119. The ESR. Spectrum of the Diphenylcyclopropenone Radical Anion

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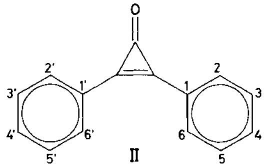
Summary

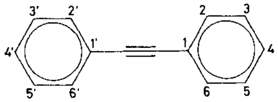
The ESR. spectrum of the relatively unstable radical anion of diphenylcyclopropenone (II) has been observed upon electrolytic reduction of II in *N,N*-dimethylformamide and 1,2-dimethoxyethane. Simple MO models account well for the π-spin distribution and for the restricted rotation of the phenyl substituents in II$^{\ominus\cdot}$. A rather facile loss of a CO molecule by II$^{\ominus\cdot}$ results in formation of the radical anion of tolane (diphenylacetylene; III). No ESR. spectra could be obtained for the radical anions of dialkylcyclopropenones which are even shorter-lived than II$^{\ominus\cdot}$, although decay by decarbonylation seems to be less favoured with them than with II$^{\ominus\cdot}$. In presence of air, electrolytic reduction of either II or its dimethyl and di-*t*-butyl analogues yields the correspondingly disubstituted semidione anions.

Introduction. - Although cyclopropenone (I) and a number of its mono- and disubstituted derivatives have been synthesized in the course of the last two decades [1], no ESR. spectra of the corresponding radical anions have been reported. As indicated by experiments in our laboratory (see Appendix), these radical anions exhibit rather low stability which renders their studies by ESR. difficult. For such studies, the most promising candidate among the radical anions of the hitherto known cyclopropenones is that of the diphenyl derivative (II), due to the stabilizing effect of the two aryl substituents. An unsuccessful attempt to observe its ESR. spectrum has been mentioned in the literature [2] through a brief statement that reduction of II with alkali metals yields the radical anion of biphenyl. In the present paper, we describe the ESR. spectrum of II$^{\ominus\cdot}$; the secondary radical anion is identified as that of tolane (diphenylacetylene; III).

I



II



III

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Results. - The radical anion $\mathrm{II}^{\ominus\cdot}$ was generated at low temperatures by electrolytic reduction of diphenylcyclopropenone (II) in a cylindrical cell containing a helical cathode of amalgamated gold and an anode of platinum wire placed along the axis [3]. This cell proved particularly advantageous for ESR. investigations of relatively unstable radical anions. Both *N,N*-dimethylformamide (DMF) and 1,2-dimethoxyethane (DME) were used as the solvent; the perchlorate salts of tetraethylammonium ($Et_4N^{\oplus}$) and tetrabutylammonium ($Bu_4N^{\oplus}$) cations served as the respective supporting electrolytes. The radical anions $\mathrm{II}^{\ominus\cdot}$ produced under these conditions had a half-life of *ca.* 20 min in DMF at −60° and in DME at −90°.

Figure 1 shows the ESR. spectrum of $\mathrm{II}^{\ominus\cdot}$ taken at −60° with $DMF/Et_4N^{\oplus}$ as the solvent/counterion. The analysis of the hyperfine structure is straightforward in terms of five coupling constants $a_{H\mu}$, each arising from a pair of equivalent protons:

$a_{H2,2'} = 3.11$; $a_{H3,3'} = 0.96$; $a_{H4,4'} = 4.28$; $a_{H5,5'} = 0.78$ and $a_{H6,6'} = 2.76$ Gauss[3]).

These values remain unaltered within the limits of experimental error (±0.01 Gauss) when the conditions are changed from $DMF/Et_4N^{\oplus}$ and −60° to $DME/Bu_4N^{\oplus}$ and −90°. Their assignment to the individual positions μ in the phenyl substituents is based on a MO model presented in the Discussion.

It is interesting to note that the 2,2'- and 6,6'-protons, on the one hand, and the 3,3'- and 5,5'-protons, on the other hand, are not equivalent, and that this situation persists at −20°, *i.e.*, at the highest temperature where the ESR. spectrum of $\mathrm{II}^{\ominus\cdot}$

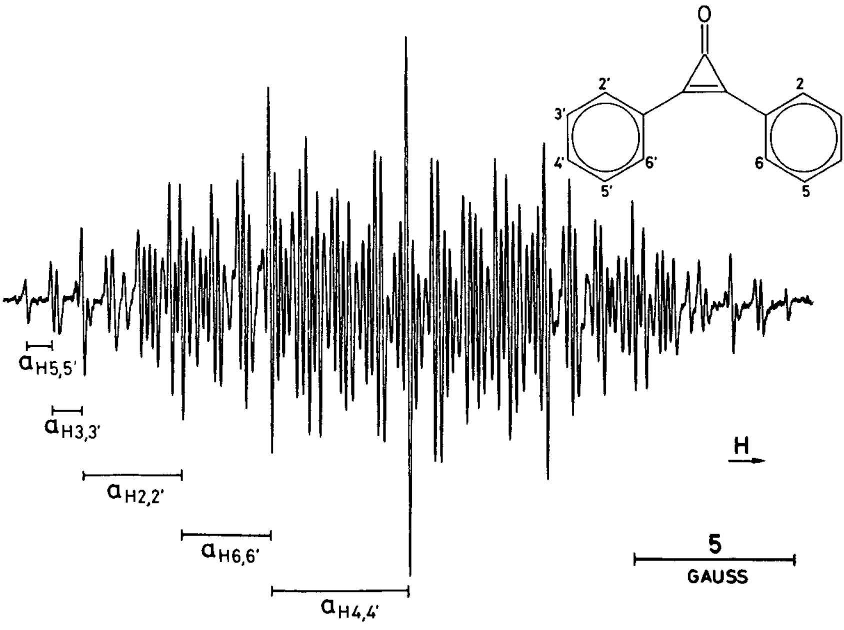

Fig. 1. *ESR. spectrum of the radical anion* $\mathrm{II}^{\ominus\cdot}$. Solvent: DMF; counterion: $Et_4N^{\oplus}$; temp.: −60°.

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[3]) 1 Gauss = 10^{-4} Tesla.

could still be observed. The rotation of the phenyl substituents about the essential single bonds linking them with the cyclopropenone moiety must thus be slow on the hyperfine time-scale (*ca.* $10^7\ s^{-1}$) even at $-20°$.

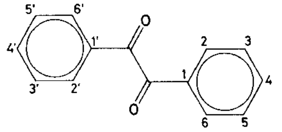
Decay of the primary radical anion ($II^{\ominus\cdot}$) is accompanied by formation of a secondary one, the proton coupling constants of which are diagnostic of the radical anion of tolane (III) [4][4]):

$a_{H,2,2',6,6'} = 2.71$; $a_{H3,3',5,5'} = 0.59$ and $a_{H4,4'} = 4.85$ Gauss
(exper. error: ± 0.01 Gauss; solvent/counterion: DMF/$Et_4N^{\oplus}$; temp.: $-60°$).

Also $III^{\ominus\cdot}$ has a low stability, its half-life being comparable to that of $II^{\ominus\cdot}$ under the same conditions. It converts into the radical anion of *trans*-stilbene [5] [6], whereby two hydrogen atoms are abstracted from the solvent.

When, prior to or during electrolysis, a contact of the solution of II with air is not avoided, the ESR. spectrum of a long-lived paramagnetic species appears at a voltage which is considerably less negative than that required for the generation of $II^{\ominus\cdot}$. This species is readily characterized as the radical anion of benzil (diphenylethanedione; IV) [7] by virtue of its proton coupling constants:

$a_{H2,2',6,6'} = 1.00$; $a_{H3,3',5,5'} = 0.35$ and $a_{H4,4'} = 1.11$ Gauss
(exper. error: ± 0.01 Gauss; solvent/counterion: DMF/$Et_4N^{\oplus}$; temp.: $-60°$).



IV

The *g* factor of $IV^{\ominus\cdot}$ amounts to 2.0050 ± 0.0001 as compared to 2.0026 ± 0.0001 for both $II^{\ominus\cdot}$ and $III^{\ominus\cdot}$.

Discussion. - *MO models.* The lowest unoccupied orbital (LUMO) of cyclopropenone (I) is antisymmetric with respect to the perpendicular mirror plane (m) passing through the C=O bond, and the same nodal property is shared by the diphenyl derivative (II). In the HMO approximation, the LUMO's of I and II (*Fig. 2*) are identical with those of ethylene and stilbene (1,2-diphenylethylene), respectively, and thus independent of the choice of the parameters $\alpha_{\dot{O}}$ and $\beta_{C=\dot{O}}$ Accordingly, the π-spin populations ρ_μ calculated by means of the *McLachlan* procedure ($\lambda = 1.2$) [8] are almost insensitive to such a choice, being left unchanged to ± 0.0005 upon variation of the pertinent parameters in the ranges $|\alpha| < |\alpha_{\dot{O}}| < |\alpha + 2\beta|$ and $|\beta| < |\beta_{C=O}| < |2\beta|$. The *Table* lists these π-spin populations ρ_μ for the proton bearing centres μ. The correlation between the theoretical values (ρ_μ) and the experimental data (a_{H_μ}) is greatly improved when one allows for the non-equivalence within the sets of *ortho* (2,2′ and 6,6′)- and *meta* (3,3′ and 5,5′)-protons. In the frame of a HMO model, this can be done most conveniently by slightly

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[4]) It is probable that in the previously reported reduction of II [2] this spectrum was erroneously ascribed to the radical anion of biphenyl ($a_{H2,2',6,6'} = 2.68$; $a_{H3,3',5,5'} = 0.39$ and $a_{H4,4'} = 5.39$ Gauss).

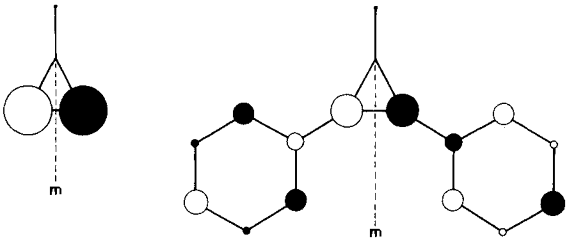

Fig. 2. *Lowest unoccupied HMO's of cyclopropenone* (I) *and its diphenyl derivative* (II). The areas of the circles are proportional to the squares of the LCAO coefficients. Filled and blank circles symbolize different signs of these coefficients. The dashed line is the trace of the perpendicular mirror plane m.

modifying the parameter of the spatially proximate centres 6 and 6′ [6]5). As evident from the *Table*, use of $\alpha - 0.1\beta$ for the two centres leads to an excellent correlation of the calculated π-spin populations ρ_μ and permits one to assign the latter unambiguously to pairs of equivalent protons in the positions μ.

The HMO model of II indicates that - owing to the strong positive contributions of the LUMO (*Fig. 2*) - the essential single bonds linking the phenyl substituents with the cyclopropenone moiety acquire some double bond character on passing from the neutral molecule (II) to its radical anion ($\mathrm{II}^{\ominus\cdot}$). Consequently, the energy barrier to rotation of the phenyl groups about the linkages in question is enhanced, which may, at least in part, account for the relative "slowness" of this motion in $\mathrm{II}^{\ominus\cdot}$ (see Results).

Steric hindrance. X-ray crystallographic studies of II [9] show that the phenyl substituents can assume a nearly coplanar arrangement with the cyclopropenone moiety (twisting angle of *ca.* 6°), because the steric hindrance by the 6- and 6′-hydrogen atoms is only slight. It is tempting to assess the relative extent of such hindrance by comparing the differences $\Delta a_{\mathrm{H},o} = a_{\mathrm{H}2,2'} - a_{\mathrm{H}6,6'}$ and $\Delta a_{\mathrm{H},m} = \Delta a_{\mathrm{H}3,3'} - a_{\mathrm{H}5,5'}$ observed in this work for the *ortho*- and *meta*-protons, respectively, with the analogous values found for structurally related species. Suitable for such comparison are the radical anions of 1,2-diphenylcyclobutene (V) and 1,2-diphenylcyclopentene

Table. *π-Spin populations ρ_μ calculated for the radical anion of diphenylcyclopropenone* (II)

μ	ρ_μ a)	ρ_μ b)	$a_{\mathrm{H}\mu}$ c)
2, 2′	+0.099	+0.107	3.11
6, 6′		+0.091	2.76
3, 3′	−0.032	−0.036	0.96
5, 5′		−0.026	0.78
4, 4′	+0.135	+0.137	4.28

a) Standard parameter α for $\mu = 6$ and 6′.
b) Parameter $\alpha - 0.1\beta$ for $\mu = 6$ and 6′.
c) Experimental proton coupling constants in Gauss.

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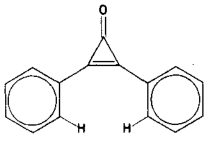
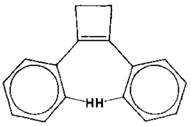
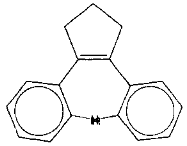
5) The assignment made in the reference paper [6] for the 2- and 6-protons in the radical anions of *trans*-stilbene and *trans*-azobenzene should be reversed. The same holds for the corresponding 3- and 5-protons.

(VI), since both contain the *cis*-stilbene π-system and thus - in accord with the HMO model (*Fig. 2*) - display a π-spin distribution similar to that in $\mathrm{II}^{\ominus\cdot}$ [10]. The expectation that the steric hindrance should augment in the sequence $\mathrm{II}^{\ominus\cdot} < \mathrm{V}^{\ominus\cdot} < \mathrm{VI}^{\ominus\cdot}$ is borne out by the increase in the pertinent differences $\Delta a_{\mathrm{H},o}$ and $\Delta a_{\mathrm{H},m}$ (values in Gauss).





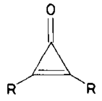


	II	V	VI
$\Delta a_{\mathrm{H},o}$	0.35	0.46	0.57
$\Delta a_{\mathrm{H},m}$	0.18	0.25	0.42

Secondary products. The conversion of $\mathrm{II}^{\ominus\cdot}$ into the radical anion of tolane (III), with a concomitant loss of a CO molecule, requires only little comment. An analogous reaction was also observed for the neutral compound II either by thermal or photochemical initiation [1], the release of strain inherent in the cyclopropenone moiety being presumably the driving force for the formation of III.

In contrast to $\mathrm{III}^{\ominus\cdot}$, the radical anion of benzil (IV) cannot be formed from $\mathrm{II}^{\ominus\cdot}$, since it is generated at a voltage insufficient for the reduction of II (see Results). Our experimental findings show that $\mathrm{IV}^{\ominus\cdot}$ is also produced when, prior to the electrolysis, the solution of II is bubbled with air for *ca.* 30 min and subsequently degassed. Evidently, diphenylcyclopropenone (II) can be converted into the neutral benzil (IV) by a prolonged contact of the DMF or DME solution (containing 0.1 M tetraalkylammonium perchlorate) with oxygen[6]). Further studies are desirable to clarify the reaction mechanism which, apart of taking up two oxygen atoms by II, implies a decarbonylation of this compound. In the latter context, it is noteworthy that the ESR. spectrum of $\mathrm{IV}^{\ominus\cdot}$ is not observed upon direct electrolytic reduction of tolane (III) in presence of air.

Appendix. - Considerable effort has been deployed in the electrolytic reduction of dialkylcyclopropenones such as the dimethyl (VII) and the di-*t*-butyl derivative (VIII).



VII, R=Me
VIII, R=t-Bu

$\mathrm{O{=}\overset{1}{HC}{-}\overset{2}{CR}{=}\overset{3}{CHR}}$

IX, R=t-Bu

However, even under the same experimental conditions as those successfully applied to the diphenyl analogue II, no ESR. spectra of the primary radical anions $\mathrm{VII}^{\ominus\cdot}$ and $\mathrm{VIII}^{\ominus\cdot}$ could be obtained. Whereas, in absence of air, reduction of VII failed to give any signals at all, a well-defined spectrum of a secondary paramagnetic product appeared upon the electrolysis of VIII. We ascribe this spectrum, shown in *Figure 3*, to the hitherto unknown radical anion of 2-*t*-butyl-4,4-dimethyl-2-pentenal (IX) where the two nonequivalent protons in the positions 1 and 3 give rise to the four broad hyperfine components and

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[6]) Oxidation of II to IV takes place with $KMnO_4$ in acetone [11] or *m*-chloroperbenzoic acid in methylene chloride [12], but it does not occur with oxygen in apolar solvents such as benzene [13]. Presumably, under the conditions of our experiments, this reaction is facilitated by the higher polarity of the solution.

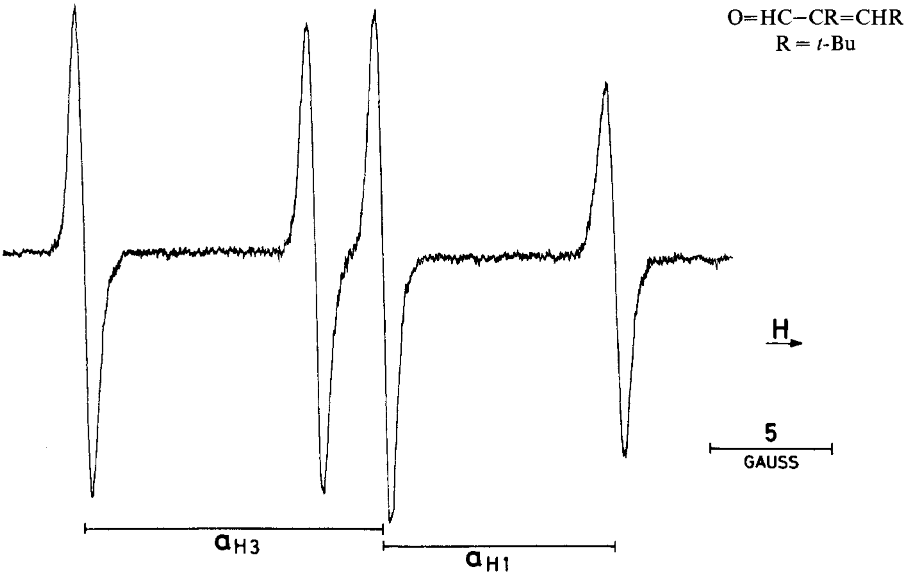


Fig. 3. *ESR. spectrum of the radical anion IX*$^{\ominus}$. Solvent: DMF; counterion: $Et_4N^{\oplus}$; temp.: – 60°.

the two sets of nine *t*-butyl protons contribute to the line-width through unresolved splitting. The coupling constants measured at – 60° with DMF/$Et_4N^{\oplus}$ as the solvent/counterion are

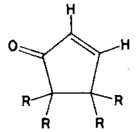
$$a_{H1} = 9.40 \pm 0.05 \text{ and } a_{H3} = 12.15 \pm 0.05 \text{ Gauss}$$

and the *g* factor amounts to 2.0037 ± 0.0001.

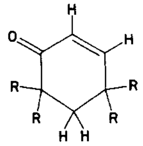
This assignment is supported by comparison of the a_{H3} value with 11.67, 11.0 and 11.8 Gauss found for the corresponding protons in the radical anion of 2,2,6,6-tetramethyl-4-hepten-3-one (X) [14], 4,4,5,5-tetramethyl-2-cyclopentenone (XI) [2] and 4,4,6,6-tetramethyl-2-cyclohexenone (XII) [2] respectively.

$O{=}RC{-}CH{=}CHR$

X, R=t-Bu



XI, R=Me



XII, R=Me

Conspicuous features in the spectra of IX$^{\ominus}$ are different line-widths of the four components (*Fig. 3*) as well as a marked dependence of the coupling constants a_{H1} and a_{H3} on the temperature and solvent/counterion. Both effects can be attributed to an occurrence of conformational and configurational isomers.

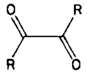
When in the electrolytic reduction of di-*t*-butyl-cyclopropenone (VIII) the perdeuteriodimethylsulfoxide (DMSO-d_6) is used as the solvent, the ESR. spectrum of the radical anion of 2-*t*-butyl-4,4-dimethyl-1,3-dideuterio-2-pentenal (IX-d_2) is observed, in which the proton coupling constants a_{H1} and a_{H3} are replaced by the corresponding deuteron splittings:

$$a_{D1} = 1.44 \pm 0.01 \text{ and } a_{D3} = 1.87 \pm 0.01 \text{ Gauss.}$$

The relative stability of IX$^{\ominus}$ and IX-$d_2^{\ominus}$ (half-life of 30 min at – 60°) is undoubtedly due to the two *t*-butyl substituents which render polymerization more difficult. Its formation from the transient radical anion VIII$^{\ominus}$ by a scission of one essential single bond in the cyclopropenone system and an uptake of two hydrogen or deuterium atoms from the solvent indicates that for VIII$^{\ominus}$ such a reaction can effectively compete with decarbonylation. This statement is in line with reports [1] that a thermally initiated loss of a CO molecule takes place less readily with VIII (*ca.* 320°) than with its diphenyl analogue II (*ca.* 150°).

In presence of air, electrolytic reduction of VII and VIII affords the radical anions of correspondingly disubstituted diones (XIII and XIV) [15], as evidenced by the observed coupling constants of the alkyl protons;

$a_H(\mathrm{Me}) = 5.65 \pm 0.05$ for XIII$^{\ominus}$ and $a_H(t\text{-Bu}) = 0.27 \pm 0.01$ gauss for XIV$^{\ominus}$ ($g = 2.0049 \pm 0.0001$; DMF/$\mathrm{Et_4N^{\oplus}}$; $-60°$).



XIII, R = Me
XIV, R = t-Bu

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REFERENCES

[1] For recent comprehensive reviews on cyclopropenones see: *K.T. Potts & J.S. Baum*, Chem. Reviews *74*, 189 (1974); *T. Eicher & J.L. Weber*, Topics in Current Chemistry *57*, 1 (1975).
[2] *G.A. Russell & G.R. Stevenson*, J. Amer. chem. Soc. *93*, 2432 (1971), footnote 25.
[3] *F. Gerson, H. Ohya-Nishiguchi & Ch. Wydler*, Angew. Chem. *88*, 617 (1976); Angew. Chem. Int. Ed. *15*, 552 (1976); *F. Gerson & H. Ohya-Nishiguchi*, to be published.
[4] *Ch.S. Johnson, Jr., & R. Chang*, J. chem. Physics *43*, 3183 (1965); *J.G. Broadhurst & E. Warhurst*, J. chem. Soc. (A) *1966*, 351; *R.E. Sioda, D.O. Cowan* and *W.S. Koski*, J. Amer. chem. Soc. *89*, 230 (1967).
[5] *R. Chang & Ch.S. Johnson, Jr.*, J. chem. Physics *41*, 3272 (1964).
[6] *N.M. Atherton, F. Gerson & J.N. Ockwell*, J. chem. Soc. (A) *1966*, 109.
[7] *R. Dehl & G.K. Fraenkel*, J. chem. Physics *39*, 1793 (1963).
[8] *A.D. McLachlan*, Mol. Physics *3*, 233 (1960).
[9] *H.L. Ammon*, J. Amer. chem. Soc. *95*, 7093 (1973).
[10] *F. Gerson, M. Szwarc & Ch. Wydler*, to be published.
[11] *S. Andreades*, J. Amer. chem. Soc. *87*, 3941 (1965).
[12] *J.K. Crandall & W.W. Conover*, Tetrahedron Letters, *1971*, 583.
[13] *A. Krebs*, unpublished results.
[14] *K.W. Bowers, R.W. Giese, J. Grimshaw, H.O. House, N.H. Kolodny, K. Kronberger & D.K. Roe*, J. Amer. chem. Soc. *92*, 2783 (1970).
[15] *G.A. Russell*, 'Semidione Radical Anions' in 'Radical Ions' (E.T. Kaiser & L. Kevan, eds.), Interscience Publishers, New York 1968.