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DIRECTIVE EFFECTS IN ALLYLIC AND BENZYLIC POLYMETALATIONS: THE QUESTION OF U-STABILIZATION, Y-AROMATICITY AND CROSS-CONJUGATION†

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In recent years there have been important developments in metalation reactions. Propargylic, allylic and benzylic polymetalations were observed and unusual directive effects were found in these reactions. At the same time new concepts, U-stabilization and Y-aromaticity, concerning the reason for the particular conformation and configuration of anions and uncharged molecules were put forward. The present discussion will indicate the course of the developments in this field and present a new interpretation on these effects. This is not intended to be an exhaustive presentation of all the results in the literature but mainly a representation of ideas and findings following their actual development and not necessarily the order of their publication.

Our interest in allylic polymetalations started in 1964. At this time we were engaged in the metalation of derivatives of unsaturated fatty acids. This was an applied project aimed at increasing their functionality for possible utilization of the products as starting materials for polymers.[1]

The first compound we metalated was linoleyl alcohol. The metalation was carried out with butyllithium in ether. At this time butyllithium was rarely used in the laboratory for the metalation of aliphatic compounds and was applied mainly for the metalation of aromatics,[2] particularly heterocyclic compounds, and for the exchange of bromine[3] for lithium. The metalation of 1,4-dienes by butyllithium had not yet been performed at this time. Our metalation proceeded smoothly to give the pentadienylic compound, which was then reacted with carbon dioxide. These results were published[4] only several years later due to the difficulties we initially encountered in the separation of the mixture of products and the determination of the position of the substituents in the long chain. These difficulties were overcome only after considerable effort.

In the meantime, Bates[5] and Kloosterziel[6] had published elegant work on the metalation of simple 1,4-dienes and utilized NMR to establish the nature of the products. They later extended the metalation to more extended systems. We had also extended our metalations to dienes and 1,3-enynes[7] observed gem dimetalation using both NMR and UV spectroscopy, to establish the nature of the products.

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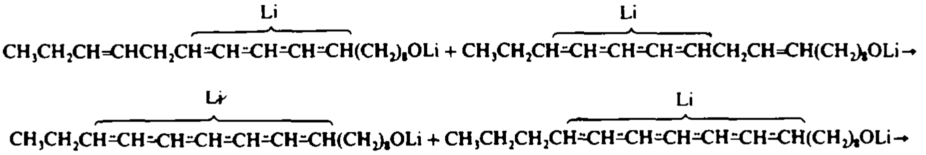
†Dedicated to Professor H. C. Brown on the occasion of his seventieth birthday.

The successful abstraction of a proton from a methylene group located between two double bonds raised the question whether the abstraction of two protons, one from each methylene group located between the two double bonds, in linolenic acid would be possible to obtain a dimetalated compound. Polymetalated aliphatic hydrocarbons containing the charges in the same delocalized system were not known at this time. The closest analogs known to such a system were the dimetalated enolates obtained from 1,3-dicarbonyl compounds,[8] but in these derivatives the charges are located mainly on the oxygens. Another group of dimetalated compounds were the products of the reaction of alkali metals with aromatic compounds.[9] Aromatic compounds containing more than one carbon metal bond were also known, but since these were σ-bonds perpendicular to the π-framework they were isolated from each other and essentially non-interacting.

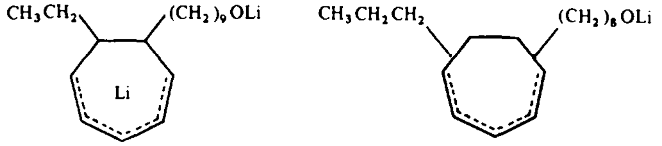
The metalation of linolenyl alcohol (eqn 1) proceeded rapidly.[10] The question of the feasibility of a second metalation on an activated methylene could not be settled since a 1,6 sigmatropic shift of a proton from the second methylene took place after the first metalation to give an entirely conjugated heptatrienylic system. Such a migration was observed by us earlier in the linoleyl derivatives.[4] However this shift in the linoleyl compounds was much faster due to the increase in conjugation after the migration. Consecutive cyclization of the heptatrienylic lithium compounds led to the cycloheptadienylic lithium derivatives. The success,

$$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_8OH + BuLi \rightarrow \qquad (1)$$



$$CH_3CH_2CH{=}CHCH_2\overbrace{CH{=}CH{=}CH{=}CH{=}CH}^{Li}(CH_2)_8OLi + CH_3CH_2\overbrace{CH{=}CH{=}CH{=}CH{=}CH}^{Li}CH_2CH{=}CH(CH_2)_8OLi \rightarrow$$

$$CH_3CH_2\overbrace{CH{=}CH{=}CH{=}CH{=}CH{=}CH{=}CH}^{Li}(CH_2)_8OLi + CH_3CH_2CH_2\overbrace{CH{=}CH{=}CH{=}CH{=}CH{=}CH{=}CH}^{Li}(CH_2)_8OLi \rightarrow$$



(2)

that we experienced in the polylithiation of acetylenic fatty acids[11] turned our attention to the polymetalation of simpler acetylenes,[12] but later we turned back to the problem of allylic polymetalation, this time with simpler substrates, using phenyl as one of the activating groups.

ALLYLIC POLYMETALATION

At this time no case of allylic polymetalation had been recorded. The questions we asked ourselves were the following:

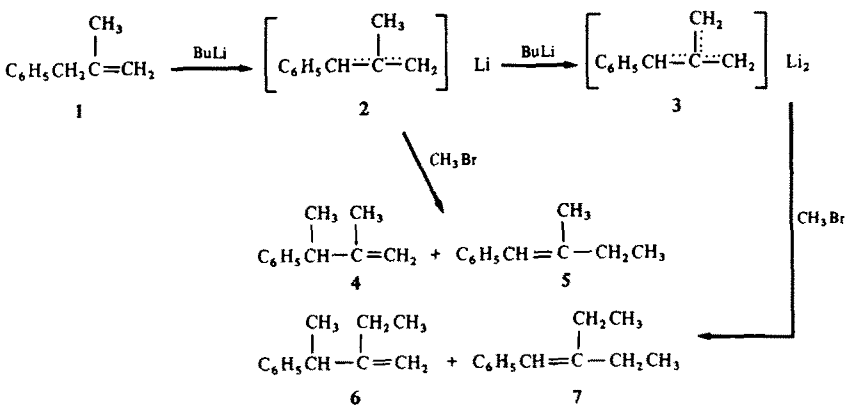
(1) Can olefins or polyenes be polymetalated at allylic positions?

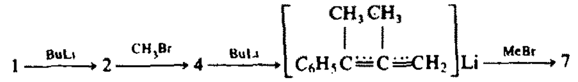
(2) If this were possible, what would be the structure of the polyanion: planar or divided into perpendicular subunits?

(3) Will it be possible to abstract more than one proton from one allylic position?

(4) With more than one allylic position in the monoanion, will there be a structural preference for proton abstraction from one of them?

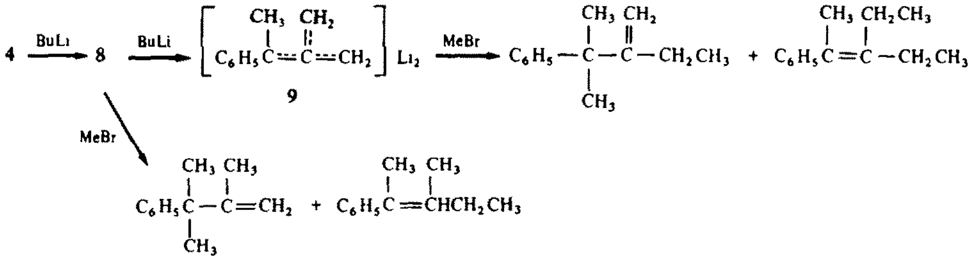
Metalation at room temperature of methallylbenzene[13] **1** with butyllithium (BuLi) and tetramethylethylenediamine (TMEDA) in hexane or in ether with various proportions of reagents led to the mono **2** and then to dilithio **3** derivatives. Alkylation at various stages of the reaction with methyl bromide yielded the mono **4** and **5** and dimethyl **6** and **7** derivatives. The metalation in hexane with BuLi–TMEDA was faster than in ether. These results were not a consequence of consecutive monometalations and alkylations (eqn 3) since the amount of the dialkylated products increased with the duration of the reaction with butyllithium and since the monometalation of **4** is slower than dimetalation of **1**. The reaction of **1** with 2.5 equivalents of commercial butyllithium (0.6 M) and a ratio BuLi/TMEDA of one, was after 24 hr practically all dimetalated whereas the reaction mixture of **4** in the same conditions contains 40% of unmetalated substrate (equation 4), together with **8** and an equal amount





(3)

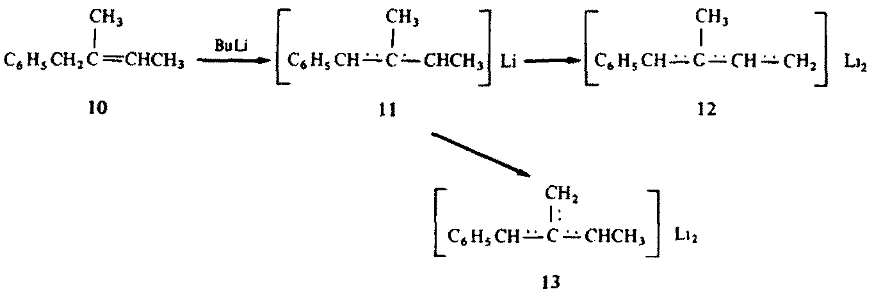
of the dimetalated derivative **9**. The slow monometalation of **4** is of steric nature, since the transformation of a tetrahedral carbon, bearing a methyl into a trigonal one should be easier than of an unsubstituted one, due to the decreased C–H bond dissociation energy and



(4)

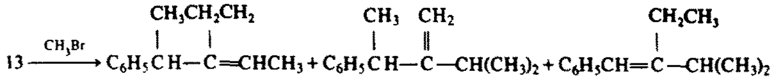
increased C–Me bond strength.[15] Departure from this behavior was interpreted as a manifestation of steric effects. The second step of metalation is less hindered, since it takes place on a methyl and proceeds in **4** faster than the first one. The methyl at the benzylic position was not attacked, only the allylic methyl and **9** as well as **3** were derivatives of cross-conjugated dianions. Dimetalation on **1** was also performed using butyllithium and potassium t-butoxide (Schlosser's and Lochmann's method[16]). In this case the formed precipitate of the dimetalated product was separated from the solution and alkylated in THF with methyl bromide yielding the same products as those obtained with BuLi–TMEDA.

The question what type of dianion will be formed preferentially, a cross-conjugated or extended one was settled by submitting **10** to a similar metalation (**10** has two different allylic methyl groups). The monometalated **11** can give either the derivative of the extended **12**, or cross-conjugated **13** dianion or both of them (equation 5).



(5)

Unexpectedly, only **13** was obtained, as proved by the methyl derivatives formed on treatment with methyl debromide (6).

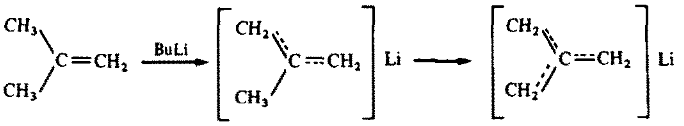


$$13 \xrightarrow{CH_3Br} C_6H_5\overset{CH_3CH_2CH_2}{\overset{|\qquad |}{CH-C}}=CHCH_3 + C_6H_5\overset{CH_3}{\overset{|}{C}}H-\overset{CH_2}{\overset{\|}{C}}-CH(CH_3)_2 + C_6H_5CH=\overset{CH_2CH_3}{\overset{|}{C}}-CH(CH_3)_2 \qquad (6)$$

The progress of the metalation was followed also by NMR. Particularly the para proton in the phenyl ring was shifted considerably upfield in each stage, to 6.15 in **2** and then to 5.82 ppm in **3**.

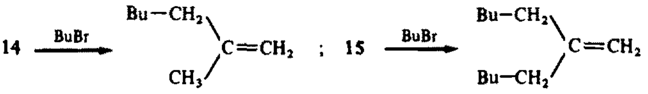
The ease of dimetalation of the methallylbenzene compounds raised the question of the role of phenyl in the reaction. How much charge is delocalized into the aromatic ring to permit further metalation? CNDO calculations performed by us[13] have shown that a larger percentage of the charge is located in the side chain of the dianion than in that of the monoanion. The phenyl absorbed part of the introduced additional charge, but more of it remained in the side chain. This seemed to us unusual, since even in the monoanion there is more charge in the side-chain than in the ring and addition of charge was supposed to be less in the part of the molecule that already was highly charged, because of charge repulsion. This calculation indicated to us that the charge in the side chain in the dimetalated compounds is stabilized perhaps even more than in the monometalated ones and that the phenyl group is perhaps not necessary for the formation of a dilithium compound.

Inspection of the structure of the dimetalated products has shown that they are derivatives of trimethylenemethane dianion. The preparation of the parent compound **15** was therefore undertaken[17] by metalation of isobutene with BuLi and TMEDA in hexane (equation 7). The intermediate methallyllithium **14** was metalate faster than isobutene and only a short time after the beginning of the reaction was it possible to trap it with butyl bromide (equation 8). After some time the dibutyl derivative was obtained exclusively.



(7)

14 **15**



(8)

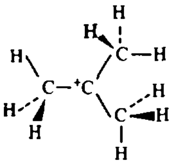
It was found by Hooz[18] that by carrying out the reaction in ether, once can stop the reaction at the stage of **14**. Disodium and dipotassium derivatives of trimethylenemethane have apparently been prepared previously,[19] although no direct proof for their formation has been provided.

The stability of **15** is outstanding compared to the high reactivity of the non-Kekule[20] hydrocarbon trimethylenemethane[21,22] itself.

The selectivity of the cycloaddition of the singlet and triplet trimethylene methane biradical has been elucidated by Berson.[23] Also transition metal complexes of trimethylenemethane (TMM) have been found to react in cycloadditions.[24-27] The structure of their complexes has C_{3v} symmetry in the case of iron tricarbonyl complexes, but the palladium (O) complex showed non-equivalence of the methylene carbons[29] and exhibited nucleophilic character.[29]

The electronic structure of TMM was of continuing great interest[30] and the planar triplet was found to be of lower energy than the perpendicular singlet.

The amazing easy formation of **15**, its stability in solution and the strange coincidence that it contained six π electrons, dispersed around the periphery of the system suggested aromatic stabilization,[17] and through-space delocalization of the π electron sextet between the three methylenes. Such a stabilization of a cross-conjugated compound with three groups linked to a central atom and containing six π-electrons was discussed in the case of heteroatom containing compounds, such as guanidinium ion,[31] and given the name of Y-aromaticity. This concept was and is still widely used. The conformation of the t-butyl cation **16**[32] and those of dimethyl ether, dimethylamine, propane,[17] acetone and isobutane[33] **18**, as opposed to isopropyl cation **19** were explained by the six quasi π electron interactions related to aromatic interactions.



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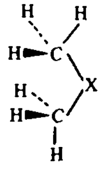
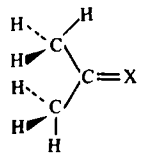


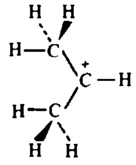
$X=CH_2, NH, O$

17



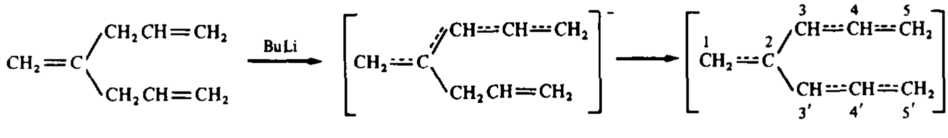
$X=CH_2, O$

18



19

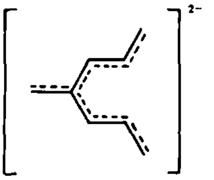
A CNDO calculation of the geometry of trimethylenemethane dianion has found,[34] that it is all-planar, the negative charges are all on the external carbons, and the central carbon has some positive charge on it. A similar calculation for the dication showed a partial negative charge on the central carbon. However the dianion showed a slightly negative instead of a positive overlap between the external carbons. This seemed to be in contradiction with the hypothesis of through-space delocalization.



(9)

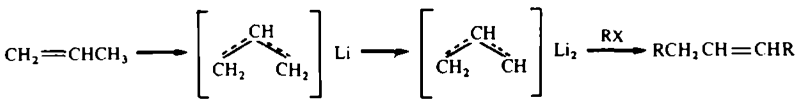
20

The next acyclic "aromatic" dianion **20** containing 10 π electrons[34] was therefore prepared (eqn 9). The reaction proceeded in ether and THF even without TMEDA. All the protons in the mono and dianions were assigned in the NMR. The coupling constants showed that the protons between the carbons C_3–C_4 and $C_{3'}$ and $C_{4'}$ are trans. Conformation **20a** was attributed to **20**. The activation energy for rotation around the C_4 and C_5 and $C_{4'}$ and $C_{5'}$ bonds was found from NMR to be 14.5 kcal/mol^{-1} and in a derivative of **19** with a phenyl group on C_1 the rotation around C_1–C_2 was found to be 11.5 kcal/mol^{-1} (the rotation around C_4–C_5 in the phenyl derivative was 14 kcal/mol^{-1}). All these data do not support the assumption that there is some unusual stabilization of the planar aromatic conformation, different and in addition to that found in pentadienyl or heptatrienyl-lithium compounds and that the dianion does assume a conformation with the terminal carbons close to each other that will permit through-space delocalization of the electrons. However, there should be some special feature in the structure of the starting material or of the dianion that accounts for its stabilization.



20a

Allyllithium itself has undergone an additional metalation[35] (equation 10) and surprisingly the second proton was abstracted from a terminal carbon already carrying a charge to yield **21**. This was established by alkylation that took place on both terminal carbons. However, this reaction was sluggish and did not go to completion. Allylbenzene was therefore dimetalated (equation 11) to **22**.



(10)

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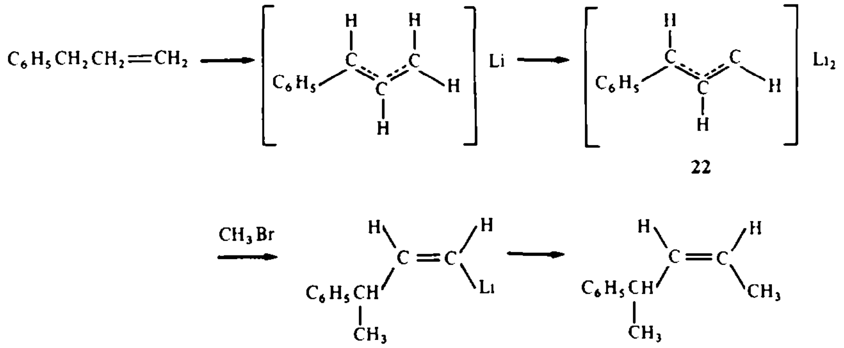


22

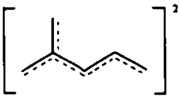
23

(11)

Again, the second proton was abstracted from the terminal carbon[35] already carrying a charge and not from the central or benzylic carbon. The conformation established by NMR is as in **22** with the protons on C_2 and C_3 anti and those on C_2 and C_1, syn. This conformation is supported by the formation of the cis methylated derivative **23**, formed via a vinylic lithium intermediate.

Ab initio calculations[36,37] performed on **21** showed it to have the protons on C_1 and C_2 syn, but the lithium atoms were found to be located one above and the other below the plane containing the carbon and hydrogen atoms.

A great contribution to the study of polyanions was made by Bates. The branched-chain dianion **24** and trianion **25** were prepared easily,[38] with BuLi-TMEDA but **26** was formed very reluctantly. Bates has also prepared the unbranched butadiene dianion **27** by metalation of butene although **27** was formed with greater difficulty than the branched ones **24** and **25**, Dilithium hexatriene **28** was also prepared by Bates by metalation and its structure was determined by X-ray crystallography, as having the folded conformation. Similar butenediyls **29**, **30**, **31** have been prepared by the reaction of magnesium with dienes[39] such as butadiene, isoprene and myrcene. Monomeric and polymeric structures were assigned to these products. Another compound of this type is the dianion of a sulfolene **32**.[40] 2,3-Dimethylbutadiene[41] gave



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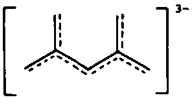

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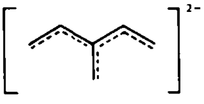

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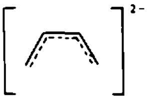

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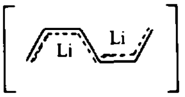

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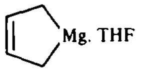

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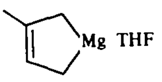
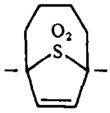


30

$-(Mg-CH_2CH{=}CHCH_2)_n$

31



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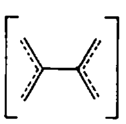

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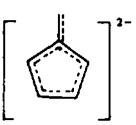

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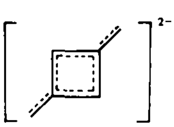
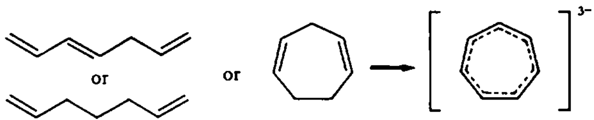


35

on metalation the dianion **33** and methylcyclo-pentadiene yielded fulvene dianion **34**. Metalation of 2,3-dimethylenecyclobutane gave **35**, and **26** was prepared by Schlosser's method.[16]

Interesting results were obtained by Bates on metalation of heptatriene and heptadienes.[12] Metalation[43] of 1,3,6-heptatriene or of 1,6-heptadiene gave the aromatic seven-membered trianion **36**, but 1,4-heptadiene yielded the open-chain trianion **37** (equation 13). Schleyer[44] lithiated methylenecycloheptane (equation 14) and obtained first the cross-conjugated dianion **38** that was subsequently converted into the stabilized methylenecycloheptatriene dianion **39**.



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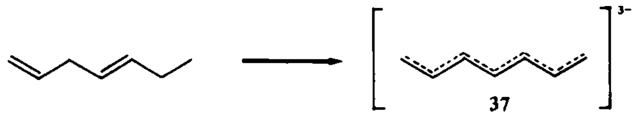

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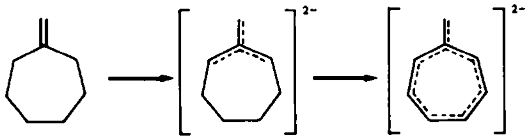
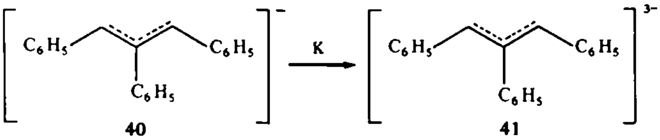


38 39

(14)

The trianion **41** was prepared by Boche[45] by a different route, the reaction of the monoanion **40** with alkali metals. A dilithium **42** and tetralithium **43** compound was prepared from 1,2,3,4-tetraphenylbutadiene by the action of lithium metal.



40 41

$$C_6H_5CH{=}C(C_6H_5)C(C_6H_5){=}CHC_6H_5 \xrightarrow{Li} C_6H_5CHLi{-}CC_6H_5{=}CC_6H_5CHLiC_6H_5 \rightarrow$$

42

$$C_6H_5CHLi{-}CLiC_6H_5{-}CLiC_6H_5{-}CHLiC_6H_5$$

43

The greater thermodynamic stability of a cross-conjugated dianion over that of the extended one was proved by Mills though the observation that the isomerization of the dilithium derivative of **44** into **45**. The accurate value of the chemical shift of the protons in trimethylenemethane dianion was established and its position fell on the line correlating the

44 45

chemical shift with the charge in aromatic systems. This point is upfield to that corresponding to the same charge in a polyenylic monoanion system. This raises an interesting question. Is it possible in an aromatic system, that exerts a paramagnetic shift to have a proton on a charged carbon shielded more than in a non-aromatic one? The chemical shift of the protons in the ten π electron acyclic compound **20**, was rather like in normal acyclic anions. Another possibility is, that chemical shifts of the protons in dianions and polyanions have also a different proportionality coefficient in their relation with the charges, from that in monoanions. Moreover a fitting of the straight lines to the experimental points seems to make the point of **15** correspond not less well to the acyclic than to the aromatic series.

U AND Y AROMATICITY

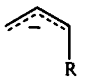
The formation of butadiene **27** and hexatriene **28** dianions and their conformations fitted nicely the concepts of stabilization and "aromaticity" as developed by Hoffmann[48] and Epiotis.[46] The symmetrical orbitals were found to be lowered in energy in a six-electron U conformation[48] of butadiene dianion **27** hexatriene dianion **28** or pentadienyl anion **46**. The U conformation of the latter **46** was predicted to be more stable than the sickle S **47** or extended W **48** conformation. This was the first time that a relation was proposed to exist between the number of π-electron in an acyclic system and the stabilities of its particular conformations. Such a relation and in addition the geometry of the stable conformations, where the terminal atoms of the system were close to each other was very reminiscent of aromaticity. Dilithium hexatriene[38] was indeed found to be more stable in the conformation **28**. The syn form of the alkylallyl anion **49** was found to be kinetically[50] and thermodynamically[51] preferred as it was also by calculation.[52] The lithium derivative of **49** was also more stable[53–55] than its anti conformer, as were the potassium derivatives.[55–57] It seems however that the anti-isomer of **49** is more stable in the gas phase.

Allyl anions containing heteroatoms carrying lone pairs of electrons thus forming a 6 π electron system were also found to be more stable in the syn conformation, e.g. with sulfur **50**,[59] oxygen **51**,[60–62] and nitrogen **52**.[63] Syn anions are also preferentially stabilized, when nitrogen takes one or more positions of the allylic system, e.g. **53**,[64] **54**,[65] **56**,[66] and in an anion **56** derived by abstraction of a proton α to nitrogen of an amide[67] or of a nitrosamine[68] **57**.


46


47


48



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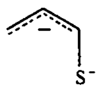

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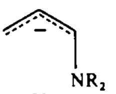

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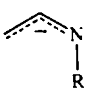

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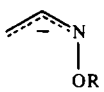

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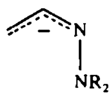

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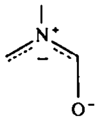

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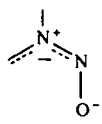

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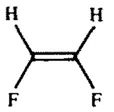
On the other side, pentadienylic lithium compounds have been found by NMR studies to be more stable in the W conformation[5,69] **48**, as were also substituted pentadienylic lithium and potassium compounds prepared with potassium in liquid ammonia.[6] However, dimethoxyboration-oxidation of pentadienyl potassium prepared in THF by BuLi and potassium t-butoxide[16] or trimethylsilylmethylpotassium,[71] yielded Z-penta-2,4-dien-1-ol.[72] Substituted pentadienes gave also products supporting the U conformation **46** for pentadienylpotassium. Similar results[73] have been obtained by reacting chlorotrimethylsilane with pentadienylpotassium prepared from 1,3- or 1,4-pentadienes with potassium in THF in the presence of a tertiary amine. It was concluded the pentadienylpotassium is present in the U conformation in solution, but has the W or S conformation in the solid state. This was also confirmed by ^{1}H and ^{13}C NMR spectra.[74] SCF MO calculations[75] support the W conformation **48** for pentadienylic anions. It is possible that the electrostatic interactions between the three carbons carrying the charge in the pentadienylic anion and the large potassium cations are the reason for the preference of the U conformation of potassium derivatives in solution, but the small lithium can interact or birdge only the 1,3-carbon atoms and therefore does not favor **46**.

Epiotis[49] has analyzed carefully by MO calculations the reasons for the greater stability of cis olefins having two vicinal substituents with lone pairs relative to their trans isomers, i.e. 1,2-difluoroethylenes **58**. This was initially attributed to attractive interactions in the symmetrical combination of the lone pair orbitals, since their antisymmetrical combination interacted strongly with the π orbital of the double bond. Here again was a six π electron system, similar to butadiene dianion **27**. This system was considered to have π-aromaticity **59**, as well as σ aromaticity **60** involving the σ lone pairs and C–C bond orbitals e.g. for **58** and **61**. This treatment was also extended to a great number of olefins, including those having methyl substituents instead of heteroatoms as contributors of π-orbitals, e.g. **62**.

58



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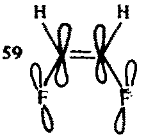

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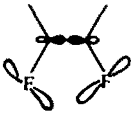

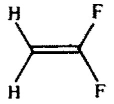

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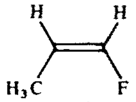


62

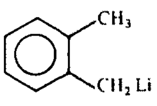
The concept of σ-aromaticity in **61** was challenged,[76] since no electron density was found in the region between the fluorine atoms. A different interpretation for the greater stability of **58** and related compounds than of their trans isomers was advanced.[77] According to this approach, this is not because of the stabilization of the *cis* but of the destabilization of the trans isomers due to the four electron repulsion between the lone pairs. Such four electron interactions are known to be stronger with the groups in a trans or anti disposition as evidenced by NMR coupling or π–π absorption maxima. The greater stability of trans than of *cis* 1,2-difluorocyclopropane[78] was claimed as support for Bingham's[77] interpretation.

A more complete assessment of all the stabilizing and destabilizing interactions[79] has shown that the four electron-two orbitals overlap repulsion is an important contributor to aromaticity and in addition the two electron two orbital interaction stabilizes the *cis* **58** more than its trans isomer. This was supported by additional MO calculations.[80]

BENZYLIC POLYMETALATION

Irrespective of the answer to the question whether the greater stability of the cis reactive to the trans 1,2-disubstituted olefins is due to the U-aromatic stabilization of the *cis* or the destabilization of the *trans*, it is clear that the cross conjugated allylic anions are more stable than the extended ones e.g. **15**, **12**, **45** vs **27**, **13** and **44** respectively. It is therefore of geat interest to know what is the reason for the stabilization of these cross conjugated dianions. The initially postulated acyclic Y aromaticity[17] was later questioned[13] because of the repulsive overlap population between the peripheral methylenes. Later, the aromaticity of the cross conjugated dianions was claimed[47] again because of the ^1H NMR shift of **15**. Since our calculations were by CNDO method and could not be relied too much upon, we looked for a system, where the question of $4n+2$ π-electron through space aromatic delocalization could be tested experimentally. The requirement for such a system was to have in it the terminal charge-bearing methylenes removed rigidly from each other to prevent through space delocalization. Another requirement was to have the possibility of comparing the stability of this system with an isomer with extended delocalization. Such a system could be formed from isomeric xylenes, if metalation at each of the methyls were possible. The meta dimetalated xylene corresponded to the trimethylenemethane dianion, where a benzene ring replaced a double bond. It is derived from th Kekule' meta xylyene by addition of two electrons. The para dimetalated xylene is an extended conjugated system and the ortho isomer has the U conformation. Toluene[81] was polymetalated previously. The monometalation of xylenes[82] was studied extensively, and the dimetalation of m-xylene with amylsodium and TMEDA was reported.[83]

Metalation of o-xylene[84] with BuLi–TMEDA in hexane yielded a mixture of lithiated products **63**, **64**, **65**, **66**. The composition of this mixture was determined by NMR and by subsequent reactions, e.g. silylation with chlorotrimethylsilane and it depended strongly on the ratio BuLi–TMEDA. A high ratio of these reagents gave a larger amount of the ring **65** and gem-metalated **66** products, but a ratio of 1:1 yielded almost exclusively **64**. The low ratio of reagents e.g. 4:1 favored coordination of one TMEDA to benzyl- and butyllithium simultaneously and because of this favored proximate gem. or ortho dimetalation. A similar observation was made also in the case of the other benzylic compounds studied.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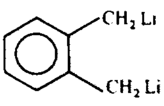
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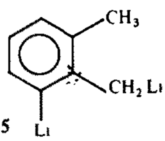
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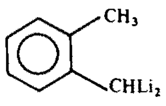
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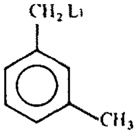
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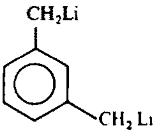
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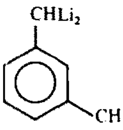
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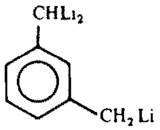
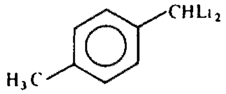

70

The polymetalation of m-xylene in similar conditions was faster than of its ortho isomer and led to the products **67**–**70**. Again, decreasing the ratio of BuLi–TMEDA to 1:1 gave mostly **68**. The mixture of products was silylated. The progress of the reaction was followed by NMR, particularly in the region of the aromatic protons. The disappearance of the starting material was accompanied by an upfield shift of C$_4$–H appearing as a doublet and the C$_2$–H, C$_6$–H as a multiplet. The C$_5$–H appeared as quartet in **67** and a triplet in **68**.

The behaviour of p-xylene during the metalation was different than that of its isomers. Not only was the metalation much slower, but a single dimetalated product **71** was formed slowly. However, metalation at both methyls could be performed with BuLi–t–BuOK yielding **72** and **73**.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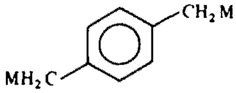
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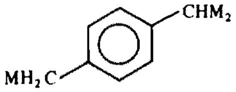
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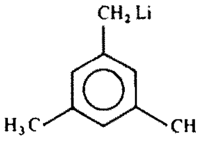
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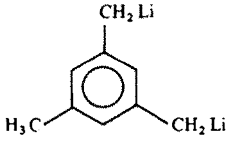
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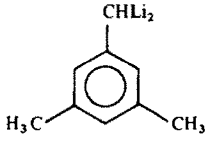
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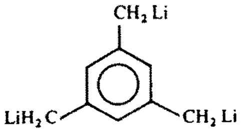
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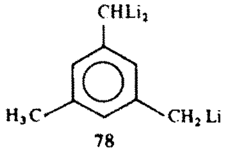
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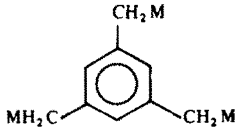
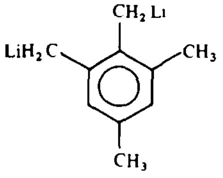

79

A facile trilithiation was observed in the case of mesitylene. A mixture of products **74**–**78** was obtained with various ratios of reagents, but **77** was obtained almost exclusively when a large proportion of TMEDA was present. The reaction was followed by NMR, that permitted to establish from intensity ratios that aromatic protons o, p to two CH$_2$Li groups appear at higher field than the o,o-protons. Metalation of mesitylene with BuLi-t-BuOK gave the trimetalated product **79** and no ring metalation.

These results have shown that the preference for dimetalation is in the sequence meta > ortho > para. Only meta tri-dubstituted benzenes can lead to trimetalation with BuLi–TMEDA, but BuLi–t–BuOK (acting as BuK) can polymetalate at para positions, because of its higher basicity.

The preferential meta dimetalation with BuLi–TMEDA was observed in several additional cases. Thus 1,2,3,5-tetramethylbenzene yielded two dimetalated products **80** and **81** but only one trimetalated product **82**, with the metalated methyls in meta positions. Metalation with BuLi–t–BuOK gave the tetrametalated product **83**.



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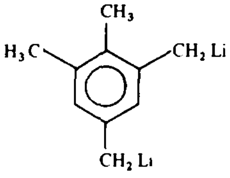

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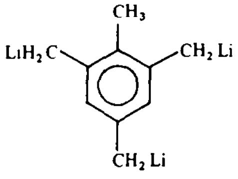

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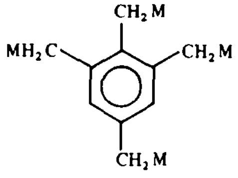

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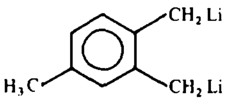

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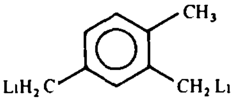

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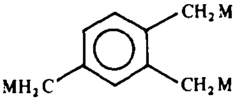

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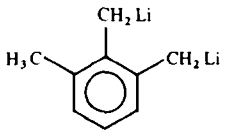

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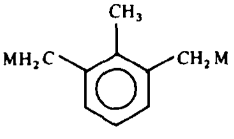

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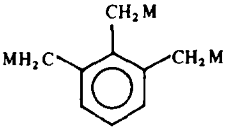
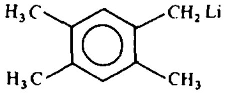


89

1,2,4-Trimethylbenzene produced again an ortho **84** and meta **85** but no para dilithiated product, with the amount of **85** twice that of **84**. The use of BuLi–t–BuOK as metalating agent increased the ratio of **85**:**84** to 5:1, and produced also the trimetalated **86** derivative.

The only case where ortho dimetalation was preferred to meta was that of 1,2,3-trimethylbenzene that gave with BuLi–TMEDA the ortho-dimetalated product **87** exclusively. However metalation with BuLi–t–BuOK gave more of the meta dimetalated product **88** and its amount relative to **87** increases with time. It appears that the **87** is the kinetic product but **88** is favored thermodynamically. The trimetalated product **89** was also formed. The lithiated products undergo proton exchange and isomerization slowly, but potassium derivatives do it much faster and permit to obtain the more stable products.

An intramolecular competition for either ortho or meta or para dimetalation took place in durene where all these processes can take place from the monolithiated compound **90**. Only ortho **91** and meta **92** and no para dimetalation took place.



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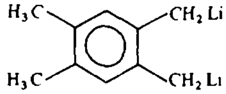

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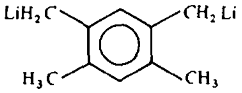


92

The products of metalation were characterized partly by NMR and always by derivatization with chlorotrimethylsilane and in addition two more reagents were utilized—methyl bromide and borane in THF. The product of the last reaction gave after hydrolysis and oxidation hydroxy derivatives, generally benzylic alcohols and also phenols when ring metalation took place. This method is an extension of the preparation of diols from allylic[86] and propargylic[87] lithium compound with borane. The NMR data and particularly the strong upfield shifts of the proton para to the charged methylenes prove that despite the multiple charges in the system all the methylenes carrying most of the charge are in the plane of the aromatic ring.

At this stage it was clear that the cross-conjugated m-xylylene dianion is more stable than its ortho and para isomers and the U shaped ortho is more stable than its para isomer. It follows therefore that the stabilization of the cross-conjugated polyanions is not due to aromatic through-space delocalization, since the meta methylenes are too far away from each other to permit this. The U-shaped ortho isomer should have been the most stable if aromatic delocalization were the most important effect, but it appears to be less stable than its meta isomer. The larger stability of the ortho relative to the para isomer may be due to U-stabilization or to a stronger stabilizing interaction of both methylenes with both lithium cations (see later for a further discussion of this interaction). Since the heat of formation of ortho, para and meta xylylenes[88] are 53, 50 and 76 kcal mol^{-1} more respectively, the introduction of two electrons in each of them to give the corresponding dianions, stabilizes the meta relative to he ortho and para isomers by more than 23 or 26 kcal mol^{-1} respectively.

CALCULATIONS

The phenomenon of polymetalation, when the charges are introduced into the same delocalized system seemed incomprehensible. One would expect these polyanions to be much more basic than perhaps even BuLi, but not only are the lithium derivatives formed; they are formed at similar rates to those of the monolithium derivatives. We have carried out some CNDO calculations[85] of the energy of ΔE of the gas reaction of ionizations of the carbon acid to the monoanion (eqn 15a), of the monoanion to the dianion (eqn 15b) as well as of the energy E′ of the displacement of a hydrogen by a lithium atom (16a)

$$AH_2 \rightarrow AH^- + H^+ \qquad \Delta E = E_{AH^-} - E_{AH_2} \tag{15a}$$

$$AH^- \rightarrow A^{2-} + H \qquad \Delta E = E_{A^{2-}} - E_{AH^-} \tag{15b}$$

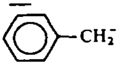
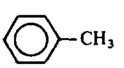
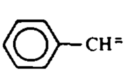
and (16b). We did not consider the absolute energies as very reliable, but

$$\Delta E' = E_{AHLi} - E_{AH_2} \tag{16a}$$

$$\Delta E' = E_{ALi_2} - E_{AHL_i} \tag{16b}$$

hoped that a comparison of the differences ΔE for the formation of the mono- and dianions could provide valuable information and similarly for the formation of the mono and dilithium compounds. Some of the results[84,89] are given in Table 1. The ΔE for the ionization of the one of the other anion. Consider the union of a methyl anion with an allyl anion (equation 17).

Table 1.

Product	ΔE (ev) anion	ΔE' (ev) Lithium der.
63	23.81	6.72
64	29.88	0.16 - 5.16
68	28.66	4.83
72	29.7	7.11
74	23.76	6.67
75	28.58	5.91
77	32.99	5.40
	23.85	6.77
	26.056	10.73
	34.61	0.65

hydrocarbons to all the three isomeric methylbenzyl-anions are similar, as is that for benzyl and dimethyl–benzyl anion. The ΔE for the ionization of the mono to the dianions is by several eν more endothermic than for the hydrocarbons, and is similar for the ortho and para, but less endothermic for the meta isomer. It should therefore, as expected, be much more difficult to form the di than the mono-anions. However, the formation of the mono-, di- and tri-lithium derivative of the corresponding anions derived from mesitylene is approximately of the same energy. The formation of the dilithium m-xylylene and of dilithium derivative of the dianion derived from mesitylene is also more favorable than that of dilithium p-xylylene. These results are internally consistent since the same ionization processes for several different substrates are of similar energy except for the meta isomers, where apparently an electronic effect is at work. In the lithium derivatives there are departures from regularity when the lithium atoms are close to both charged methylenes and $\Delta E'$ in this case depends on the relative disposition of the lithium atoms. Apparently, the electrostatic interactions in such arrangement lower the energy of these compounds. All the lithium derivatives were calculated for the geometry found by Stucky[90] for benzylithium, with lithium above the plane of the molecule and bridging the benzylic and ortho positions. An arrangement with lithium occupying a tetrahedral position on the benzylic carbon is of higher energy. Strangely, the form having both lithium atoms in dilithium o-xylylene on the same side of the plane of the aromatic ring is of lower energy than the form with the lithium atoms on opposite sides, despite expected lower electrostatic repulsion in the last form. Such an arrangement would correspond to the concept of Schleyer,[91] that the two lithium atoms in a Mobius system are at opposite sides of the plane. A different geometry would therefore be expected for our Hückel system.

The benzylidene dianion is of higher energy than xylylene dianions, as anticipated, because of a greater charge concentration. Its dilithium derivative is of lower energy than that of meta and para xylylene derivatives and similar to that of their ortho isomer. Again, the most stable geometry is with the lithium atoms on the same side of the aromatic ring. The electronic configuration of this molecule is then similar to a phenylcarbene coordinated with a dilithium molecule.

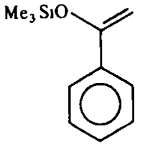
The strong effects of the positions of the lithium atoms is undoubtedly exaggerated in magnitude and probably an artifact of the calculation method. We think nevertheless that the trend of the energy changes found in the calculation reflects the real situation, although only a very limited number of geometries have been examined. One would expect that a more extensive search in the manner of the very elegant, and innovating way Schleyer[92] has been doing, could lead to a better understanding of the structures of these polylithium compounds. However, it is not certain at all that orbital interactions between the lithium atoms and the polyanions are responsible for the stabilization of these compounds. The fact that similar potassium derivatives of polyanions with the charges in the same delocalized system are formed suggests that these interactions might be mainly ionic and so may be in the lithium compounds. The polylithium compounds are prepared in hexane solution preferentially in concentrated solution of excess butyllithium, but with difficulty in THF, and supports the view that aggregation and formation of contact ions, solvated externally by TMEDA is the driving force for the stabilization of the compounds. Electrostatic interactions between polyanions and cations are much stronger than that of monoanions. Thus, the lithium and sodium salts of cyclononatetraenyl anion[93] exist in THF as a mixture of contact and solvent-separated ion pairs, whereas the K, Rb and Cs salts as contact pairs, but all the salts of cyclooctatetraene dianion exist as contact pairs in all solvents examined. The driving force for the disproportionation of salts of radical anions, e.g. of naphthalene into the hydrocarbon and the salt of the dianion is the large coulombic interaction in the salt of the dianion.[94] This disproportionation is unexpectedly (if the solvation of the dianion only is taken into account) much more extensive in the less polar diethyl ether than in THF and for lithium tetracenide it is ten orders of magnitude larger in diethyl ether than in THF.

9,10-Dihydroanthracene was the only compound where both the first and second acidity constant were measured[95] by Streitwieser. A particularly small difference of only 4 pKa units was found. This is particularly striking in view of the antiaromaticity of the system formed on introduction of the second charge. However the pKa's were determined for anion–cesium ion-pairs and triplets (first and second acidity constant respectively) and increased electrostatic interaction on going from the ion-pair to the ion-triplet undoubtedly contributes to the ion triplet stabilization. The stabilization of a large number of polyanions has been calculated.[42]

POLYMETALATION OF ENOLATES

The CNDO calculations and our experimental results support the larger stability of the meta dianions relative to their isomers. It was of intersest to examine, whether the introduction of a heteroatom in the system will maintain the same sequence of stabilities of polyanions. We undertook therefore to study the metalation of enolates derived from acetophenones substituted in the ring.[96]

Metalation of **93** with BuLi–TMEDA in hexane[96] yielded the ortho metalated product **94** exclusively. The enolate **95** is formed in the first step. Metalation of **96** in the same conditions gave in addition to the ortho metalated product **97** two derivatives, one metalated at the para **98** and one at the α-position **99**. However, metalation of **96** in THF with BuLi alone yielded **98** exclusively. It seems that in hexane there is association between the enolate and BuLi that favors chelation and metalation at neighboring positions. In THF, this effect is weaker and para metalation is favored.



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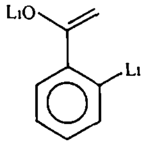

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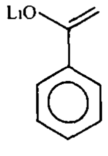

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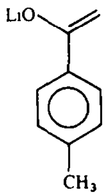

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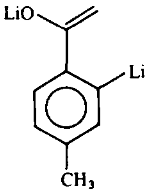

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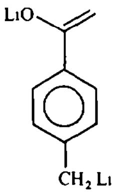

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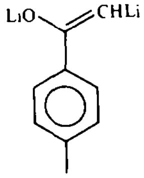
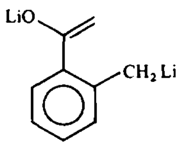


99

The enolate of 2-methylacetophenone has undergone mono-metalation of the methyl yielding **100** and two modes of dimetalation, both metalations at the methyl **101** and one of the methyl and the other at the α-position **102**. Moreover, the acetylene **103** was obtained. probably by lithium oxide elimination from **102**. Additional cases of two metalations α to a carbonyl group have been observed recently in **104**[97] and **105**.[98]

2,4,6-Trimethylacetophenone gave with BuLi–TMEDA in hexane products of monometalation of one ortho methyl **107** both ortho methyls **106** and of ortho- and para methyls **108**.



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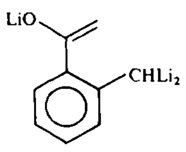

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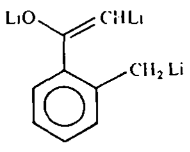

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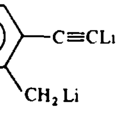

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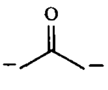

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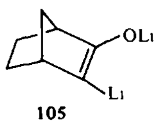

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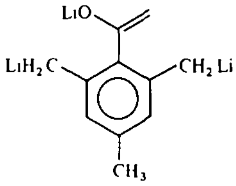

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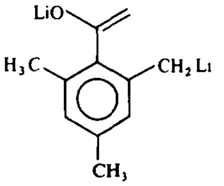

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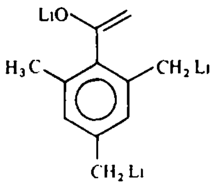

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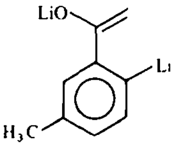


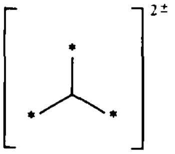
109

The only substituted enolate of acetophenone that does *not* undergo metalation of the methyl is that of 3-methylacetophenone. In this case the only product was that of ortho-metalation **109**.

CHARGE ALTERNATION AND UNION OF IONS

There seems to be a very basic discrepancy between the directive effects in the metalation of substituted benzyl anions and that of enolates of acetophenones. In the first case the metalation of a methyl at the 3-position is the preferred reaction, but in the enolates this methyl is not metalated at all, whereas the ortho and para methyls are metalated easily.

This discrepancy, however, is only apparent. In the allylic as well as in the benzylic compound the cross-conjugated polyanions corresponding to non-Kekulé hydrocarbons are the most stable isomers. These compounds contain a number of branchings equal to the number of charges. If we divide the atoms into a starred and unstarred set, the number of nonbonding molecular orbitals (NBMO) of the molecule will be equal to the difference between the number of atoms of the starred and unstarred sets e.g. two for **110** and **112** and three for **111** and **113**. Such a situation makes the introduction of a number of charges, negative or positive, equal to the number of NBMO's easier for these cross-conjugated than for their extended isomers. Another consequence of cross-conjugation is that the additional charges enter th same starred set, where the first charge was introduced. Moreover, the unstarred atoms carry a partial opposite charge. In the extended polyanions the charges are "smeared out" over all the atoms of the conjugated system. Acyclic and unbranched mono-anions or cations have charge alternation when containing an odd number of carbon atoms.



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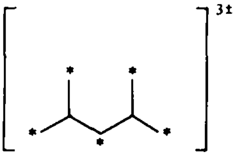

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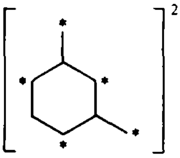

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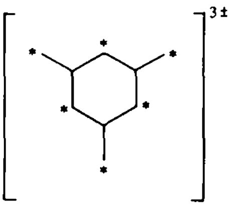

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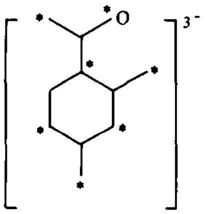

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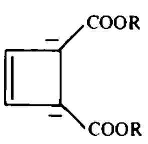
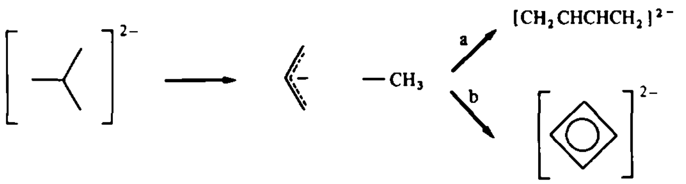


115

The stability of the polyanions (and polycations) can be analyzed by an extension of the PMO method of Dewar,[99] by a union of two odd alternant anions, or of a polyanion and a radical. In those cases however the set of rules formulated by Dewar for hydrocarbons has to be changed. According to Dewar the union of two odd alternant hydrocarbon radicals or of an anion and a cation involved their NBMO's to be stabilizing had to take place via the atoms of the starred set, the "active" atoms. These unions involved the NBMO's since the sum of the electrons in these NBMO's was that required for the formation of the bond, and the electron in the NBMO's is located on the active atoms exclusively. However the number of electrons in two NBMO's of two odd alternant anions is four and such a two orbital-four electron interaction is destabilizing. On the other side the interaction of a filled NBMO of one with the LUMO of the other anion should be stabiling. Such an interaction can be obtained by overlap of the starred ("active") set of atoms of one anion with either the starred or unstarred one of the lther anion. Consider the union of a methyl anion with an allyl anion (equation 17). There are three modes of carrying out this union: (a) at one starred extremity of the allyl to yield butadiene dianion; (b) at both starred extreme carbons to give the cyclobutadiene dianion; and (c) at the central unstarred carbon atom of the allyl anion with formation of trimethylenemethane dianion. In all the cases, there is a stabilizing interaction (equation 18) of p with the LUMO ψ_3. However in formation of the cyclobutadiene dianion (mode b) the interaction is twice that of mode a, formation of butadiene dianion. Mode c involves also the interaction of p with ψ_3, but via the central carbon with the highest coefficient in ψ_3. Moreover, in this mode of union there is no next neighbor repulsive interaction with the HOMO ψ_2. The difference between modes (b) and (c) is that in the former the union is between atoms carrying the same charge initially and of the end the charges are evenly distributed over all the carbons, but in the last—the union starts between a charged and uncharged atom and gives a product where there is charge alternation. The last is therefore the most favored mode and trimethylenemethane dianion can be obtained easily and stored whereas the aromatic cyclobutadiene dianion was postulated an ephemeric intermediate.[100] The absence of aromatic stabilization was found in **114**, where no evidence was found for the contribution of cyclobutadiene dianion.[101]



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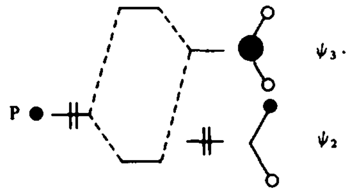
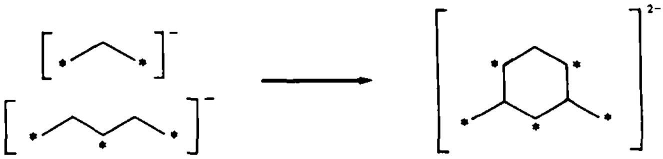


(18)

In a similar manner one could make a union of an allyl anion with a pentadienyl anion (equation 19) to give the m-xylylene dianion, of trimethylenemethane dianion (equation 20) with pentadienyl anion to yield the trianion derived from mesitylene.



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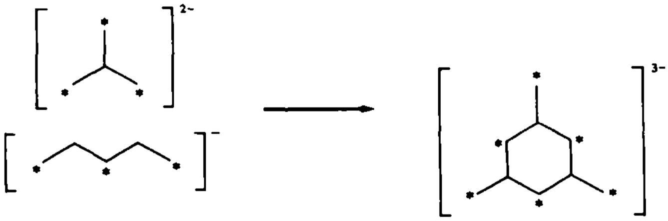
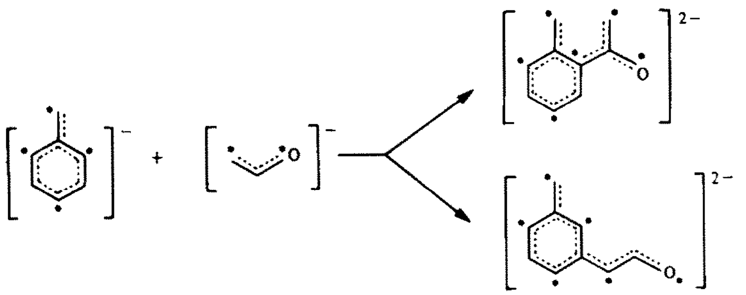


(20)

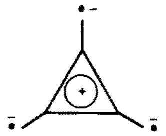
The polyanions derived from the enolates of aromatic ketones can be seen as formed by a union of a benzylic anion with an enolate (eqn 21). The best way to make the union via the terminal carbon of the enolate is with the meta position of the benzylic anion. However, the central atom of the enolate is preferentially linked to the ortho or para position. Charge alternation is maintained in both cases.



21

Charge alternation is a very powerful factor. It makes gem-dimetalation preferred to metalation of an unstarred position. It seems to support the view that this is mainly charge stabilizing and not an orbital effect.

A ring substitued fully with identical substituents has for symmetry reasons the same charges on all the atoms of the ring. It can then be considered as one superatom and the systems will be stabilized when all the substituents carry a full or partial charge opposite to that in the ring. Thus the dianion on trimethylenecyclopropane **116** is similar to trimethylenemethane dianion **117**. The negative charges in **116** should be located on the methylenes, whereas the cyclopropyl carbons should carry a partial positive charge. This was confirmed[102] by the ^{13}C NMR spectra of **118a** and **118b** and by the calculated and the experimental spin densities of the radical anions of **116** and **118a**.



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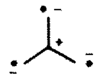

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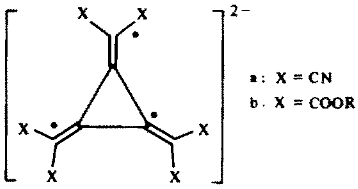

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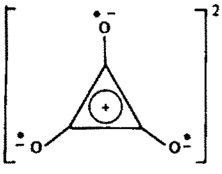

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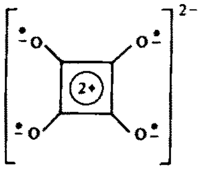

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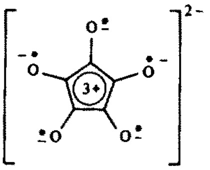

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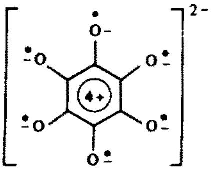

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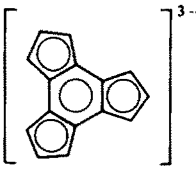
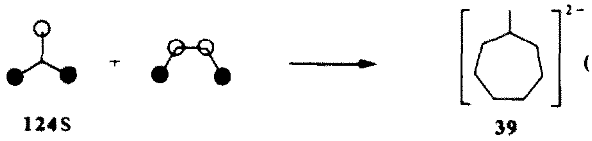


123

A similar approach could be taken for the analysis of the stability of the aromatic oxocarbons[103] **119**, **120**, **121** and **122**. All these compounds are dianions and could formally be considered as an aromatic positively charged ring with negatively charged oxygens on it. The charges are of course not full, neither on the carbons nor on the oxygens, but charge alternation between oxygens and the uniformly opposite charged ring can be assumed. It would be of interest to examine, whether the trindene trianion[104] **123** that has all the benzylic carbons negatively charged will induce a partial positive charge on the ring carbons.

Odd cyclic dianions containing an exocyclic methylene **34** and **39** cannot be formed by a union of the unstarred atoms of one anion to the starred ones of another anion. It was suggested by Schleyer[44] that **39** can be considered stabilized by a delocalization of the charges of trimethylenemethane dianion into the LUMO of butadiene during the union of these two components. In this case it is the symmetric NBMO of trimethylenemethane dianion **123S** that is delocalized (eqn 22), so that the exocyclic methylene has very low electron density in **39**, since the antisymmetric NBMO **124A** has a node on this methylene.



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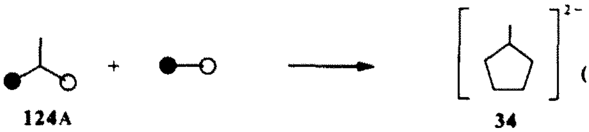

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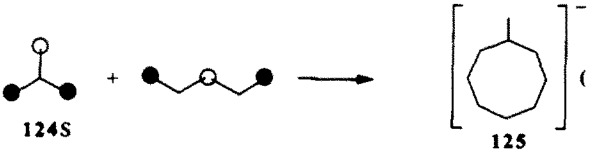


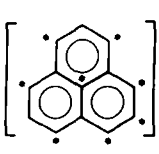
(24)

However in **34** it is **124A** that interacts with the LUMO of ethylene (23) so that the electron density of **124S** remains on the exocyclic methylene. The trimethylenemethane dianion can therefore interact with olefins and polyenes containing either 4n or (4n + 2) carbon atoms.

Methylenecyclooctaheptatrienyl anion **125** can be considered as formed by the union of radical anion of trimethylenemethane and pentadienyl radical or of the trimethylenemethane dianion and the pentadienyl cation (eqn 24). In both cases **124S** will be involved in the union and therefore no electron density will be expected on the exocyclic methylene, as indeed was found.[105]

In planar monocyclic fully conjugated, unsubstituted, closed-shell, odd-membered anions containing an odd number of π-charges and in even-membered anions containing an even number of π-charges the situation is different. In these systems the electron density is equal at all ring atoms for symmetry reasons. A number of such cyclic anions has been studied recently,[106] particularly compounds containing more than one charge e.g. cyclooctatetraene dianion,[107] annulene dianions,[108] pentalene dianion,[109] heptalene dianion,[110] dibenzononalene dianion,[111] dimethyldibenzopentalene dianion,[112] dibenzopentalene dianion,[113] and pyracyclene dianion.[114] Also tetraanions have been prepared recently, e.g. acepleiadylene tetraanion,[115] pyrene and perylene tetraanion.[116] All these compounds were prepared by reaction of the cyclic unsaturated compounds with alkali metals. The tetraanions were prepared from aromatic compounds and were also aromatic. The aromatic dianions containing 4n atoms in the ring are more stable than the antiaromatic dianions with 4n + 2 atoms. The charges in these compounds are distributed over all the atoms of the ring.

However, there is a group of non-Kekulé hydrocarbons, that are unstable being radicals or diradicals, that give very easily anions, dianions and also cations. These are of the phenalene type[117] **126**. An expanded version of it is the triangulene dianion[118] **127**, that can be obtained by metalation of its dihydro derivative with BuLi. Another compound of this type is dibenzonaphthacene dianion **128** and dication[119,120] dibenzopentacene dianion **129** and dication.[121] All these compounds are cross-conjugated and can be divided into a starred and unstarred set of atoms. The charges are not distributed over all the atoms of the ring as in aromatic and



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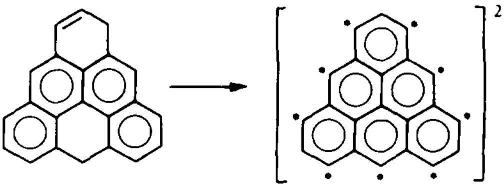

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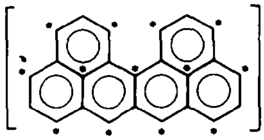

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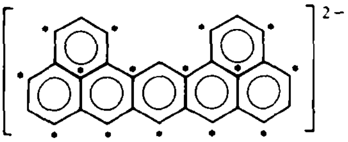
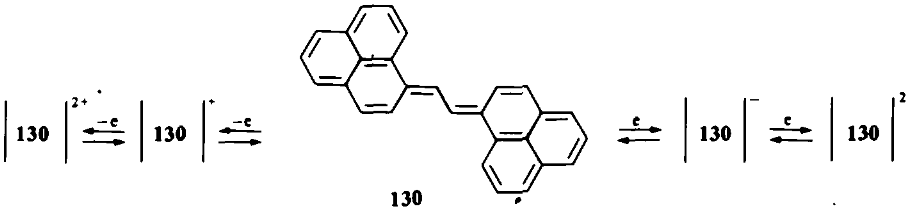


129

antiaromatic ions formed from Kekule hydrocarbons, but are located on the starred set only. They form easily cations and anions. However they cannot be isolated as hydrocarbons. Recently, a dimer of the phenalenyl type[122] was prepared as a stable molecule **130** and it can undergo reversible electron transfer to give a mono and dication, a mono and dianion (eqn 25). The difference between the oxidation and reduction potentials is very low. The compound **130** has therefore useful amphoteric redox properties.

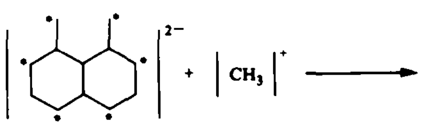


(25)

These phenalenyl type compounds are very similar to our cross-conjugated benzylic type polyanions. They can also be obtained formally by union e.g. of a dianion with a cation (eqn 26). They are cross-conjugated, easily polymetalated giving an alternating charge distribution with the second charge entering the same set of atoms where the first one was located. It seems that charge alternation is very important in the stabilization of the polyanions. This charge alternation is necessarily associated with cross-conjugation, when the number of charges corresponds to the number of points of cross-conjugation. The increased stability of such polyions relative to their isomers with extended conjugation and dispersal of the charge over the whole system derived from increased stabilizing interaction between all the neighboring atoms. Since there is charge alternation, each atom is located next to one, two or three atoms of opposite charge. This leads to a donor acceptor stabilizing interaction. A similar explanation was recently offered by Epiotis[123] for the larger stability of gem relative to vicinal difluoroethylenes. An LCFC treatment[124] of these compounds has shown that the sum of the energies of the fragments of each of the isomers was equal and the differences in the energy of the isomers is in the interaction of the fragments. This is more stabilizing in 1,1-difluorethylene due to a kind of donor–acceptor interaction which is stronger than in the 1,2-isomer. Epiotis rejected an explanation[125] based on electrostatic interactions, since a calculation has shown that these interactions should be destabilizing. One can see directly that 1,1-difluoroethylene is an alternating system **131**, where both fluorines are starred but in 1,2-difluorethylene **132** they are not.

RULES OF STABILIZATION OF DELOCALIZED SYSTEMS

It is important to underline that cross-conjugation is not a resonance effect. In fact, resonance considerations should lead to a conclusion that cross-conjugation in polyanions should be destabilizing. Very often arguments are brought to the effect that two electron-



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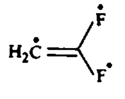

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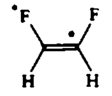

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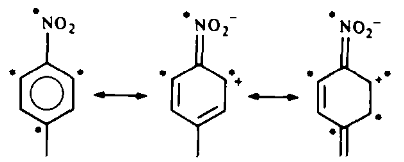

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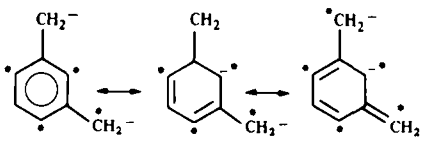

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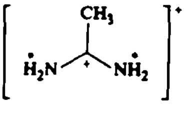
withdrawing or two electron-donating groups in an ortho or para disposition one to another are destabilizing since charges of equal sign are introduced next to each other, e.g. **133**. In the cross-conjugated polyions the charges are transferred not to the neighboring but to the same atom **134**, and this should have an even larger energy-raising effect. The destabilization in **133** and the stabilization in **134** have the same origin, i.e. diminished or increased charge alternation respectively relative to the mono-substituted compound or the other isomer. This is a new effect, that is very general as seen from the examples below.

Charge alternation in conjugated compounds is not restricted to polyions. It may occur in uncharged compounds or compounds with one charge only. The effect appeared in a more pronounced manner in polyanions, since it defied our usual concepts of greater stabilization in systems with extended delocalization. Here we raise again the question: what is energetically preferred: extended or cross-conjugation? The answer to this question is simple. The most stable delocalized system having charges or electron-donating and accepting groups will be that where there is charge or donor–acceptor alternation. In polyions this will occur in cross-conjugated systems, and in monoions, in extended or cross-conjugated systems. A few examples of compounds are given below for ionic and neutral systems. Thus allyl anion and cation **135**, pentadienyl anion and cation **136** are extended ions with alternating charges and at the extremities of the system. However the amidinium ion has the charge formally in the centre with the electron donors at both ends **137**. The borane anion[126] **138** has the negative charge in the center stabilized by two acceptors. Three donor acceptor interactions of a central atom with its neighbors will stabilize a charge on this atom even more than two interactions **139–149**. The quanidinium ion **146** is not stabilized by Y-aromaticity, since a π-electron sextet is already present in quanidine **145** itself, and one would have therefore expected it to have a lower basicity than amidine. This is not the case. The pKa of **146** is 13.5[127] and that of **137** is 12.41.[128] It is of interest that the pKa of **147** is 12.13[128], since although the two nitrogens are not on the same carbon, they are both on the starred carbons. It is the protonated form that is stabilized more in **146** than in **137**, but not very much. This is a clear saturation effect, since the change from methylamine with a pKa of 10.62[129] to that of **137** is much larger. A similar conclusion can be reached from the results of the calculations of the barrier for C–N rotation[130] in **146**. The barriers for a single, double and triple C–NH_2 rotation were 17.43, 45.35 and 111.63 kcal mol^{-1}. Removal of aromatic character occurs in

135

136



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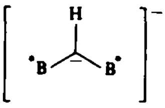

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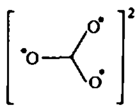

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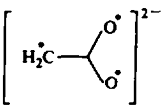

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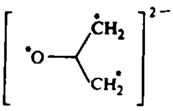

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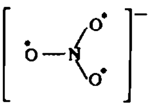

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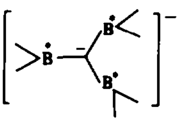

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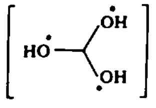

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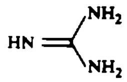

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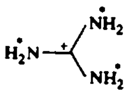

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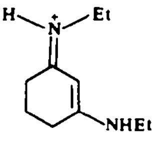
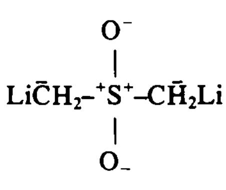


147

the single rotation and nonetheless it is there, where the lowest barrier appears, as expected if one considers that this is the third group to stabilize the positive charge on the central carbon and its contribution to stability should be the smallest. Gem dimetalation is a course taken often by the reaction, although this is less preferable than dimetalation at different starred positions. This was shown before in **21, 22, 66, 69, 70, 71, 73, 76, 78, 99, 101, 102, 105** and also α-to a nitro group[131] **148** to a nitrile[132] **149**.

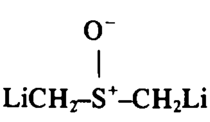
$[\mathrm{RCNO_2}]\mathrm{Li_2}$ **148** $[\mathrm{PhC\ CN}]\mathrm{Li_2}$ **149**

Planarity is not a condition for dimetalation. Charge alternation is found also in **150** and **151**.[132]



$$\underset{\mathrm{O_-}}{\overset{\mathrm{O^-}}{\mathrm{Li\bar{C}H_2{-}{}^{+}S^{+}{-}\bar{C}H_2Li}}}$$

150

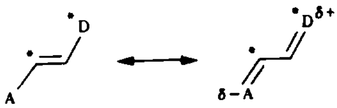


$$\overset{\mathrm{O^-}}{\mathrm{LiCH_2{-}S^{+}{-}CH_2Li}}$$

151

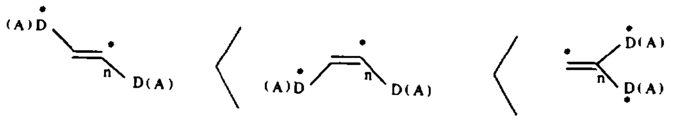
One has to conclude therefore that a donor and acceptor are preferentially linked directly and two donors or two acceptors are in the most stable arrangemnt when linked tthe same atom. Applying the principle of vinylogy one can formulate the general rules for stabilities of the relative arrangements of substituents: (1) A conjugated system containing atoms of different electronegativities or charges reaches highest stabilization when the number of donor–acceptor interactions is the largest possible. This can be obtained by alternating partial charges on neighboring atoms. (2) Two or more substituents of the same kind (donors or acceptors) are stabilized in a delocalized system, when they are placed all on the starred set of atoms in the molecule. (3) Two substituents of different kinds are stabilized when one is one a starred and the other on an unstarred atom of the molecule.

Both these arrangements lead to charge alternations, e.g. for a donor–acceptor (eqn 27). Methylenes carrying positive or negative charges are considered acceptors and donors respectively. Even in the case of polyions, there is charge alternation, since an opposite partial charge is induced on the atoms neighboring the charge-bearing group.



(27)

For olefins and aromatics the sequence of stabilities can be assumed as in eqn (28)–(31).



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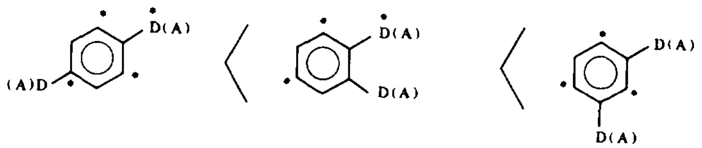

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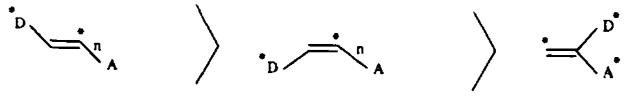

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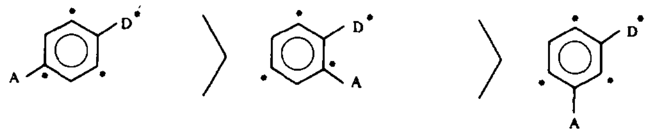
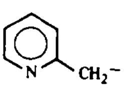


(31)

An apparent contradiction to our rules is the stabilization of a radical by a donor and an acceptor substituent on the odd electron carbon, Viehe's "capto-dative" effect.[133,134]

No direct resonance between the donor and acceptor can be involved in this system. However, the odd electron center is amphoteric and can interact with each of the groups. In these interactions a situation is developed where charge is transferred from the donor via the central atom to LUMO of the acceptor.

The two substituents of the same kind need not be identical. As an example one can take the much discussed question of larger stabilities of the **152** and **153** relative to **154**. The usual explanation is that the charge in **152** and **153** can be delocalized on th electronegative nitrogen,



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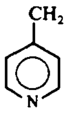

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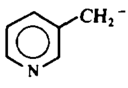

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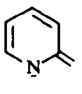

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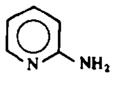

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157

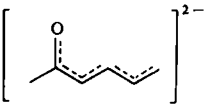
e.g. **155** but this is impossible in **154**. A similar situation is in **156**. However, recent calculations have shown [135] that introduction of a π-electron donor, e.g. NH_2, OH or F on the 2 and 4 position of pyridine increases the π-electron density at the 5-position almost to the same extent as on nitrogen and at the same time decreases even more strongly the π-electron density at the 2, 4 and 6 positions. One has therefore a much more pronounced charge alternation than in the unsubstituted pyridine or in the 3-substituted one. No change in geometry of pyridine was found on introduction on substituents as expected if the electron density were introduced on nitrogen alone. All these substituents stabilize pyridine relative to benzene (calculation of isodesmic energies).

A careful study of acidities of 3- and 4-substituted pyridinium and anilinium ions have been carried out recently.[136] In this study MO calculations of the energies of the bases and their conjugate ions had been carried out at the STO-3G level. A good Hammett relationship has been found between the acidities of the 3-substituted pyridinium and anilinium ions Analysis of the data for the 4-substituted compounds by the method of Taft and Lewis, taking the substituent effects as the sum of field/inductive and resonance effects gave also a reasonably good correlation. It is clear from the MO calculations that this correlation is a result of various effects sometimes acting in opposite directions in both series. First, the 3-substituent is two carbon atoms away from nitrogen in pyridine, but four carbon atoms away in aniline. However this is not the most important factor. The effect of the position of the substituents on the energy of aniline and the anilinium ion are in opposite directions. Thus π-electron donors are more stabilizing in the 3- than in the 4-position in aniline, but are energy-lowering in the 4-relative to the 3-position in the anilinium ions. This is expected since three atoms separate the two groups in the meta substituted aniline and this is a stabilizing arrangement for two donors. An electron acceptor will be more stabilizing at the 4- than at the 3-position. In the pyridines, the situation is different. Here the 4-substituent is three carbons away from nitrogen and an electrondonating group will be more stabilizing there than at the 3-position. However, pyridine is different from anilines, since protonation at nitrogen still leaves an orbital with electrons on it that can interact and one could envisage, e.g. p-aminopyridine as **157**, where a pentadienylic cation is stabilized by amino groups in the 1-, 3- and 5-positions. The effect is much larger in the pyridinium ion than in pyridine itself due to the charge that couples more strongly the two donors.

Charge alternation is of course not a necessary condition for polymetalation to take place and neither is cross-conjugation. A number of polymetalated compounds were prepared with no cross-conjugation, although they were shown to be less stable than the cross-conjugated ones, e.g. **26**, **27**, **28**, **29**, **72**, **84**. However, **28** was shown to be composed of two allyllithium parts. To this group belong also the α,β-dimetalated nitro compounds[137] **158**, that are formed from nitro compounds with one α-hydrogen only. Unsaturated ketones[138] can give di- **159** and tri-metalation **160**. The metalation of an unsaturated amide[139] **161** gave the kinetically preferred **162**, since chelation is easier at the β' than β position. This course of metalation is taken probably because of chelation to the β' position.

$\left[\mathrm{RCHCR'NO_2}\right]^{2-}$

158



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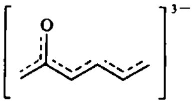

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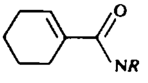

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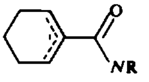

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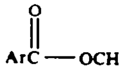


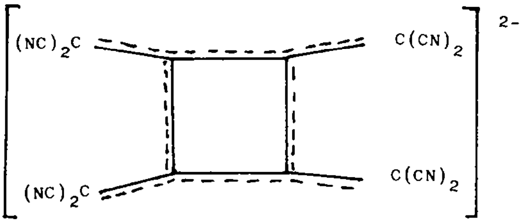
$\mathrm{Ar\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_2}$

163

An important group of compounds where a charge is introduced next to oxygen or nitrogen are the dipole stabilized carbanions,[140] e.g. **163**. Recent calculations have shown[141] that an electronegative heteroatom as σ^- acceptors can stabilize considerably a charge on carbon next to it.

We have shown that delocalized polyions are stabilized relative to their isomers, when cross-conjugated. The reason for this stabilization is not resonance, but charge alternation, where donor–acceptor interactions between nearest neighbors lower the energy of the molecule. Similar stabilization can be achieved in monoions or in uncharged molecules, when the number of donor–acceptor interactions is maximized.

Note added in proof. A derivative of the tetramethylenecyclobutane dianion **164** was recently prepared[142,143] and the charge was found to be located mostly on the exocyclic groups.



164

The relative instability of cyclic delocalized ions vs their cross-conjugated and even extended analogs was found by MO calculations and was attributed to Coulomb repulsions in the cyclic ions.[144]

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