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A CHEMICAL AND THERMOCHEMICAL STUDY OF NON-OBSERVED SYMMETRY ALLOWED REACTIONS†

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Abstract—A variety of reactions, whilst predicted to be symmetry allowed, are not observed experimentally. Several such non-observed yet allowed reactions have been studied in order to understand them and to possibly bring about, with suitably modified substrates, their observation. For example, although ozone adds to π-bonds, the isoelectronic nitro group does not, due to a high activation energy barrier. This reaction is of the type $A \rightleftharpoons B \rightarrow C$. Molecular orbital calculations of a series of 1,3-dipolar species reveal a correlation of the π bond order with their effectiveness in [4 + 2]-additions. Based on this, the nitro group as well as ozone should be considered as poor dipolar agents. The exceptionally high ΔH_f° of ozone (+ 34.00 kcal mol^{-1}) as compared with that of nitrobenzene (+ 3.8 kcal mol^{-1}) could possibly explain the reactivity of the former. This is reflected in an estimated ΔH° value of -45.5 kcal mol^{-1} for the ethylene–ozone addition as compared with + 7.5 kcal mol^{-1} for the *non-occurring* ethylene–nitrobenzene addition. Thermochemical calculations demonstrate that the nitrogroup is more prone to undergo addition as a 2π partner than as a 1,3-dipolar reagent.

The thermal, nitro group—olefin addition has been examined using a variety of electrophilic nitrobenzenes with tetracyclone as the common substrate. The extent of cyclo-addition was assessed on the basis of the isolation of 2-benzoyl-3,4,5-triphenylfuran. 4-Nitro-4′-methyl diphenyl sulfone and 4,4′-dinitro diphenyl sulfone have been identified as efficient reagents for these reactions. The former compound has been found to add to even non-conjugated olefins.

The clean thermal transformation of crystalline 7,7-dimethyl-bicyclo[2.2.1]heptane-1-nitrile oxide to the corresponding isocyanate is an example of the observable $A \rightleftharpoons B \rightarrow C$ change. In this case, the oxazirine corresponding to B, arising from conrotatory cyclisation, undergoes irreversible rupture ($B \rightarrow C$). Such transformations are not observed with the stereochemically more favoured nitrones since these belong to the type $A \rightleftharpoons B$.

The $\pi^4s + \pi^2s$ addition of carboxylates to olefins would lead to a carbon base at the expense of an oxygen one. This is clearly unfavourable and is not observed. On the other hand, the reverse of this reaction, namely, the fragmentation of ketal conjugate bases to carboxylates would be expected to be facile. This is indeed so and the process has been shown to be concerted. Ketals from p-nitrobenzaldehyde are shown to undergo fragmentation with 1,5-diazabicyclo[3.4.0]nonene-5 (DBN) to olefins. The carboxylate–olefin addition belongs to the general category $\pi + A^- \rightleftharpoons B^-$, that encompasses cycloadditions, electrocyclic reactions and sigmatropic shifts. An equation $\Delta G^\circ = [1.4(pK_a^{BH} - pK_a^{AH}) + X]$ kcal mol^{-1}, wherein X is dependent on the reaction type has been derived for predicting the ΔG° for these $\pi + A^- \rightleftharpoons B^-$ processes.

Of practical interest is the development of perturbed $\pi + A_1^- \rightleftharpoons B_1^-$ systems that are predicted to occur in the forward direction, where the parent type $\pi + A^- \rightleftharpoons B^-$ is not favoured. Although no worthwhile synthon may be devised that might simulate either the carboxylate–olefin addition, or the enolate–olefin addition, the perturbation of the allyl anion is possible, principally by substitution with electron-withdrawing substituents at 2 position. Thus, the anions derived from propenes that carry $-CN$, $-NO_2$, $-SO_2Ph$, $-SO_2CF_3$, $-COO^tBu$, $-CO^tBu$ and $-N_2^+$ as 2-substituents are predicted to add to olefins thereby providing novel routes to functionalised cyclopentanes.

In preliminary investigations, the 2-nitropropene anion unit, generated *via* the collapse of nitrocyclopropane-9,9′-fluorene conjugate base, underwent rapid nitrite elimination leading to allene, thus precluding cycloaddition to added styrene. A preference for [2,3] shift over [3,3] is exhibited by oxime–O–allyl ethers as predicted by the above equation. Several observed and non-observed symmetry allowed reactions have been rationalised using the pK$_a$ concept.

Highly unfavourable $\pi + A^- \rightleftharpoons B^-$ changes can be, in principle, realised via the strategy $\pi + A^- \rightleftharpoons B^- \rightarrow C^-$. This is possible by appropriate incorporation of weak bonds such as N–O, S–S and O–O with the B^- unit. Endeavours to illustrate this with an unusual oxadiazolinone carrying a particularly fragile N–O bond and with 3-lithiomethyl benzisoxazole are presented.

The principle of the conservation of orbital symmetry[1] enables a prediction of the feasibility of a concerted process. However, a variety of reactions, whilst predicted to be symmetry allowed, are not observed experimentally. In the present work, using experiment and theory, several such non-observed, allowed reactions have been studied in order to understand them and to possibly bring about, with suitably modified substrates, their observance.

As a first step, non-observed allowed reactions can be separated into two categories, namely, I: $A \rightleftharpoons B \rightarrow C$ and II: $A \rightleftharpoons B$

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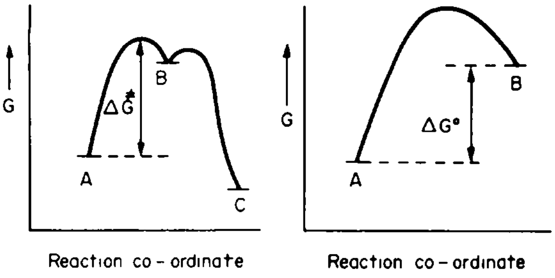
†We respectfully dedicate this work to the memory of Professor R. B. Woodward. This paper will be included in the Book version of the special Woodward Memorial Supplement.



Type I Type II

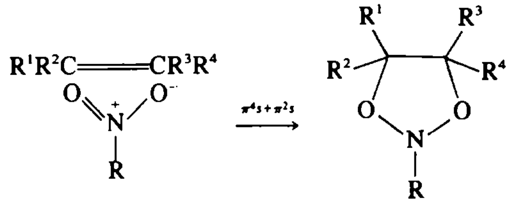
The non-observance of a symmetry allowed A ⇄ B change can be either due to the absence of B in the reaction mixture or because the amount present may be so small that it cannot be detected by the probe employed.

A reaction of the Type I: A ⇄ B → C, offers a method to differentiate the two possibilities mentioned above. In this category, compound B is expected to be rapidly converted to C either on the basis of its preparation by other means or on the basis of reaction mechanisms. If, even after incorporation of such a step, the allowed reaction is not observed, it could be concluded that in the A ⇄ B change, the barrier, which normally is moderate for allowed reactions, is overwhelmingly large. On the other hand, formation of C could be an indication of the presence of B and therefore a demonstration of the occurrence of the symmetry allowed A ⇄ B change.

In spite of a surmountable activation energy barrier and the stability of A and B, an allowed reaction of the Type II may not be observed because of highly unfavourable equilibrium. Each of these types are further discussed below.

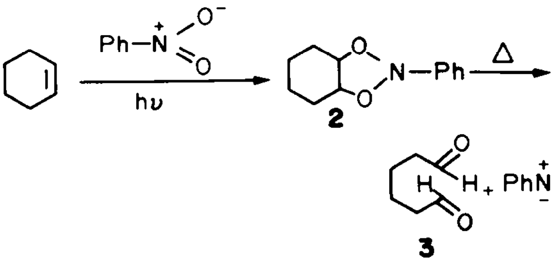
Type I: A ⇄ B → C where A ⇄̸ B. Cycloadditions involving the nitro group

The nitro group being isoelectronic with ozone can be expected to add to olefins leading to **1**:

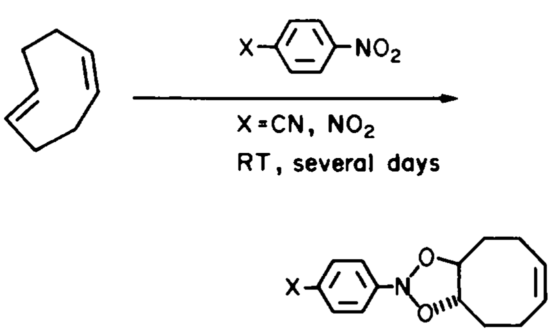


1

However such additions, potentially of great practical significance, are not generally observed.[2] Adducts related to **1** prepared by non-concerted additions are thermally unstable. Thus, the cyclohexene–nitrobenzene adduct **2** decomposes on reaching room temperature to phenylnitrene and the 1,4-dialdehyde **3**:[3]



The ready change **2**→**3** should enable the identification of the thermal olefin–nitro group addition, even though the adduct **2** is formed in extremely small amounts. The complete absence of any reaction on refluxing a variety of 2π-components in nitrobenzene[4] indicates a high barrier to the addition. This conclusion finds support from a study of the cycloaddition of nitro-aromatic compounds to the highly strained *E,Z*-cyclooctadiene.[5] The latter compound undergoes totally stereospecific nitrogroup cycloaddition with aromatic nitro compounds carrying electron-withdrawing substituents leading to 1,3-dioxazolidines:



With nitrobenzene, however, the addition is sluggish and competes with the dimerisation of *E,Z*-cyclo-octadiene itself. Interestingly, this addition is not effective with *E*-cyclooctene for which the "addition strain" has been estimated to be ~ 12 kcal mol⁻¹ lower than the *E,Z*-diene. Of this strain factor, only about 25% contributes to the transition state. Thus, the transition state involving nitro group-olefin cycloaddition is closer to the starting materials. The importance of this observation is discussed later (*vide infra*).

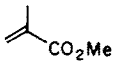
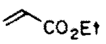
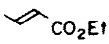
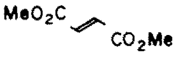
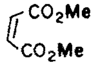
Over the past decade, we have examined diverse aspects of the thermal addition of the nitro group to π systems. Unlike ozone and nitrone, the isoelectronic nitro group does not participate in 1,3-dipolar cycloadditions. To rationalise this experimental reality, efforts were made to correlate observed reactivities in 1,3-dipolar cycloadditions to π-bond order (b.o.) and π-electron densities of the 1,3-dipolar species. Such a correlation should also enable a theoretical evaluation of perturbed nitro systems as potential partners in cycloadditions. We have found that there exists a correlation between the second order rate constants (k_2) of several [4 + 2]-additions and the 1,3-dipolar contribution of the 4π component, as reflected in the π. b.o. computed from Huckel–Molecular Orbital Theory.[6a] the contributing structures are:

$$a = b^+ - c^- \longleftrightarrow a^+ - b - c^-$$

π b.o.	1	0

Thus in Table 1 are presented k_2 values, all converted to 25° using the Arrhenius equation, for the cycloaddition of seven 2π components of diverse character to five 1,3-dipolar components, each one having a central sp nitrogen. The calculated π b.o. are also given. These data have

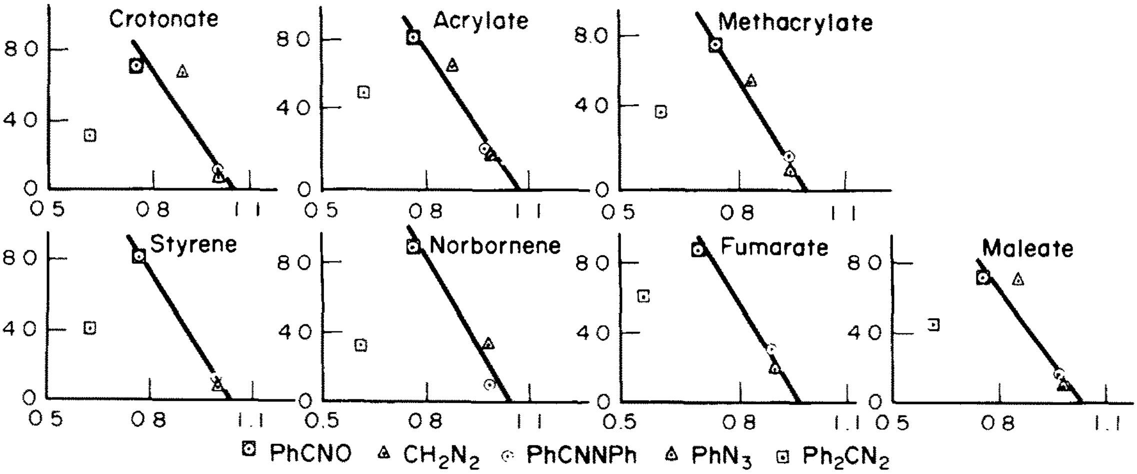
Table 1. Second order rate constants in l mol^{-1} s^{-1} ($k_2 \times 10^8$), all converted to 25°, for the addition of 1,3-dipolar systems with 2π components

1, 3 dipolar system	π b.o.							
$Ph\text{-}\overset{+}{C}{\equiv}\overset{+}{N}\text{-}\overset{-}{O}^{a}$	0.769	2.72×10^8	7.81×10^8	0.12×10^8	11.12×10^8	0.19×10^8	1.10×10^8	11.48×10^8
$H_2C{=}\overset{+}{N}{=}\overset{-}{N}^{b}$	0.873	1.6×10^6	23×10^6	0.19×10^6	—	14×10^6	—	—
$Ph_2C{=}\overset{+}{N}{=}\overset{-}{N}^{c}$	0.617	3.45×10^4	55.1×10^4	0.344×10^4	203×10^4	4.76×10^4	0.0798×10^4	0.169×10^4
$Ph\text{-}C{\equiv}\overset{+}{N}\text{-}\overset{-}{N}-Ph^{d}$	0.981	2.42×10^2	8.65×10^2	0.0881×10^2	37×10^2	1.03×10^2	0.154×10^2	0.339×10^2
$Ph\text{-}N{=}\overset{+}{N}{=}\overset{-}{N}^{e}$	0.997	7.2	98.5	2.7	85	3.4	4	1880

[a] R. Huisgen, R. Grashey and J. Sauer, *Chemistry of Alkenes* (Edited by S. Patai), p. 739–953; [b] A Ledwith and Y. Shih-Lin, *J. Chem. Soc.* (B), 83 (1967); THF; [c] R. Huisgen, H. Stangl, H. J. Sturm and H. Wagenhofer, *Angew. Chem.* **73**, 170 (1961); DMF; [d] A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey and E. Spindler, *Chem. Ber.* **100**, 2192 (1967); [e] R. Huisgen, G. Szeimies and L. Mobius, *Chem. Ber.* **100**, 2494 (1967); CCl_4.

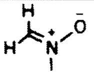
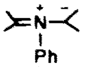
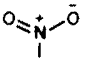
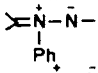
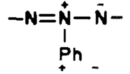
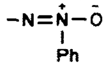
been presented in Chart 1 wherein $\log k_2$ values are plotted against the calculated π b.o. The reasonably good correlation that is found, in spite of the great divergence in the nature of the 2π component is noteworthy.[6b] These correlations bring out the contribution of the 1,3-dipolar character to the kinetic parameters. It should be possible, in principle to isolate the energy factors from the overall interactions that are reflected in the π b.o. We feel, however, that since the utility of this relationship is only to assess the efficacy of a given 1,3-dipole, this simple representation is adequate. It must be pointed out that in all the figures in Chart 1, diphenyldiazomethane exhibits a lower rate than predicted. This must be related to the increased steric crowding in the transition state.

Chart 1. π bond order vs $8 + \log K_2$ for the addition of 1,3-dipolar systems with 2π components (see Table 1).



In Table 2 diverse 1,3-dipolar systems are

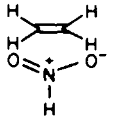
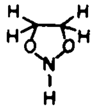
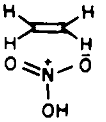
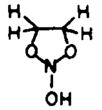
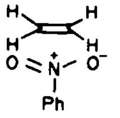
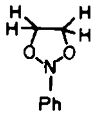
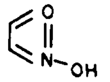
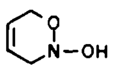
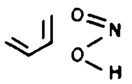
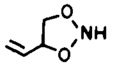
Table 2.

System	π b O	System	π b O	System	π b O	System	π b O
$N{\equiv}\overset{+}{N}-\overset{-}{C}<$	0 873	 $H_2C{=}\overset{+}{N}(-)-\overset{-}{O}$	0.819	 $>{=}\overset{+}{N}(Ph)-\overset{-}{C}<$	1.042	$-N{=}\overset{+}{O}-\overset{-}{N}-$	0 763
$-C{\equiv}\overset{+}{N}-\overset{-}{O}$	0.903	 $O{=}\overset{+}{N}(-)-\overset{-}{O}$	1 262	 $>{=}\overset{+}{N}(Ph)-\overset{-}{N}-$	1 058	$>{=}\overset{+}{O}-\overset{-}{N}-$	0.865
$-C{\equiv}\overset{+}{N}-\overset{-}{C}<$	1 107			 $-N{=}\overset{+}{N}(Ph)-\overset{-}{N}-$	1 109	$>{=}\overset{+}{O}-\overset{-}{O}$	0 899
$-C{\equiv}\overset{+}{N}-\overset{-}{N}-$	1.113			 $-N{=}\overset{+}{N}(Ph)-\overset{-}{O}$	1.165	$>{=}\overset{+}{O}-\overset{-}{C}<$	1.060
$N{\equiv}\overset{+}{N}-\overset{-}{N}$	1.147					$-N{=}\overset{+}{O}-\overset{-}{O}$	1.105
$N{\equiv}\overset{+}{N}-\overset{-}{O}$	1.330					$O{=}\overset{+}{O}-\overset{-}{O}$	1 250

arranged in the order of their π b.o. Although needed kinetic data are not available, a cursory examination of Table 2 brings out, again, a correlation between the calculated π b.o. and the reactivity of the 1,3-dipolar system in cycloaddition. From Table 2 it would be predicted that ozone should be a poor 1,3-dipolar agent just as the nitro group. This conclusion is certainly in error! Ozone has a special feature that makes it a good 1,3-dipolar agent. The exceptionally high heat of formation (ΔH_f°, ° referring to the standard state of 1 M or 1 atm, 25°C) $+34.00\ \mathrm{kcal\ mol^{-1}}$ of ozone compared with a ΔH_f° of $+3.80\ \mathrm{kcal\ mol^{-1}}$ for nitrobenzene[7a] might be making an important contribution, particularly since, in such additions, the transition state is closer to starting materials. To test this, ΔH° for the ethylene–ozone addition as well as that of ethylene to nitrobenzene, nitric acid and nitrous acid were estimated employing group addition methods developed by Benson *et al.*[7b] The important result that whilst the ΔH° estimated for the *occurring* ethylene–ozone addition is $-45.5\ \mathrm{kcal\ mol^{-1}}$, that for the *non-occurring* addition of ethylene to nitrobenzene, nitric acid and nitrous acid are respectively +7.5, +9.6 and $+4.4\ \mathrm{kcal\ mol^{-1}}$ (Table 3).

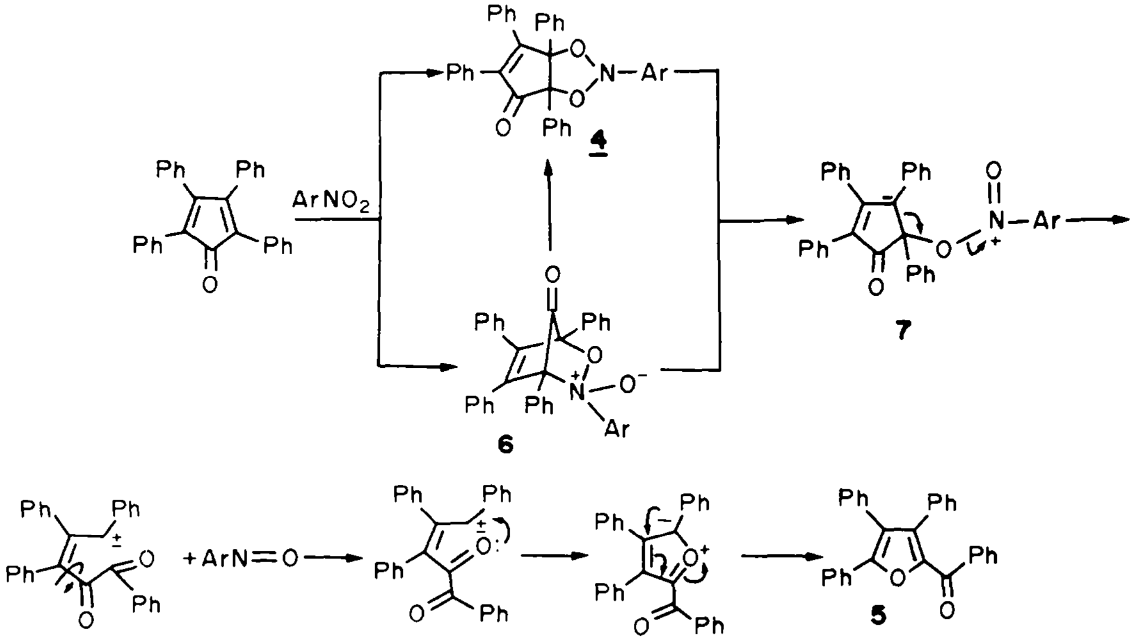
Parenthetically, such calculations demonstrate that the nitro group is more prone to undergo cycloaddition as a 2π partner than as a 1,3-dipolar agent (Table 3). The experimental realisation of $\mathrm{ArNO_2}$–*E*,*Z*-cyclo-octadiene cycloaddition at room temperature suggests that the energy barrier to nitro group cycloaddition can be overcome with perturbed nitro systems. We have calculated the π b.o. for a variety of such perturbed systems. None of them was predicted to be an effective reagent. Simultaneously, however, the cycloaddition of the nitro group to π systems was explored with a wide variation of both the components.

Table 3. Estimated ΔH° values in kcal mol⁻¹

			ΔH°
	→		+4.4
	→		+9.6
	→		+7.5
	→		−26.07
	→		+22.28

Of great significance in this context was the transformation of tetraphenylcyclopentadienone (tetracyclone) to pentaphenylpyrrole in boiling nitrobenzene discovered by Dilthey in 1941![8] We examined this reaction extensively and our results demonstrate that the primary interaction of the two components leads to the formation of the key adduct **4** (Chart 2). This then fragments to nitrosobenzene and 3,4,5-triphenyl-2-benzoylfuran **5**. The adduct **4** might also result by further transformation of the initially formed [4+2]-adduct **6**. The possibility that the oxygen transfer takes place by initial Michael addition of $\mathrm{PhNO_2}$ leading to **7** can be ruled out since $\mathrm{PhNO_2}$ can not parti-

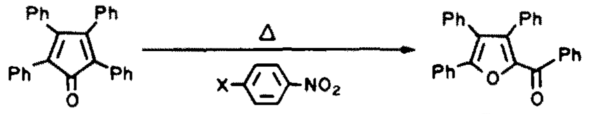
Chart 2



cipate in such processes. Indeed that is the reason for its use as a solvent in Friedel–Craft reactions! The yield of the crystalline furan **5** is then a measure of the extent of addition involving nitrobenzene and tetracyclone. We have examined the yield of the furan **5** as a function of substitution of nitrobenzene. Our results are presented in Table 4.

As in the photochemical cycloadditions, the carbonyl components present were complex. The isolation of azo-compound from reaction of tetracyclone with aromatic nitro compounds (see experimental) clearly establishes the intermediacy of nitrenes. The formation of **8** is not surprising since it is a good substrate for nitrene insertion.

Table 4.



1 m mole

5

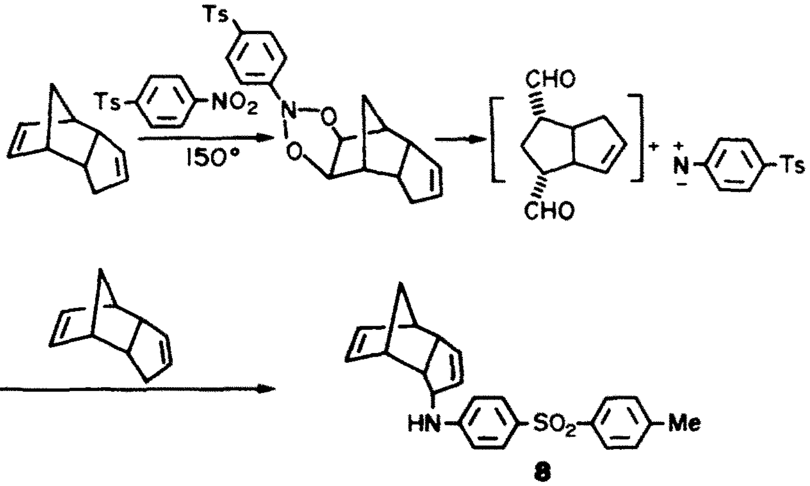
X	Reagent (m moles)	Condition	% Yield of 5
H	excess	$PhNO_2$ reflux; 15 hr	6
CN	10	o-dichlorobenzene reflux; 48 hr	22
CN	10	200°; 7 hr	20
NO_2	10	200°; 7 hr	18
T_s	1	200°; 10 hr	48
N_2^+	1	200°; 6 hr	—

As anticipated, substitution of the nitrobenzene with electron withdrawing groups does increase the furan formation. The fact that a 50% yield of **5** could be realised with equivalent amounts of the reagent 4-nitro-4′-methyl diphenyl sulfone was indeed satisfying.

With a view to clearly establish a thermal nitro group-2π cycloaddition, 4-nitro 4′-methyl diphenyl sulfone, a good reagent for conversion of tetracyclone into **5** change, was reacted with equivalent amounts of acenaphthylene, tolan, maleic anhydride, and indene at 200°C. No reaction was observed. However, 4-nitro 4′-methyl diphenyl sulfone in dicyclopentadiene was rapidly consumed at 150°C and work-up gave a 32% yield of the insertion product **8**.

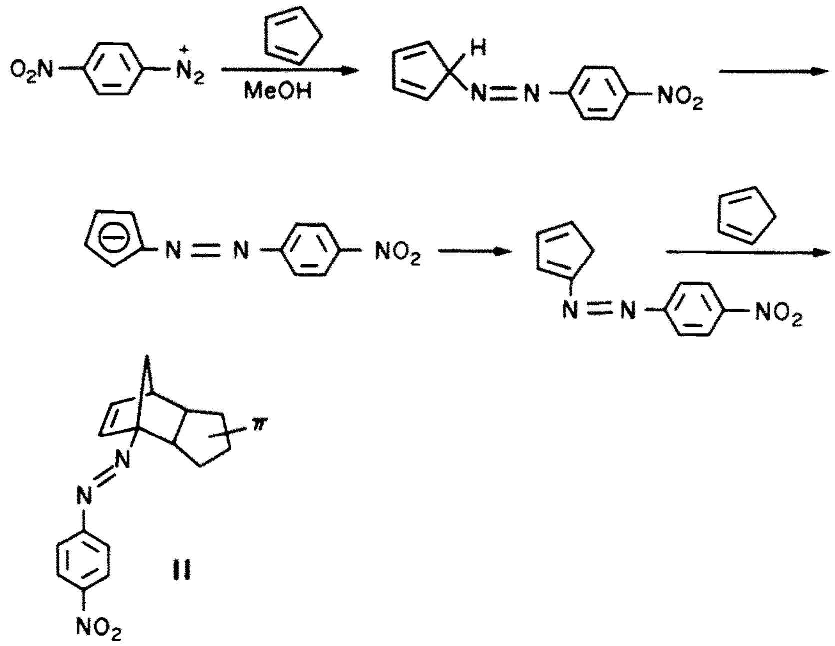
The formation of the nitrene *via* addition to monomeric cyclopentadiene and fragmentation is excluded from blank experiments. The versatility of 4-nitro 4′-methyl diphenyl sulfone in cycloadditions is being further examined.

The crystalline and stable *p*-nitrophenyl diazonium fluoborate **9** was also reacted with a number of π components. However, there was no evidence for the involvement of the nitro group. The major pathway was coupling leading to azo-compounds. Thus, the reaction of freshly cracked cyclopentadiene with **9** in refluxing methanol gave the bright yellow crystalline **11** in 96% yields! The structural assignment for **11** is supported by analysis, IR, NMR, MS, UV, UV(H^+), UV(OH^-) and its formation rationalized in Chart 3.



8

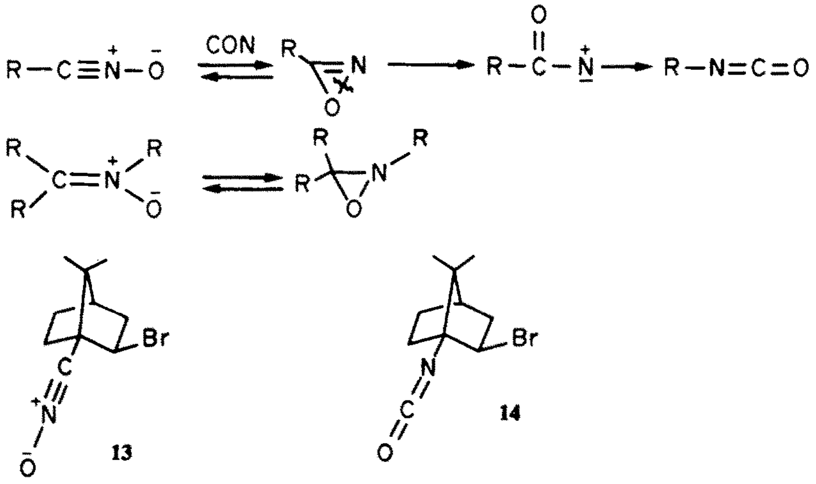
Chart 3



Type I: $A \rightleftarrows B \rightarrow C$. *The nitrile oxide⟶isocyanate rearrangement*

Nitrile oxides which do not dimerize are converted thermally to isocyanates. This change is concerted as evident from studies with labelled substrates[9] and from our own observation[10] of the smooth transformation of the stable bridgehead nitrile oxide **13** to the corresponding isocyanate **14**. The rearrangement therefore, must be taking place *via* a conrotatory cyclization followed by an irreversible oxazirine opening and Curtius rearrangement (Chart 4). The occurrence of the cyclization is discernable because of the irreversible removal of the intermediate oxazirine. Thus this change belongs to the type I: $A \rightleftarrows B \rightarrow C$. Interestingly, the related nitrone ⟶ oxazirane change, although stereochemically more favourable, is not observed.[11] Indeed, the observed transformation is oxazirane ⟶ nitrone.[12] The reaction is not observed since it belongs to the type $A \rightleftarrows B$ wherein the forward change is not favoured (Chart 4).

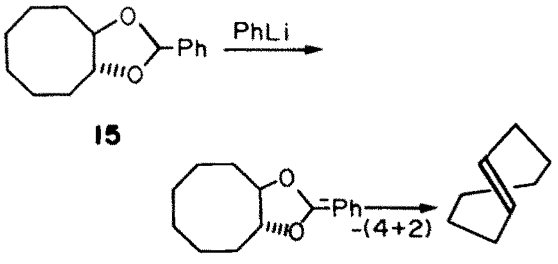
Chart 4



Type II: $A \rightleftarrows B$. $\pi + A^- \rightleftarrows B^-$ *cycloadditions*

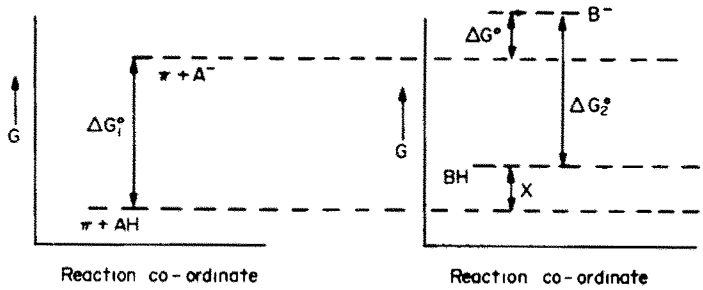
A surprisingly large number of reactions involve the concerted transformation of an electron excess species ($\pi + A^-$) to another (B^-) wherein the process $\pi + A^- \rightleftarrows B^-$ is not complicated by irreversible side reactions. In such cases, provided the kinetic barrier is surmountable the direction of a symmetry "allowed" reaction will be dictated by ΔG° factors. This rationalization finds much support in numerous examples that have come up recently. The (4 + 2) addition of carboxylates and enolates to olefins, *inter alia*, represents an important class of non-observed allowed, $\pi +$

$A^- \rightleftarrows B^-$ reactions. In these and related systems, the $B^- \rightarrow A^- + \pi$ change takes place with great ease and has become a useful method in organic synthesis. Such a fragmentation can be clean and must be proceeding in a concerted manner as evidenced by the formation of *E*-cyclooctene in 85% yield from ketal conjugate base generated from **15**:[13]



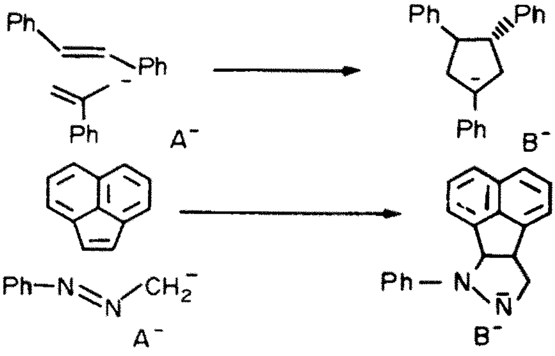
15

We have derived a relationship that correlates ΔG° of a $\pi + A^- \rightleftarrows B^-$ change with the pK_a of the respective conjugate acids AH and BH. The genesis of this relationship, represented by eqn (1) becomes apparent with the following illustration:



$$\Delta G_2^\circ - \Delta G_1^\circ + X = \Delta G^\circ = [1.4(pK_a^{BH} - pK_a^{AH}) + X](\text{kcal mol}^{-1}) \qquad (1)$$

Since the pK_a of AH and BH are available or could be approximated,[20] the realization of the magnitude of X would enable the estimation of the ΔG° that is responsible for the non-observance of a symmetry allowed reaction. Fortunately, in cycloaddition reactions, a fair idea of the importance of X can be extracted from experimental observations. That this is modest is brought out by the following observed reactions where the pK_a differences are very marginal.[14,15]

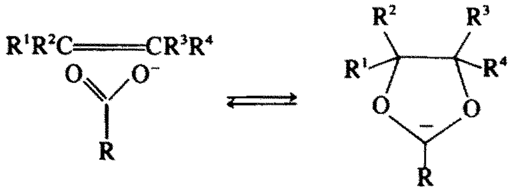


The π strain of acenaphthylene is responsible for the above cycloaddition since $Ph{-}N{=}N{-}CH_2^-$ does not add to normal double bonds. Thus, it could be concluded that the allowed $\pi + A^- \rightleftarrows B^-$ change would be observed if the first term of the right hand side of eqn (1) is not very unfavourable. We feel that eqn (1) could be used with great advantage and this aspect is illustrated below.

THE APPLICATION OF EQN (1) TO ALLOWED $\pi + A^- \rightleftarrows B^-$ REACTIONS

Cycloaddition reactions

Carboxylate–olefin cycloaddition. The $\pi^4s + \pi^2s$ addition of carboxylate to olefins leads to a ketal conjugate base:



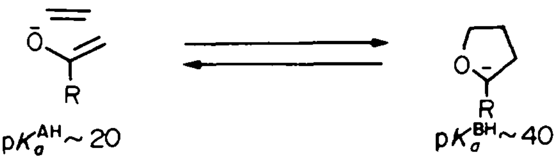
$pK_a^{AH} \sim 5$ $\qquad$ $pK_a^{BH} \sim 35$

$$\Delta G^\circ \cong 1.4(35 - 5) + X = [42 + X]\text{ kcal mol}^{-1}$$

One could readily see that the free energy difference here is truly formidable and the great propensity for the reverse fragmentation is understandable. It can also be concluded that the reaction would proceed in the forward direction in the event the product carbon acid is stronger than the starting oxygen acid. It is difficult to suggest such an example with uncomplicated substrates and therefore we hold little hope of designing a carboxylate that would add to olefins. However, the reverse process could be exploited for the transformation, *vic*-diols to olefins.

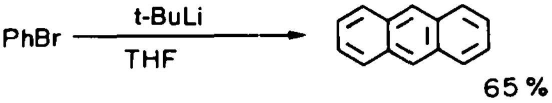
The fragmentation of ketal conjugate bases is complicated in the case of substrates having other similar acidic sites. Thus, *meso* hydrobenzoin–benzaldehyde ketal gave only 6% *trans* stilbene from complex mixture arising from treatment with ^{n}BuLi.[16] We felt that an enhancement of the acidity of the proton involved in ketal fragmentation would enable the reaction to proceed well and therefore *p*-nitrobenzaldehyde could be a useful reagent for the transformation of *vic* diols to olefins. In the event, the ketal from *p*-nitro-benzaldehyde and *meso* hydrobenzoin **16** resisted fragmentation under mild conditions, where the initially formed *cis* stilbene is stable. However a 43% yield of *trans* stilbene was obtained on treatment of the ketal at 200°C for 2 hr with DBN.

Enolate–olefin cycloadditions



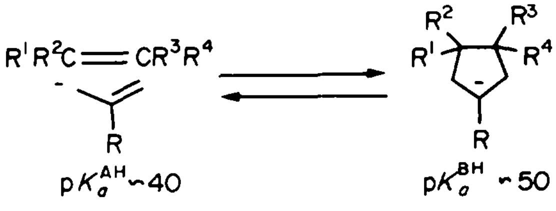
$$\Delta G^\circ \cong [28 + X] \text{ kcal mol}^{-1}$$

As in the previous case, this reaction is also highly unfavourable and as anticipated, the reverse process is exceedingly facile. Conjugate bases of tetrahydrofurans readily fragment to enolates and indeed this method has been exploited for the clean generation of enolates.[17] The ubiquitous nature of this fragmentation is best illustrated with the following fascinating transformation:[18]



In view of the highly unfavourable ΔG° associated with the enolate + π system, it is difficult to tailor perturbed simple synthons that would take the reaction in the forward direction.

Allyl anion–olefin cycloadditions. It should be noted that in the above reaction one carbon base is transformed to another and, in contrast to the previous cases, the allyl anion system presents maximum versatility for perturbation leading to observable $\pi + A^- \rightleftarrows B^-$ reactions. Indeeed, the only $\pi + A^- \rightleftarrows B^-$ reactions, thus far observed, belongs to this type, wherein an initially formed carbon base is transformed either to a more stabilized carbanion or a nitrogen equivalent.[19] In both cases, the ΔG° can be predicted to be favourable (Chart 5). We feel that the allyl anion-olefin cycloaddition with perturbed substrates can be used to advantage in organic synthesis. A few of the possibilities, each predicted [20] on the basis of eqn (1) to take place, are presented in Chart 6.



$$\Delta G^\circ \cong [14 + X] \text{ kcal mol}^{-1}$$

An excellent method for the generation of 2-substituted propenyl carbanions envisaged in Chart 6 is *via* collapse of appropriate cyclo-

Chart 5

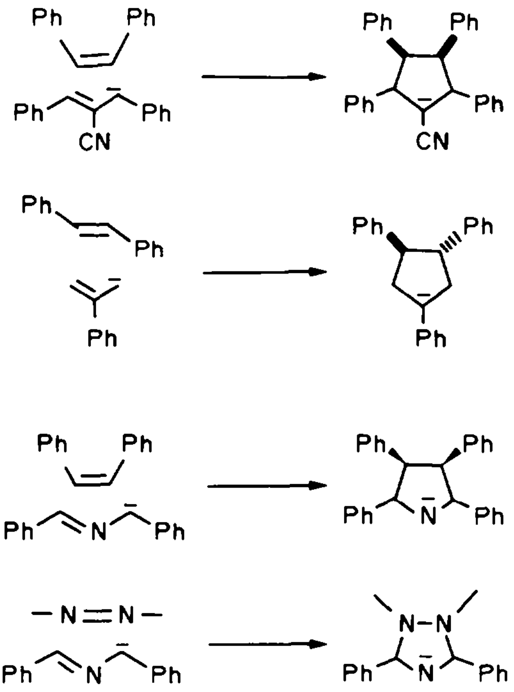
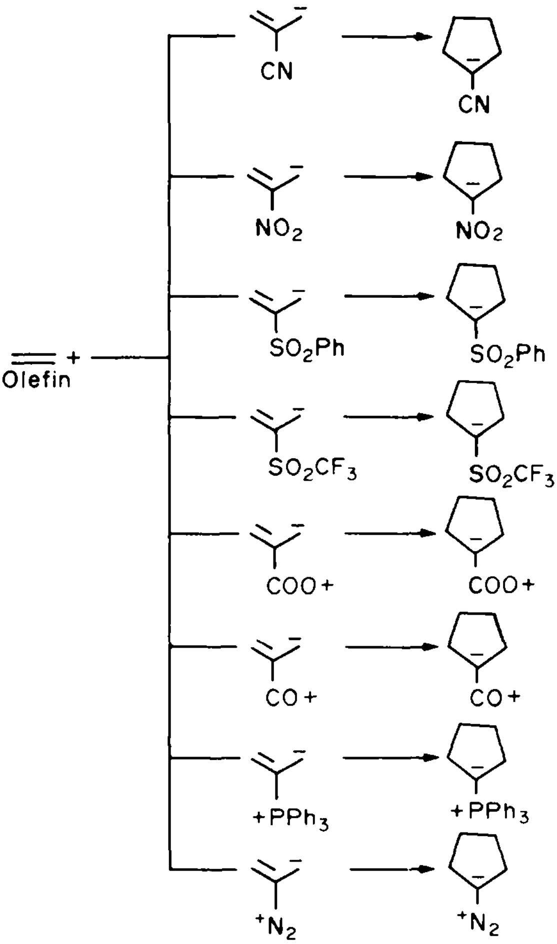
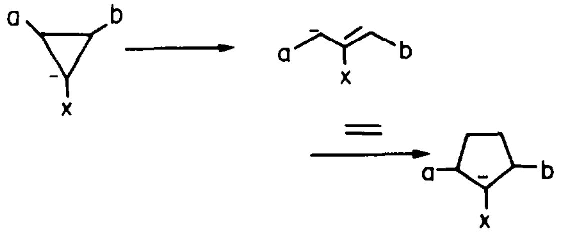
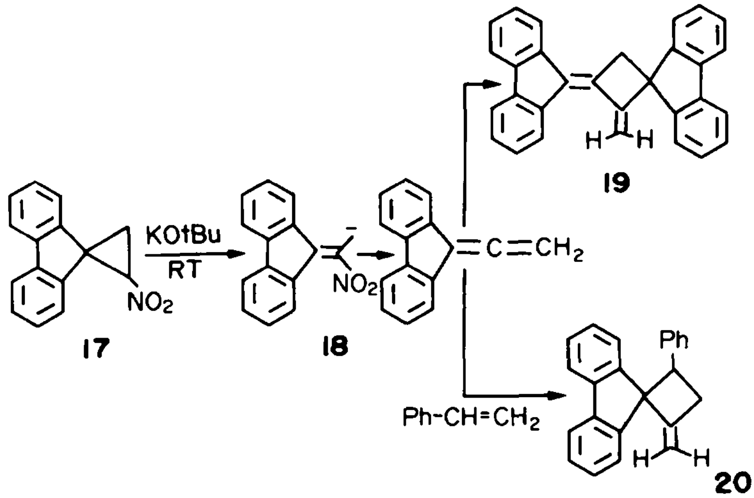


Chart 6





propane anions.[21] In this approach the cyclopropane strain is exploited to generate a stronger carbon base. Employing this strategy we generated the 2-nitropropenyl anion **18** by collapse of nitronate generated from the nitrospiro compound **17**:[22]

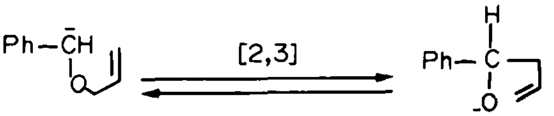


17 **18** **19** **20**

Unfortunately, at room temperature, **18** eliminated nitrite leading to allene which partly dimerised to **19** and partly underwent [2 + 2]-addition with styrene, introduced to capture **18** to give **20**. Modified conditions to curb the tendency of compounds related to **18** to eliminate and the generation of several species presented in Chart 6 are being explored.

Sigmatropic reactions

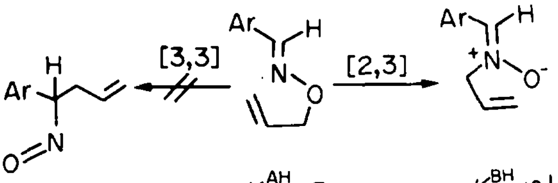
The pK_a considerations represented by eqn (1) become even more significant in the area of sigmatropic reactions of the type $A^- \rightleftarrows B^-$ since the value of X now principally associated with the activation energy ceases to be a major consideration. Thus the facile [2,3] shift represented by the following can be readily rationalized:[23]



$pK_a^{AH} \sim 35$ $pK_a^{BH} \sim 20$

$\Delta G^\circ \cong [-21.0 + X]$ kcal mol^{-1}

Indeed a great majority of the [2,3] shifts can be analysed in terms of such favoured $A^- \rightleftarrows B^-$ changes.[24] Our earlier unexpected finding that oxime–O–allyl ethers undergo [2,3] sigmatropic shift in preference to [3,3] can now be rationalised:[25]

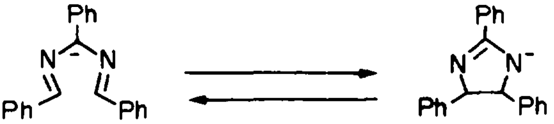


$pK_a^{AH} \sim 5$ $pK_a^{BH} \sim 1$

$\Delta G^\circ \cong [-5.6 + X]$ kcal.mol^{-1}

Electrocyclic reactions

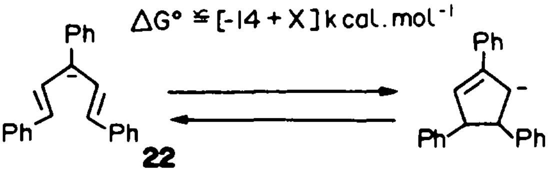
Equation (1) provides a ready rationalisation for the fact that whilst **21** undergoes ready cyclisation[26] such a process does not take place either with **22** or with **23**.[27]



21

$pK_a^{AH} \sim 30$ $pK_a^{BH} \sim 20$

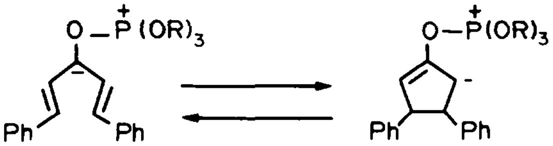
$\Delta G^\circ \cong [-14 + X]$ kcal.mol^{-1}



22

$pK_a^{AH} \sim 33$ $pK_a^{BH} \sim 35$

$\Delta G^\circ \cong [2.8 + X]$ kcal.mol^{-1}

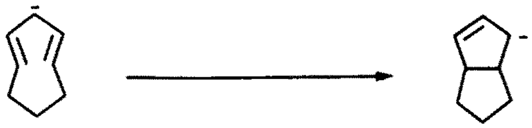


23

$pK_a^{AH} \sim 25$ $pK_a^{BH} \sim 35$

$\Delta G^\circ = [14 + X]$ kcal.mol^{-1}

Nearly all treatises on Woodward–Hoffmann rules cite the following as a typical disrotatory cyclisation:[1]

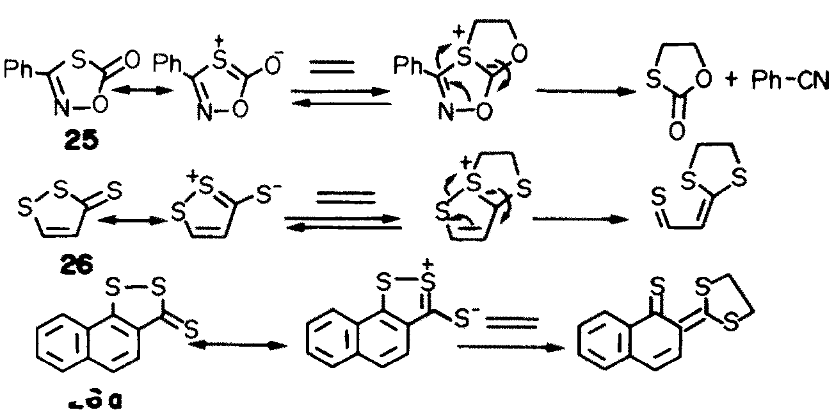


24

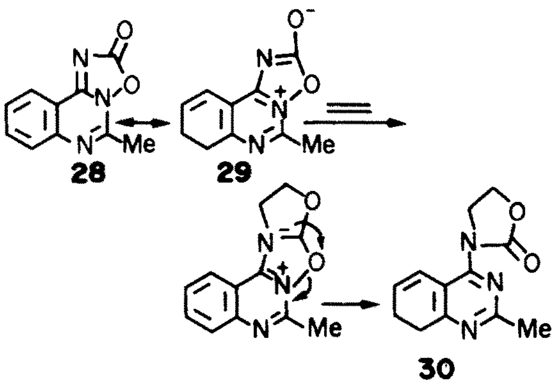
The above reaction represents a cyclopentadiene anion–allyl anion type cyclisation which according to eqn (1) would be predicted to be unfavourable. A ready explanation that seems to have been overlooked thus far was provided in the original paper itself.[28] Models, confirmed by NMR studies, clearly show that the five-centred dienide ion cannot achieve coplanarity. The best conformation associated with the observed cyclisation is one where the middle carbon is lifted from the plane by as much as 30°. The cyclisation then transforms a relatively destabilized carbanion to a stable allyl anion. This has been clearly pointed out by Bates,[28] who estimated the $\Delta G°$ for this change to be $-3\ \mathrm{kcal\ mol^{-1}}$. Indeed, he has made the interesting prediction that when the ring size that incorporates the penta-dienide anion unit is increased, the cyclised form would be destabilized and therefore, the reaction may not take place. The cyclo–octadiene anion cyclisation is not an electrocyclic process in the normal sense.

THE DEMONSTRATION OF $A \rightleftarrows B \rightarrow C$ REACTIONS BY INCORPORATION OF WEAK BONDS

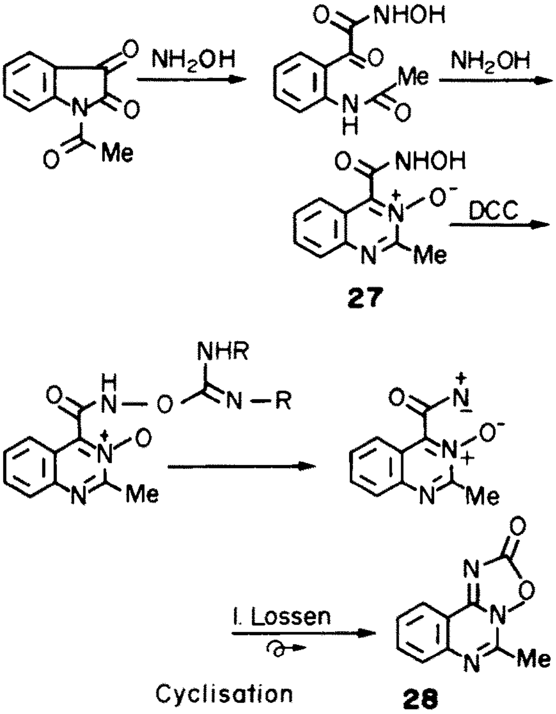
As stated earlier it is, in principle, possible to demonstrate the occurrence of non-observable $A \rightleftarrows B$ change by incorporating the feature $A \rightleftarrows B \rightarrow C$. For example in the nitrile oxide → isocyanate change the key step is the rupture of the weak N–O bond of oxazirine arising from con-rotatory cyclisation. Even the most unfavourable carboxylate–olefin cycloaddition may be, accomplished by this strategy. Thus, the weak bonded systems **25**,[29] **26**[30] and **26a**[31] could be considered as masked equivalents of the thiocarboxylate in cycloadditions:



We have examined the unusual oxadiazolinone **28** as a carboxylate equivalent in cycloadditions. Because of the major contributing structure **29** it should lead to the quinoxaline **30** *via* a facile N–O bond rupture.

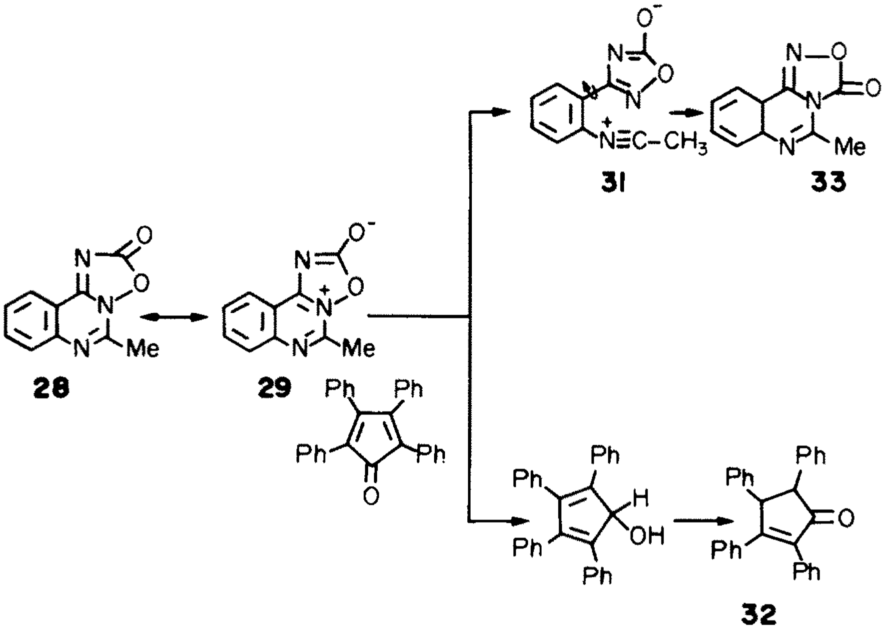


Although **28** is known,[32] details relating to its preparation as well as yields are not available. It arises from N-acetylisation *via* the interesting sequence. Initially, we faced problems in preparing



27 as well as **28**. However, they can now be obtained by precise procedures presented in the experimental section. The thermal reaction of **28** with tetraphenylcyclopentadienone at 200° for 6 hr gave a 50% yield of the isomeric oxadiazolinone

33,[33,34] and a 20% yield of cyclopentenone 32. The formation of 33 and 32 are rationalized *via* novel pathways outlined below highlighting the importance of the contributing structure **29**:



A systematic study of **28** in cycloadditions is in progress.

The weak N–O bond of isoxazoles can be advantageously used to promote allyl anion–olefin type cycloaddition reactions. The versatility of this approach is illustrated in Chart 7 with 3,5-dimethylisoxazole. The conjugate base of 3-methylbenzisoxazole presents an unusual combination and illustrates the possible transformation of a strong carbon base to a very weak phenolate *via* cycloaddition and N–O bond rupture. (Chart 8).

3-Methylbenzisoxazole[35] was prepared by an improved procedure. Deuterium exchange experiments showed that NaH in dimethoxyethane

Chart 7

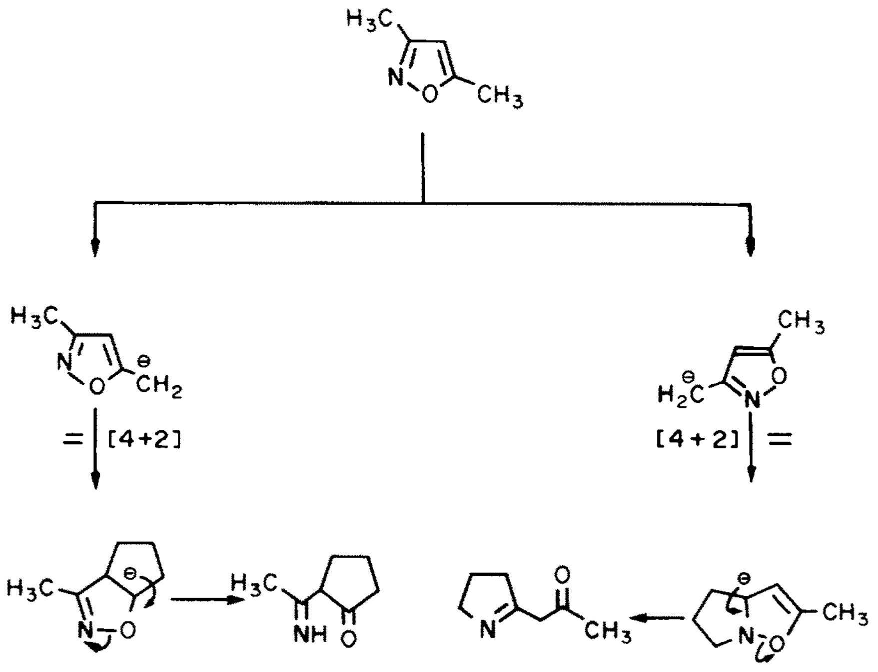
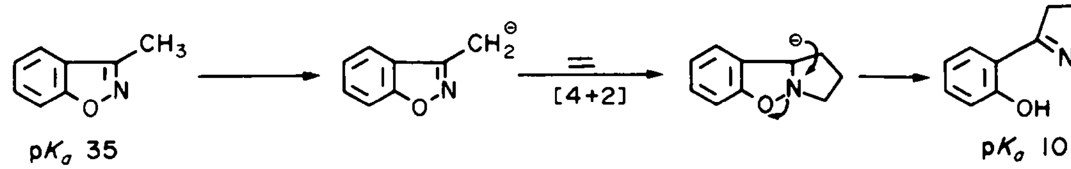
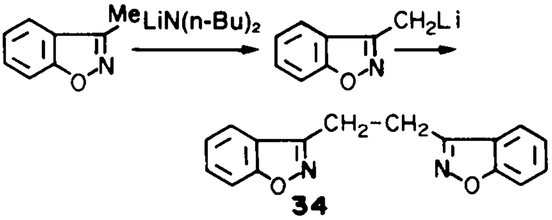


Chart 8



was ineffective. However, the involvement of 3-lithiomethylbenzisoxazole was clearly demonstrated with lithium di-n-butylamide by isolation of dimer **34**.



34

The versatility of 3-lithiomethylbenzisoxazole in cycloadditions is under study.

An understanding of a wide variety of non-observed symmetry allowed reactions, an untapped facet of Woodward–Hoffmann rules, has been attempted in this study. Further efforts in this direction could lead to the identification of new reagents, new reaction types and useful synthetic strategies.

EXPERIMENTAL

Melting points and boiling points are uncorrected. IR spectra were recorded on Perkin–Elmer Model 377 and 580 spectrophotometers as neat liquids or solids as KBr discs. NMR spectra were obtained on approximately 10–15% solutions mostly in $CDCl_3$ on A-60D and R-90 spectrometers. The chemical shifts are reported in ppm downfield from TMS at 0.00 as internal standard. Mass spectra were obtained from a Jeol instrument. Elemental analysis were carried out in Coleman automatic C, H and N analysers. Silica gel (Acme) was used for tlc and column chromatography was done on silica gel (Acme, 100–200 mesh). Reactions were monitored, wherever possible, by tlc.

Reaction of tetracyclone in boiling nitrobenzene: isolation of pentraphenylpyrrole, tetraphenyl N-phenyl 2-oxo 4-pyrroline, 2-benzoyl triphenyl furan (5) and benzanilide

A solution of tetracyclone (3.84 g, 0.01 mole) in nitrobenzene (25 ml) was refluxed for 15 h. Excess nitrobenzene was removed *in vacuo*, the residue steam distilled to remove nitrosobenzene formed in the reaction, extracted with benzene, the organic layer dried ($MgSO_4$), solvents evaporated and the residue chromatographed over silica gel. Elution with benzene : hexane (1 : 1) followed by benzene gave 0.81 g (18%) of pentaphenylpyrrole, mp 283–84° [lit[8] m.p. 283–84°; IR: ν_{max}(KBr) cm^{-1}: 1590], followed by 0.93 g (20%) of tetraphenyl N-phenyl 2-oxo 4-pyrroline m.p. 158–59° [lit[36] m.p. 158–59°; IR: ν_{max}(KBr) cm^{-1}; 1710 ($>$C=O], and 0.24 g (6%) furan **5**, m.p. 166–67° [lit[37] m.p. 166–67°; IR: ν_{max}(KBr) cm^{-1}: 1635($>$C=O]. All compounds were identified on the basis of comparison of their spectra with authentic samples.

Reaction of tetracyclone with p-cyano nitrobenzene in boiling o-dichlorobenzene: isolation of 5, tetraphenyl N-p-cyanophenyl 2-oxo 4-pyrroline and 4,4'-dicyanoazobenzene

Under nitrogen, a solution of tetracyclone (0.38 g, 0.001 mole) and *p*-cyano-nitrobenzene[38] (1.5 g, 0.01 mole) in *o*-dichlorobenzene was refluxed for 48 hr. Solvents were evaporated under reduced pressure, excess *p*-cyano-nitrobenzene removed by vacuum sublimation, triturated with benzene (10 ml), the resulting extract evaporated and the residue chromatographed over silica gel. Elution with benzene: ethyl acetate (1 : 1) gave 0.09 g (22%) of **5**, m.p. 164–66°, 0.16 g (33%) of tetraphenyl N-p-cyanophenyl 2-oxo 4-pyrroline, m.p. 213–15° [Calc. C, 86.06; H, 4.91; N, 5.73; Found C, 85.86; H, 5.02; N, 5.95%; IR: ν_{max}(KBr) cm^{-1}: 2200(CN), 1730($>$C=O)] and 0.01 g (5%) of 4,4'-dicyanoazobenzene m.p. 263–66° (lit.[39] m.p. 268–70°, Calc. C, 72.41; H, 3.44; N, 24.13; Found C, 72.58; H, 3.55; N, 24.06%; IR: ν_{max}(KBr) cm^{-1}: 2200(CN)].

Neat thermal reaction of tetracyclone with p-cyanonitrobenzene

A mixture of tetracyclone (3.84 g, 0.01 mole) and *p*-cyanonitrobenzene (14.8 g, 0.1 mole) under N_2 was held at 200–210°C for 7 h in a sealed tube. Excess *p*-cyanonitrobenzene was removed by sublimination and work up as described above gave 0.81 g (20%) furan **5**, m.p. 166–167°C, 1.47 (30%) of the 2-oxo-4-pyrroline m.p. 215–218°C, 0.22 g (10%) of 4-cyanobenzanilide, m.p. 160–162° and 0.11 g (5%) 4,4'-dicyanoazobenzene, m.p. 263–266°.

Neat thermal reaction of tetracyclone with p-dinotrobenzene

An intimate mixture of tetracyclone (0.384 g, 0.001 mole) and *p*-dinitrobenzene (1.68 g, 0.01 mole) was held at 200° for 7 h. under N_2 in a sealed tube. The reaction mixture was triturated with benzene and the organic extract of chromatography over silica gel gave 0.7 g (18%) of furan **5** on elution with benzene.

Neat thermal reaction of tetracyclone with 4-nitro-4'-methyl diphenyl sulfone

4-Nitro-4'-methyl diphenyl sulfone was prepared by an improved procedure. Under nitrogen, a mixture of *p*-dinitrobenzene[40] (5 g, 0.0297 mole) and sodium *p*-toluene sulfinate[41] (6 g, 0.0337 mole) in dry dimethylsulfoxide was left stirred at room temperature for 18 h, poured into ice water, the precipitated solid collected and crystallised from absolute alcohol to give 7.5 g (91%) of 4-nitro-4'-methyl diphenyl sulfone, m.p. 170° (lit[42] m.p. 170–71°). Calc. C, 56.32; H, 3.97; Found C, 56.58; H, 3.38%; IR: ν_{max}(KBr) cm^{-1}: 1535, 1350(NO_2), 1305, 1160, 1100(SO_2); NMR: $\delta_{(CDCl_3)}$: 8.06(q, 2H, 3H), 7.73(d, 2'H), 7.26(d,3'H), 2.32(S,CH_3).

In a sealed tube, an intimate mixture of tetracyclone (1.884 g, 0.0049 mole) and 4-nitro-4'-methyl-diphenylsulfone (1.108 g, 0.004 mole) was held at 200° for 10 h. The reaction mixture was triturated with benzene and the organic extract on chromatography over silicagel gave 0.770 g (48%) of furan **5** m.p. 164–65° on elution with benzene and 0.921 g (37%) of pale yellow tetraphenyl N-p-tosylphenyl-2-oxo 4-pyrroline m.p. 244° on further elution with benzene: ethylacetate (19 : 1) Calc. C, 79.74; H, 5.02; N, 2.27; Found C, 79.84; H, 5.20; N, 2.27%; IR: ν_{max}(KBr) cm^{-1}: 1730($>$C=O), 1305, 1150, 1105(SO_2); NMR: $\delta_{(CDCl_3)}$: 7.8–6.7(m, aromatic protons); 2.28(s, CH_3).

Reaction of 4-nitro-4'-methyl-diphtnyl sulfone with dicyclopentadiene: isolation of nitrene insertion product **8**

A solution of 4-nitro-4'-methyl diphenyl sulfone (2.0 g, 0.0072 mole) in dicyclopentadiene (25 ml) was heated at 150° for 3 h, diluted with hexane, decanted and the residue chromatographed on silica gel. Elution wth ethyl acetate: benzene (1 : 19) gave 0.891 g (32%) of **8** as a foam. IR: ν_{max}(KBr) cm^{-1}: 3400(NH), 1305, 1160, 1105(SO$_2$); NMR: $\delta_{(CCl_4)}$: 9.5(m, N$\underline{H}$), 7.55(d, 2H, 3H), 7.1(m, 2'H), 6.75(b, 3'H), 5.5(m, olefinic), 2.25(s, C$\underline{H}_3$). In addition to **8**, a carbonyl containing compound was also isolated.

Reaction of p-*nitrobenzene diazonium fluoborate with cyclopentadiene: isolation of adduct* **11**

Freshly cracked cyclopentadiene (10 ml) was added, in drops, to a refluxing solution of *p*-nitrobenzene diazonium fluoborate[40] (1.1 g, 0.0046 mole) in methanol (75 ml). The reaction was complete after 1 h reflux (tlc). Solvents were evaporated, the residue washed with benzene and chromatographed on silica gel. Elution with hexane: benzene (1:9) gave 1.25 g (96%) of **11** as a yellow solid which was crystallised from dilute ethanol m.p. 175–178°. Calc. C, 64.2; H, 5.35% (hydrate). Found. C, 64.6; H, 4.8; *m/e*: 281(M$^+$); IR: ν_{max}(KBr) cm^{-1}: 1510, 1325(NO$_2$); NMR: $\delta_{(CDCl_3)}$: 7.95(d, J = 9 Hz), 6.9(d, J = 9 Hz, π isomer a), 6.85(d, J = 9 Hz, π isomer b), 5.9(m, olefinic).

Reaction of meso-*hydrobenzoin 4-nitrobenzaldehyde acetal with DBN: isolation of* trans-*stilbene*

A solution of *meso*-hydrobenzoin-4-nitrobenzaldehyde acetal[43] (0.35 g, 0.001 mole) m.p. 110–11° in DBN (2 ml) was held at 200° for 2 h, triturated with water (30 ml), decanted, the residue extracted with benzene (20 ml), solvents evaporated and chromatographed over silica gel. Elution with hexane gave 0.08 g (44%) of *trans*-stilbene m.p. 118–21°.

Reaction of 2-nitrospirocyclopropane 1,9'-fluorene (**17**) *with potassium t-butoxide: attempted cyclo-addition of 2-nitropropenyl anion* **18** *with styrene: isolation of allene dimer* **19** *and allene-styrene adduct* **20**

Under nitrogen and stirring, to a heterogeneous solution of KO^{t}Bu (0.61 g, 0.0054 mole) in dry benzene (15–20 ml) was added **17**[22] (1.2 g, 0.005 mole), soon followed by a dry benzene solution of freshly prepared styrene (5.2 g, 0.05 mole). The resulting yellowish red reaction mixture was left stirred for 4 h, cooled (ice), acidified with 2 ml of 1N H$_2$SO$_4$, diluted with water, extracted with benznee, washed with saturated NaCl, dried (MgSO$_4$), solvents evaporated and the residue (1.3 g) chromatographed on silica gel. Elution with hexane : benzene (1:9) gave 0.09 g (6.2%) of **20**: m.p. 83–84°: Calc. C, 93.87; H, 6.12%; Found C, 93.88; H, 6.35%; NMR: $\delta_{(CDCl_3)}$: 7.8–6.4(m, aromatic), 4.82(t, *exo*-CH$_2$), 4.5(t, *exo*-CH$_2$), 4.25(d, benzylic), 3.42(m, ring CH$_2$).

Further elution with hexane : benzene (1 : 4) gave 0.26 g (13%) of the yellow allene dimer **19**. m.p. 247°. Calc. C, 94.73; H, 5.26; Found C, 94.60; H, 5.13%; NMR: $\delta_{(CDCl_3)}$: 8.15–6.82(m, aromatic), 6.2(d, highly shielded aromatic), 5.38(s, *exo*-C$\underline{H}^a_2$), 4.75(s, *exo*-C$\underline{H}^b_2$), 2.6(s, ring C$\underline{H}_2$).

Preparation of Oxadiazolinone **28**

2-Methyl-3-N-oxidoquinazoline-4-hydroxamic acid **27**. Sodium acetate (2 g) and hydroxylaminehydrochloride (1 g, 0.014 mole) were separately dissolved in the minimum amount of water, mixed, and added to N-acetylisatin[44] (1 g, 0.0056 mole). Ethanol was added gradually and with stirring to the mixture until a clear solution was obtained (~ 30 ml EtOH), then refluxed for 0.5 h, concentrated to half the volume and left overnight in the refrigerator. The white crystalline **27** was collected, washed with alcohol : water (1:1) and crystallised from hot ethanol m.p. 239–40°. (lit[32] m.p. 240°); yield 0.66 g (57%); Calc. C, 54.79; H, 4.11; N, 19.1; Found C, 54.60; H, 4.00; N, 18.8%; IR: ν_{max}(KBr) cm^{-1}: 3120, 1655, 1600, 1538, 1490; NMR: $\delta_{(DMSO)}$: 7.9–7.55(m, aromatic), 6.15(b, N$\underline{H}$O$\underline{H}$), 2.72(S, C$\underline{H}_3$).

Lossen rearrangement followed by cyclisation of **27**: *preparation of oxadiazolinone* **28**

A mixture of the hydroxamic acid **27** (2 g, 0.009 mole) and dicyclohexylcarbodiimide (2 g, 0.009 mole) in dry dioxan (50 ml) was refluxed for 1 hr, the clear solution left aside at room temperature overnight, dicyclohexyl urea was filtered off, washed with ethylacetate, the combined filtrates evaporated *in vacuo* and the residue on crystallisation from hot ethyl acetate gave 1.10 g (60%) of **28** as colourless needles m.p. 230–231° (lit[32] m.p. 232–233°); Calc. C, 59.7; H, 3.48; N, 20.09; Found C, 60.02; H, 3.08; N, 19.80%; *m/e* 201(M$^+$); UV: λ^{MeOH}_{max} 330, 316, 284, 274, 260 nm; IR: ν_{max}(KBr) cm^{-1}: 1810, 1790, 1620, 1560, 1530, 1460; NMR: $\delta_{(DMSO)}$: 8.3–7.5(m, aromatic), 2.72(s, C$\underline{H}_3$).

The filtrate on concentration gave a gummy residue which was chromatographed on a column of silica gel. Elution with EtOAc : benzene (15:85) gave the isomeric oxadiazolinone **33** (0.16 g, 9%) which on crystallisation from methanol yielded colourless prisms m.p. 189–90° (lit[32] m.p. 195–97°); Calc. C, 59.7; H, 3.48; N, 20.09; Found C, 59.73; H, 3.45; N, 19.5%; *m/e* 201(M$^+$); UV: λ^{MeOH}_{max}: 318, 306, 295, 285, 250, 243, 235 nm; IR: ν_{max}(KBr) cm^{-1}: 1825(shoulder), 1795, 1635, 1610, 1590, 1480, 1460; NMR: $\delta_{(CDCl_3)}$ (500 MHz): 8.08(d, 1H), 7.77(t, 1H), 7.7(d, 1H), 7.55(t, 1H) (aromatic protons), 2.85(s, 3H, C$\underline{H}_3$).

Thermal reaction of oxadiazolinone with tetracyclone: isolation of cyclopentenone **32** *and the isomeric oxadiazolinone* **33**

In a sealed tube a mixture of **28** (0.201 g, 0.001 mole) and tetracyclone (0.384 g, 0.001 mole) was held at 200° for 10 h, cooled, extracted with ethylacetate, solvents evaporated and the residue chromatographed on silica gel. Elution with benzene gave unchanged tetracyclone (0.15 g), and with benzene : ethylacetate (19 : 1) 0.075 g (20%) of **32**, m.p. 163–64° (lit[45] m.p. 162°) *m/e*: 386(M$^+$); UV: λ^{MeOH}_{max}: 295 nm; IR: ν_{max}(KBr) cm^{-1} 1680, 1620, 1600, 1490, 1348.

Further elution with ethyl acetate : benzene (3 : 7) gave 0.1 g (50%) of the isomeric oxadiazolinone **33**, m.p. 189–90°.

Attempted cycloaddition of 3-lithiomethylbenzisoxazole with styrene: isolation of dimer **34**

3-Methylbenzisoxazole was prepared from *o*-hydroxyacetophenone by an improved procedure. Sodium acetate (2.5 g) and hydroxylamine hydrochloride (2 g) were separately dissolved in minimum amount of water, mixed and added to *o*-hydroxyacetophenone (3.4 g, 0.025 mole). Ethanol was then added until a clear solution was obtained, the reaction mixture refluxed for 0.5 h, concentrated to half the volume, cooled, poured into crushed ice (~ 200 g), the white crystals collected, washed with cold water and dried *in vacuo* to give 3.2 g (85%) of *o*-hydroxyacetophenone oxime m.p. 112–15°. *o*-Hydroxyacetophenone oxime (1 g; 0.0066 mole) was admixed with acetic anhydride (3 ml) and the clear solution left stirred at room temperature for 1 h. The precipitated N-acetoxy derivative was washed with petroleum ether and crystallised from benzene m.p. 141–43°, 0.96 g (75%). The N-acetoxy oxime (5 g, 0.026 mole) was held at 170–80° for 1 h, then at 100° for 1 h. The dark residue on distillation gave 3 g (87%) of 3-methylbenzisoxazole b.p. 89–90°/10 mm.

Under nitrogen and stirring, n-dibutyl amine (11.4 g, 0.088 mole) was gradually added to a solution of *n*-BuLi prepared at 0°C from Li(0.63 g, 0.09 mole) and *n*-BuBr

(12.3 g, 0.09 mole) in dry ether (50 ml), followed by, in drops, a solution of 3-methylbenzisoxazole (2 g, 0.015 mole) in dry ether (10 ml). After 0.5 h, freshly distilled styrene (2 g, 0.019 mole) was added, the reaction mixture left stirred for 5 h, poured into cold, saturated aqueous ammonium chloride adjusted to pH 2 (dil. H_2SO_4), extracted with ether (3 × 200 ml), washed with water, dried ($MgSO_4$), solvents evaporated and the residue chromatographed on silica gel. Elution with benzene : ethyl acetate (3 : 1) gave 0.05 g (5%) of **34** which was crystallised from ethylacetete–benzene; yellow needles. m.p. 215–18°; *m/e*: 264(M^+); IR: ν_{max}(KBr) cm^{-1}: 1610, 1593, 1530, 1500, 1452, 1430, 1380.

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