ACTA CHEMICA SCANDINAVICA 24 (1970) 550–560

ESR Spectra of Some Sterically Hindered Dinitro Dianion Radicals R-$\dot{C}(NO_2)_2^{2-}$. Synthesis of Geminal Dinitro Compounds and Carboxylation of Olefins

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The ESR spectra of some bulky dinitro dianion radicals $R-\dot{C}(NO_2)_2^{2-}$ have been investigated. The steric hindrance led to a non-equivalence of the two ^{14}N nuclei that gave rise to 9-line spectra exhibiting lifetime broadening of certain lines. As the temperature was increased the spectrum of the radical species with R = cyclohexyl changed into a 5-line spectrum indicating the transition to equivalence of the ^{14}N nuclei. The activation energy of the barrier was in the range 6.5 to 9.2 kcal/mole.

A secondary doublet splitting present in some of the spectra is discussed in terms of a hyperconjugative overlap between the 2*p* orbital of the central carbon atom and the *s* orbital of the proton in position α. The overlap seems to be brought about by steric hindrance produced by the asymmetry of the substituent group R.

The geminal dinitro compounds were prepared by the addition of the mercury salt of trinitromethane to the appropiate olefin followed by reduction with sodium borohydride. The dinitro function can be transformed into a carboxylic group *via* oxidation with alkaline permanganate.

In an alkaline medium the monovalent anions derived from geminal dinitro methane derivatives are easily reduced to the corresponding divalent anion radicals $R-\dot{C}(NO_2)_2^{2-}$, stable enough to be recorded by ESR spectroscopy.[1-4] In general the ESR spectra were dominated by a 5-line structure originating

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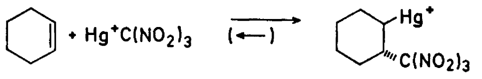
from the interaction of the unpaired electron with the two equivalent ^{14}N nuclei of the nitro groups. The coupling constants a^N were in the range 8 to 14 gauss. In several cases the spectra exhibited secondary splittings caused by magnetic nuclei present in the substituent group R.

Two members of the series, $O_2N-\dot{C}(NO_2)_2^{2-}$ and $H_2N-CO-CH{=}CH-\dot{C}(NO_2)_2^{2-}$ exhibited linewidth alternations originating from a partially hindered rotation of the nitro groups around the C—N bonds. This effect became very prominent for the bulky 2-hydroxycyclohexyl derivative,[3] which showed two non-equivalent nitro groups. Our further investigation of this effect is presented in this paper.

A new synthesis of geminal dinitro compounds is described. These substances were originally obtained as intermediate products in a series of experiments made with the intention of developing the addition of the mercury salt of trinitromethane to olefins into a carboxylic acid synthesis.

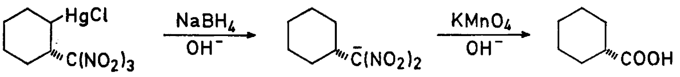
SYNTHESIS

The mercury salt of trinitromethane adds to olefins according to eqn. (1), (for a review, see Ref. 5).



(1)

The reaction proceeds well in a variety of solvents, protic as well as aprotic; an *O*-alkylated product would be in equilibrium with the components (*cf.* hydroxymercuration), and rearranges therefore to the more stable C-alkylated product. Demercuration of organomercurials has been accomplished with sodium borohydride,[6] and applied to our system, it gave geminal dinitro compounds as the main product. They were found to give carboxylic acids on treatment with permanganate, eqn. (2).

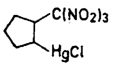
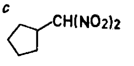
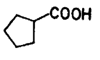
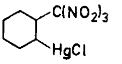
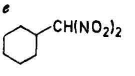
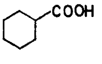
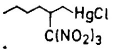
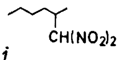
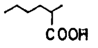
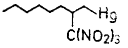
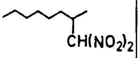
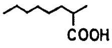
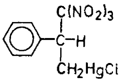
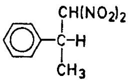
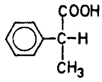
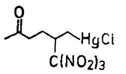
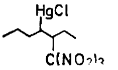


(2)

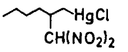
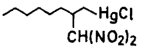
The general applicability of reaction (1) was first tested. Trinitromethane, *ca.* 40 % in water with a molar equivalent of mercuric nitrate and 1.8 moles of conc. perchloric acid (catalyst), was used as standard reagent. The reaction was carried out in 1,2-dimethoxyethane as the solvent, and the adducts were isolated as chlorides. The addition followed Markownikov's rule. Monosubstituted and *cis*-disubstituted olefins react rapidly, whereas tri- and tetrasubstituted olefins do not give adducts. 1,1-Disubstituted ethylenes react sluggishly [7] or not at all. *cis*-Stilbene was isomerized to the *trans*-isomer; *cis*-3-hexene but not the *trans*-isomer reacted under the reaction condition used, but gave a poor yield. Apparently, the addition of the bulky trinitromethyl group is strongly sterically hindered at a crowded centre. The NMR spectrum of the *cis*-3-hexene adduct in DMSO-d_6 showed only the spectrum of *cis*-3-hexene, but in chloroform, methanol, and acetone the expected spectrum was obtained. Thus, in strongly ionizing media elimination occurs, and eqn. (1) is actually reversible and in this case stereospecific.

The following olefins did not give adducts: *cis*- and *trans*-stilbene, α- and β-pinene, 1-methyl- and 1-phenylcyclohexene, 2-octene, 2-methyl-2-butene, methylenecyclohexane, allyl bromide, fumaric and maleic acids, and norbornene.

Table 1. Products from the reaction of olefins with the mercury salt of trinitromethane.

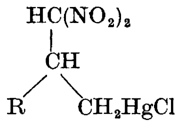
Olefin	Adduct	Yield %	Decomp. °C	Reduction product	Yield % [a]	Oxidation product	Yield % [b]
Cyclopentene		66	142 – 143	[c] 	57		27
Cyclohexene		55[d]	164 – 165[d]	[e] 	52		39(20[f])
1-Hexene	[g] 	73	88.5 – 89.5	[h] 	49		59(26[f])
1-Octene	[i] 	54	71 – 72	[j] 	49		30
Styrene		55[k]	151[k]		55		12
Allylacetone		66	112.5 – 113.5	—	—	—	—
cis-3-Hexene		15	104 – 106	—	—	—	—

[a] The yields refer to the olefins. [b] The yields are determined gaschromatographically on the methyl esters and refer to the olefins without purification of the intermediates. [c] K-salt, $C_6H_9N_2O_4K$, decomp. 147°C. [d] Lit.[7]: 75 %, decomp. 166 – 167°C. [e] K-salt, $C_7H_{11}N_2O_4K$, decomp. 180°C. Found: C 37.17; H 5.00. Calc.: C 37.16; H 4.90. [f] Yield of product obtained by distillation. Yield refers to olefin. [g] $C_7H_{12}N_3O_6HgCl$. Found: C 17.82; H 2.77. Calc.: C 17.88; H 2.57. [h] 17 % of I (see below) was obtained as a second fraction when chromatographed on SiO_2 with $CHCl_3$. [i] $C_9H_{16}N_3O_6HgCl$. Found: C 21.91; H 3.48. Calc.: C 21.69; H 3.24. [j] Na-salt m.p. 109 – 111°C. 12 % of II (see below) could be obtained as a second fraction. [k] Lit.[6a] 80 % decomp. 147°C.

I:  II: 

In the NMR spectra the CH_2Hg protons are nonequivalent; in 2-trinitromethyl-hexyl mercuric chloride and 2-trinitromethyl-octyl mercuric chloride they were found at δ 1.92 (A), and 2.25 (B), ABX-spectrum, $J_{AB} = 12.5$ cps. They couple with the methine proton (X) at δ 3.63 ppm, $J_{AX} = 7.0$ cps, $J_{BX} = 4.5$ cps. The $CH(NO_2)_2$ proton is localized at δ 5.9—6.3 ppm and is shifted to lower field in the corresponding mercury substituted derivatives. The physical data for the compounds prepared are given in Table 1.

Use of two moles of sodium borohydride per mole of adduct in aqueous tetrahydrofuran at 0—10°C reduced more than 85 % of the mercury. Simultaneously, the trinitromethyl group was reduced to a dinitromethyl group, a circumstance that actually facilitated its further transformation into a carboxylic function. Complete demercuration with sodium borohydride could not be brought about without seriously affecting the dinitromethyl group. Thus, this two step reaction gave access to new geminal dinitro derivatives. Dinitro compounds of structure I, retaining the mercury function, could occasionally be isolated in low yields.



I

The last step could be performed by adding 1.3 moles of potassium permanganate to an alkaline solution of the dinitro compound. Nametkin *et al.*[8] found earlier that aliphatic mononitro compounds are converted to aldehydes or ketones by basic permanganate. The whole carboxylation sequence can be carried out with an overall yield of 30—40 % without purification of the intermediates. When the styrene adduct was oxidized, the yield of 2-phenyl propionic acid was remarkably low. Benzoic acid was the main product, but acetophenone could also be identified.

ESR SPECTRA

The present study involved dinitro dianion radicals, $R-\dot{C}(NO_2)_2^{2-}$, in which the substituent group R was equal to: cyclopentyl, cyclohexyl, 2-hydroxy-cyclohexyl, 2-hydroxy-cyclohexyl-d_{10}, hexyl-2, and 1-phenyl-ethyl-1. The appearance of the spectra was heavily influenced by the size and bulk of the substituent group, and by the temperature of the recording. The radicals with R equal to cyclopentyl exhibited a normal 5-line spectrum without any linewidth alternations. The spectra of the other members of this series were quite different.

At temperatures between −15°C and +30°C the radicals with R = cyclohexyl showed a 9-line spectrum indicating non-equivalence of the two ^{14}N nuclei. Between −15°C and 0°C (Fig. 1a) the relative peak heights were rather close to unity, but with increasing temperature the spectra exhibited enhanced alternating linewidth variations with a broadening of the six lines with nuclear

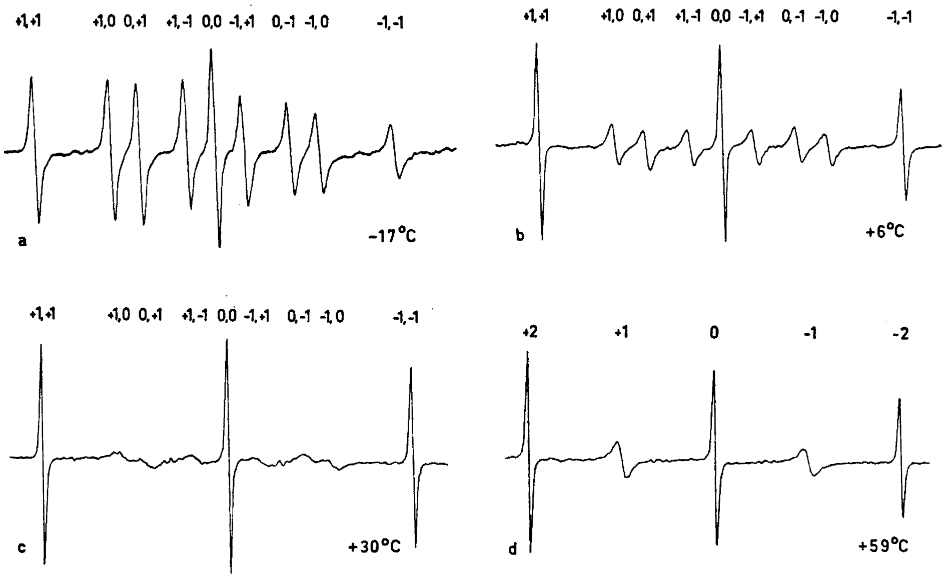


Fig. 1. ESR spectra of the radical $\text{(H)-}\dot{C}(NO_2)_2^{2-}$ at different temperatures.

quantum numbers $M_I = \pm 1(\pm 1,\ 0)$, $\pm 1(0,\ \pm 1)$, and $0(\pm 1,\ \mp 1)$, Fig. 1b. In the limit the six lines disappeared completely after a coalescence of the lines with $M_I = +1(+1,\ 0)$ and $+1(0,\ +1)$, the lines with $M_I = -1(0,\ -1)$ and $-1(-1,\ 0)$, and the two lines with $M_I = 0(\pm 1,\ \mp 1)$ into the centre line $M_I = 0(0,\ 0)$. The spectrum then consisted of the three lines of equal peak height corresponding to the quantum numbers $M_I = \pm 2(\pm 1,\ \pm 1)$, and $0(0,\ 0)$, *i.e.* the two outer and the centre lines of the original 9-line spectrum, Fig. 1c.

As the temperature was further increased the spectrum changed into a 5-line spectrum indicating that the two ^{14}N nuclei had became equivalent. The spectrum exhibited linewidth alternations with the two components with $M_I = 0(\pm 1,\ \mp 1)$ of the centre line and the two lines with $M_I = \pm 1$ broadened, Fig. 1d. As the radicals decayed rapidly on increasing temperature it was not possible to extend the recordings to temperatures above +60°C. Even at the maximum temperature accessible for recording the alternations were still very striking.

The single coupling constant, a^N, of the 5-line spectrum was found to be nearly equal to $(a_a^N + a_b^N)/2$, where a_a^N and a_b^N are the two coupling constants of the 9-line spectra $(a_a^N \neq a_b^N)$; see Table 2. On approaching the coalescence from the low temperature range, the observed difference, Δa^N, between a_a^N and a_b^N, was found to decrease, as expected (See Fig. 2).

The remaining radical species of this series also exhibited 9-line spectra with a varying extent of alternating linewidth variations. However, none

Table 2.

R in $R-\dot{C}(NO_2)_2^{2-}$	Recording temperature °C	Splitting constants in gauss 9-line spectrum a_a^N	9-line spectrum a_b^N	5-line spectrum a^N	5-line spectrum a^H	τ_0 s × 10^{15}	Activation energy *E* kcal/mole	Coalescence temperature °C
Cyclopentyl	+18			10.6				
Nitro[a]	+20			8.40[c]			6.55	< −20
$H_2N-CO-CH=CH-$[b]	+20			11.1	0.73		[d]	∼ −15
Cyclohexyl	0	12.50	8.83			105	7.97	+36
	+60			10.91				
2-Hydroxy-cyclohexyl	−10	11.64	9.10					
	+22	11.85	9.05		0.59	96	9.11	+71
	+34	11.89	9.05					
2-Hydroxy-cyclohexyl-d_{10}	+21	11.85	9.12		—	69	9.10	+62
Hexyl-2	+12	11.10	9.56		0.45	310	9.21	∼ +90
1-Phenyl-ethyl-1	+40	10.4	9.75		0.82		[d]	high

[a] Refs. 1, 4. [b] Ref. 1. [c] 3 equivalent ^{14}N: 7-line spectrum. [d] not measured.

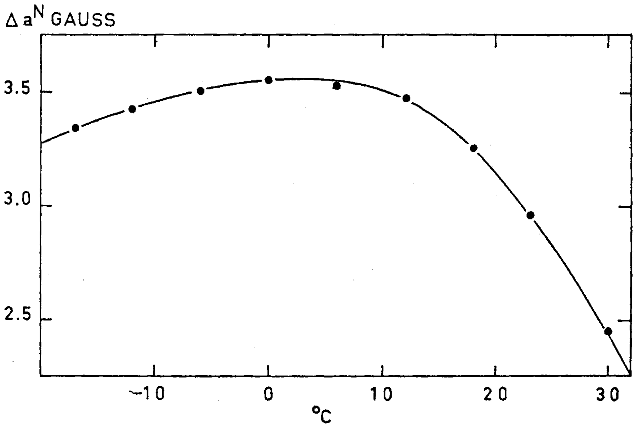


Fig. 2. The difference Δa^N between the two ^{14}N coupling constants as a function of the temperature for the radical with R = cyclohexyl.

of them did show the transition to a 5-line spectrum, even at the highest temperature accessible before the radicals decayed. Thus, the spectra of the radical with the substituent group R equal to 2-hydroxy-cyclohexyl showed strong alternations, Fig. 3, and in the limit the 9-line spectrum changed into a 3-line spectrum (+65°C).

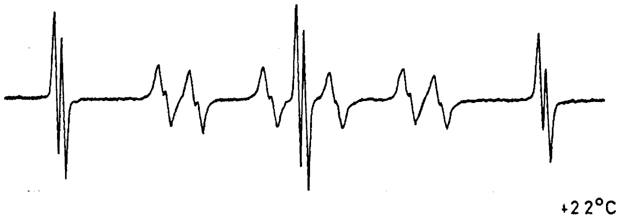
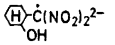


Fig. 3. ESR spectrum of the radical  $\text{C}_6\text{H}_{10}(\text{OH})\dot{\text{C}}(\text{NO}_2)_2^{2-}$.

The alternations were not so prominent a feature of the spectra of the radicals with R equal to hexyl-2 and 1-phenyl-ethyl-1, and the 9-line structure was preserved in the whole range of the temperature accessible for recording.

A secondary doublet splitting originating from the α proton was present in the spectra of the radicals in which R was equal to: 2-hydroxy-cyclohexyl, hexyl-2, and 1-phenyl-ethyl-1. The doublet had vanished in the spectrum of the deuterated radical with R equal to 2-hydroxy-cyclohexyl-d_{10}. No secondary splittings were observed for the cyclopentyl and cyclohexyl derivatives. This is further discussed below.

The temperature dependent sequence of spectral variations observed here is interpreted in terms of the general theory for chemical rate processes as studied by magnetic resonance (for reviews see Refs. 9 and 10).

The dinitro dianion radicals are assumed to be present in two conformations which arise as the result of a hindered rotation of the nitro groups around the C—N bonds caused by the bulky substituent group R, and to jump between the conformations.

In the low temperature range the rate process is rather slow, and the spectrometer sees the individual conformations, a situation which gives rise to the 9-line spectra. As the rate increases the decreased lifetime in each conformation will broaden certain lines only. At a still higher rate the spectrometer sees a mean of the two conformations, and the two ^{14}N nuclei are equivalent.

CALCULATION OF LIFETIMES AND THE ACTIVATION ENERGY

The activation energy of the barrier was estimated for some of the radical species of this series by the use of the mean lifetimes in each conformation as evaluated from linewidth measurements at different temperatures. In these calculations we used the modified Bloch equations elaborated for a two-site system with slow and rapid exchange, respectively.[11–14]

At a slow rate of jumping between the two conformations, *i.e.* in the case of non-equivalent ^{14}N nuclei, and assuming equal lifetimes in both conformations ($\tau_a = \tau_b = \tau$), τ is related to the measured linewidth $(T_2)^{-1}$, and the linewidth in the absence of jumping, $(T_2^0)^{-1}$, by eqn. (3).

$$\tau^{-1} = (T_2)^{-1} - (T_2^0)^{-1} \tag{3}$$

In the range of rapid jumping between the conformations, *i.e.* in the case of equivalent ^{14}N nuclei and alternate broadening of the lines, eqn. (4) was used for the evaluation of τ.

$$\tau = \frac{8((T_2)^{-1}-(T_2^0)^{-1})}{(\omega_a-\omega_b)^2+4((T_2)^{-1}-(T_2^0)^{-1})^2} \tag{4}$$

where ω_a and ω_b are the ^{14}N coupling constants in angular frequency units as evaluated from the 9-line spectra.*

Eqn. (4) was originally derived by Allerhand and Gutowsky for pulse echo studies in NMR in the range of moderately rapid exchange. However, the equation is also valid for steady state measurements.[15] When compared with the expression omitting the second term in the denominator which is the one usually applied to rapid exchange studies, it was found that eqn. (4) gave rise to more appropiate values of τ, especially in the temperature range close to coalescence $((T_2)^{-1} \gg (T_2^0)^{-1})$.

$(T_2^0)^{-1}$ was obtained in the case of the 9-line spectra with non-equivalent ^{14}N nuclei by the expression [10,16]

$$(T_2^0)^{-1} = A + Bm_{Ia} + Cm_{Ib} + Dm_{Ia}m_{Ib} + Em_{Ia}^2 + Fm_{Ib}^2 \tag{5a}$$

where m_{Ia} and m_{Ia} are the individual nuclear quantum numbers of the two ^{14}N nuclei a and b, respectively. At a given temperature the coefficients of eqn. (5a) may be determined from the width of the lines if it is assumed that the lifetime broadening equally affects the lines with $M_I = \pm 1(\pm 1, 0)$, $\pm 1(0, \pm 1)$, and $0(\pm 1, \mp 1)$. For the 5-line spectra, *i.e.* in the case of equivalent ^{14}N nuclei, we used the eqn. (5b), as described earlier.[4]

$$(T_2^0)^{-1} = A + BM_I(M_I-2) \tag{5b}$$

τ was also calculated from coalescence data by the use of eqn. (6).[14] (See Table 2.)

$$2\sqrt{2} = \tau(\omega_a-\omega_b) \tag{6}$$

Because of the difficulty in estimating the coalescence temperature the values of τ obtained in this way are rather uncertain.

A plot of the logarithm of the calculated lifetime against the reciprocal of the absolute temperature was found to give a straight line, from the slope of which the activation energy, E, of the barrier could be evaluated by the use of eqn. (7). (See Table 2.)

$$\tau = \tau_0 \exp(E/RT) \tag{7}$$

In the case of the radical species with R=cyclohexyl, it was found that the points corresponding to τ as evaluated by eqn. (3) and (4), respectively, fitted rather well the same straight line, Fig. 4. The point corresponding to the observed coalescence temperature also fitted rather well to the linear plot of Fig. 4.

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* In these calculations we used the maximum value of $(\omega_a-\omega_b)$ as obtained from Fig. 2.

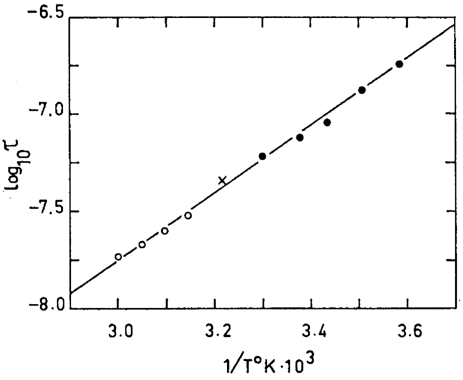

Fig. 4. A plot of the logarithm of the lifetime τ against $1/T$°K for the radical with R = cyclohexyl. ● points evaluated by eqn. (3); ○ points evaluated by eqn. (4); × evaluated from coalescence data, eqn. (6) and the observed coalescence temperature.

DISCUSSION

When the radicals were arranged according to the activation energy, the barrier was found to increase in the order: O_2N, cyclohexyl, 2-hydroxycyclohexyl, and hexyl-2, which roughly parallels the bulk of the substituent group. No hindrance in the form of a non-equivalence of the ^{14}N nuclei or alternating linewidths was observed for $R = R'-CH_2$, cyclopentyl, and aryl.[1,2]

A secondary doublet splitting originating from the α hydrogen atom was observed in the spectra of the radicals of this series, except of those species with R = cyclopentyl and cyclohexyl. Let us consider the spin density on the α hydrogen atom to be produced by a hyperconjugative overlap between the $2p$ orbital of the sp^2 hybridized central carbon atom, and the s orbital of the α hydrogen atom. In the case of such a mechanism we would expect the maximum and minimum coupling with the α hydrogen atom to prevail when the dihedral angle between the symmetry axis of the $2p$ orbital and the aliphatic C—H bond was equal to 0° and 90°, respectively. The absence of any doublet splitting from the α hydrogen atom in the spectrum of the radical with R = cyclohexyl would therefore infer a dihedral angle of 90°, and a conformation corresponding to that shown in Fig. 5a. Obviously, the conformation is the result of a symmetric repulsion between the two nitro groups and the four hydrogen atoms in positions 2 and 6 on the cyclohexyl ring.

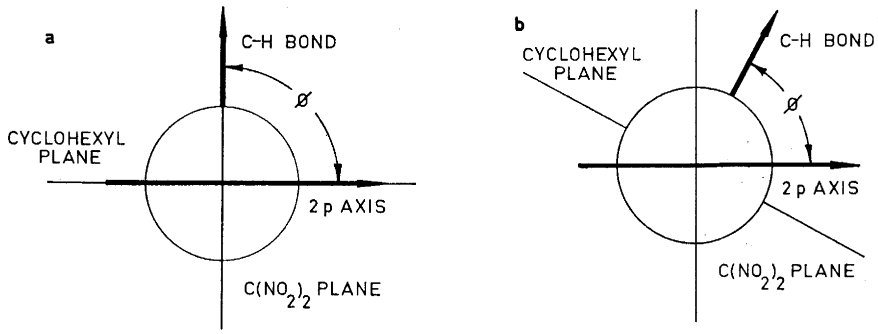

Fig. 5. Conformations in the dinitro dianion radicals $R-\dot{C}(NO_2)_2^{2-}$. *a.* R = cyclohexyl; *b.* R = 2-hydroxy-cyclohexyl.

When the symmetry of the repulsion is disturbed by the presence of a single substituent group in position 2 on the cyclohexyl ring, the dihedral angle is constrained to deviate from 90° (Fig. 5b) and a doublet splitting will be present as seen from the spectrum of the radical with R=2-hydroxy-cyclohexyl. The analogous interpretation may be also valid for the presence of the doublet splitting in the spectra of the radicals with R equal to hexyl-2 and 1-phenyl-ethyl-1. A situation similar to that discussed here has been reported for the 2,6-di-*t*-butyl-4-cyclohexyl phenoxyl radical.[17]

The absence of any doublet splitting in the case of the radical species with R=cyclopentyl, the spectrum of which did not exhibit any linewidth alternations, may be explained as follows. While the linewidth alternations (or the non-equivalence of the ^{14}N nuclei) are caused by a restricted rotation around the C—N bonds, the absence of the doublet splitting is caused by a restricted rotation around the R—C bonds which prevents coupling to the α hydrogen atom by a fixation of the steric arrangement into a symmetrical orientation analogous to that of Fig. 5a. In the case of the cyclopentyl derivative it is obvious that the restricted rotation around the R—C bond dominates.

Finally, it may be pointed out that whereas the phenomenon of alternating linewidths is a rather common feature of the ESR spectra of many dinitro anion radicals with equivalent ^{14}N nuclei (for reviews see Refs. 10 and 18), the complete sequence including also the state of non-equivalence seems not to have been described so far. On the other hand, the complete sequence of events analogous to that observed here has been reported for radicals in which the coupling involved protons only.[19]

EXPERIMENTAL

General procedure for the addition of the mercury salt of trinitromethane to olefins. The olefin (10 mmol) was added at room temperature to the reagent prepared from mercuric nitrate (10 mmol), trinitromethane (4.2 ml, 40 % aqueous solution, 11 mmol), perchloric acid, conc. (1 ml), and dimethoxyethane (*ca.* 18 ml). The mixture was left for 24 h and then sodium chloride solution was added (10 ml, 2 N). The mercury chloride derivative, occasionally obtained as a slowly crystallizing oil, was washed with water, dried, and crystallized from carbon tetrachloride, chloroform, or ethanol.

Cyclopentene, cyclohexene, 1-hexene, 1-octene, styrene, and hex-5-en-2-one gave practically quantitative yields of crude product, sufficiently pure for further reactions. The elementary analysis of the mercury compounds showed generally high C—H values, but the NMR spectra gave correct proton integrals. The IR spectra showed strong absorptions at 1595±3 and 1295±3 cm^{-1}, characteristic for the trinitromethyl group.

Reduction of the adduct. Sodium borohydride (20 mmol), dissolved in sodium hydroxide (3 M, 2 ml) was added drop by drop to the adduct (10 mmol) in tetrahydrofuran (20 ml) at 0—10°C. The mixture was allowed to reach room temperature, poured into water, and acidified with hydrochloric acid. Extraction with carbon tetrachloride and chromatography on silica (CCl_4 or $CHCl_3$ as eluent) afforded the dinitromethyl derivatives (oils). The IR spectra showed strong absorptions at 1581±3 and 1328±4 cm^{-1}. The NMR spectra showed correct proton integrals. Mercury dinitro derivatives were occasionally obtained as a second fraction. Crystalline salts could be obtained by dissolution of the dinitro derivative in alcoholic or aqueous potassium or sodium hydroxide.

Oxidation of the dinitro compound. The dinitro derivative (1 mmol) was dissolved in aqueous sodium hydroxide and potassium permanganate (13 ml of 0.1 M aqueous solution) was added at room temperature. After a few minutes MnO_2 started precipitating. About 90 min were sufficient to complete the oxidation of the dinitro compound. In order to destroy the excess of potassium permanganate, sodium sulphite solution was added to the reaction mixture until it was just pale reddish. The crude carboxylic acid was obtained by acidification and extraction with ether. The yield was determined by quantitative GC of the methyl esters, obtained by methylation with diazomethane.

Preparation of cyclohexane carboxylic acid and 2-methyl hexanoic acid. Cyclohexene (25 mmol) was transformed to cyclohexane carboxylic acid according to the method described above. However, it appeared to be preferable to raise the oxidation time to 2.5 h and the amount of potassium permanganate to 2 moles per mole cyclohexene. Distillation gave pure cyclohexane carboxylic acid (0.65 g, 20 %), b.p. 76–82°C/0.6 mm Hg. Similarly 1-hexene (1.68 g, 20 mmol) gave 2-methyl hexanoic acid (0.69 g, 26 %), b.p. 78–80°C/1 mm Hg.

Preparation of the potassium salt of dinitro 2-hydroxy-cyclohexylmethane-d_{10}. Torssell's method[3] was followed using cyclohexene-d_{10}, instead of cyclohexene.

ESR measurements. The ESR spectra were obtained on a Varian 100 kc spectrometer and a 9″ magnet as described earlier.[1,2,4]

The radicals were prepared by reduction with glucose of a solution of the parent potassium dinitro compounds dissolved in 1 N aqueous NaOH, or a 10 % solution of tetramethyl ammonium hydroxide in H_2O (*cf.* Refs. 1, 2, and 4): a few mg of the substance was dissolved together with a two to four times molar excess of glucose in about 1 ml of the solvent. After the solution had been kept standing at room temperature for 1 to 5 min, the radicals appeared. However, in the case of the 2-hydroxy-cyclohexyl derivative the induction period was found to be about 20 min.

On assuming the ESR lines to be of Lorentz shape, $(T_2)^{-1}$ and $(T_2^0)^{-1}$, respectively, were evaluated by measuring the linewidth, ΔG, in gauss between the inflexion points, *i.e.* between the peaks on the derivative curves, and by the use of eqn. (8)

$$(T_2)^{-1} = \pi\sqrt{3}\ 2.802\times 10^6\ \Delta G \tag{8}$$

The values of $(T_2)^{-1}-(T_2^0)^{-1}$ used for calculating τ (eqns. 3, 4, and 6) were the mean values of measurements on all the lines which were broadened by the jumping process.

Acknowledgements. The authors are indebted to Dr. A. Hudson, Dr. G. R. Luckhurst, and Professor L. T. Muus for valuable discussions. This work was supported by grants from *The Swedish Natural Science Research Council* and *Wilhelm och Martina Lundgrens Vetenskapsfond.*

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Received July 2, 1969.