Electron Spin Resonance Study of Air Oxidation of p-Alkyl-Substituted Phenones in Hexamethylphosphoramide. Orientation of Carbanion Formation. Extension to the Oxidation of Aromatic Cyano, Nitro, and Aldehydo Compounds[1]

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Abstract: The esr study of the air oxidation of p-alkyl-substituted phenones, $R'_{(\alpha')}$-C_6H_4-CO-$R_{(\alpha)}$ (with R' = methyl, ethyl, n-propyl; and R = methyl, ethyl), in hexamethylphosphoramide (HMPA) containing strong bases demonstrates the competitive formation of two carbanions by α or α' proton abstraction. When R = R' = ethyl, $EtC_6H_4COCH^-CH_3$ and $CH_3CH^-C_6H_4COEt$ are formed. Air oxidation of the carbanions, followed by the reduction of the intermediate diketone, leads to $EtC_6H_4CO\cdot{}^-COCH_3$ and $CH_3CO\cdot{}^-C_6H_4COEt$ radical anions observed by esr. The extent to which each carbanion is formed depends on the relative labilities of α and α' protons. When R = methyl and R' = successively methyl, n-propyl, and ethyl (para-substituted acetophenones), the α proton abstraction rate is negligible compared to that for α', and $R'CO\cdot{}^-C_6H_4COCH_3$ cis and trans isomers radical anions are observed with increasing facility for the preceding R' substituent order. INDO (closed shell) calculations of C-H bonding energies show that the proton lability is *markedly* lower in α than in α' and increases for the latter position in the same order as the facility of para diketone radical anion appearance; this fact is interpreted in terms of an auto catalytic mechanism of radical formation. Similarly, α' oxidation occurs with aromatic compounds whose α' protons are activated by groups with σ^- values greater than σ^- $COCH_3$, e.g., NO_2, CHO, CN; the corresponding para-substituted ketyls are observed by esr.

Air oxidation of $C_6H_5COCH_2R$ (R = alkyl) in aprotic media containing strong bases has been thoroughly studied by Russell, *et al.*[2] $C_6H_5COCO\cdot{}^-R$ semidione radical anions are observed by esr except for R = H;[3] the reaction is understood in terms of carbanion formation by proton abstraction from the highly acidic α-methylene group in the first step of the process. The problem with which we were concerned was the determination of the effects of any other activated site likely to compete for proton release with the α-methylene group. We considered that the methylene group (α') of the para substituent in the ketones $R'CH_2C_6H_4COCH_2R$, which is activated by the electron-attracting carbonyl group, might have comparable or even greater acidic character than the α-methylene group and would, consequently, lead to the formation of a carbanion by proton abstraction. Further oxida-

tion of that carbanion to a dicarbonyl compound, followed by reduction, would be expected to yield the ketyls of para diketones observable by esr. If these hypotheses are valid, one could reasonably expect that alkylbenzenes, substituted in the para position by groups with equal or stronger electron-attracting properties than those of the $COCH_3$ group (as defined by their σ^- values), would undergo an oxidation reaction similar to that of the p-phenones.

To check these ideas we undertook the esr study of the oxidation of p-alkyl-substituted phenones (a, R = H, R' = H, Me, Et; b, R = Me, R' = Me), p-tolunitrile, p-methylbenzaldehyde, and $R'C_6H_5NO_2$ (R' = Me, Et) in hexamethylphosphoramide (HMPA) containing sodium methoxide.

Experimental Section

Materials. Commercially available (Eastman) p-methyl- and p-ethylacetophenones were purified by glc; p-n-propylacetophenone and p-ethylpropiophenone were prepared by the Friedel-Crafts reaction and then purified by glc. Commercial HMPA (Prolabo) was distilled under reduced pressure. Water concentration, as determined by the Karl-Fischer method, was less than 300 mg/kg. Sodium methoxide (Merck) was added to HMPA in a drybox under argon atmosphere. The solvent-base system was heterogeneous. Ketones were introduced at the desired concentrations into quartz tubes in the drybox.

Computed Esr Spectra. Computations of the esr spectra from the experimental values of hyperfine splittings were performed with a PDP-7 digital computer connected to a TD 1341 Benson plotter.

Experimental Esr Spectra

Esr spectra were recorded on a Varian E-3 esr spectrometer; temperatures were controlled by means of the Varian variable-temperature accessory.

p-**Ethylacetophenone.** Traces of $EtC_6H_4COCH_3$ are added to 0.15 mol of NaOMe in 20 ml of partially deoxygenated HMPA. Immediate formation of a stable, intense esr spectrum is observed over a wide

(1) This article will be included in G. Dodin's doctoral thesis, Université de Paris VII.

(2) G. A. Russell, E. T. Strom, E. R. Talaty, and S. A. Weiner, *J. Amer. Chem. Soc.*, **88**, 1998 (1966).

(3) It could be reasonably expected that phenylglyoxal radicals could be obtained from acetophenone since, as reported by Kelly (W. L. Kelly, Ph.D. Dissertation, Pennsylvania State University, 1968), the pK_a values of ketone-enolate equilibria have, approximately, the same order of magnitude in acetophenone, as in C_6H_5COR (R = CH_2-CH_2CH_3, $CH_2CH(CH_3)_2$, for which semidiones are obtained. Acetophenone (10^{-3} mol) is added to 0.15 mol of sodium methoxide in 20 ml of HMPA, previously partially deoxygenated under an argon flow. A weak, unstable esr spectrum consisting of 27 poorly resolved lines is observed. The spectrum is tentatively attributed to the interaction of the unpaired electron with four sets of protons: 2 (0.5 G), 2 (1.55 G), 1 (1.9 G), 1 (6.95 G). These values are comparable with those reported by Russell for the radical anion of phenylglyoxal [G. A. Russell, R. D. Stephens, and E. R. Talaty, *Tetrahedron Lett.*, 1139 (1965)]. The spectrum computed from the experimental values of hfs appears to be somewhat simpler than the experimental one. One may postulate the existence of another paramagnetic species, characterized by the same overall splitting, which could be formed in a cis-trans isomerization process. When an excess of air is allowed to enter the reaction tube, the epr signal vanishes. No resonance signal was detected when acetophenone is introduced in a nondeoxygenated NaOMe-HMPA solution.
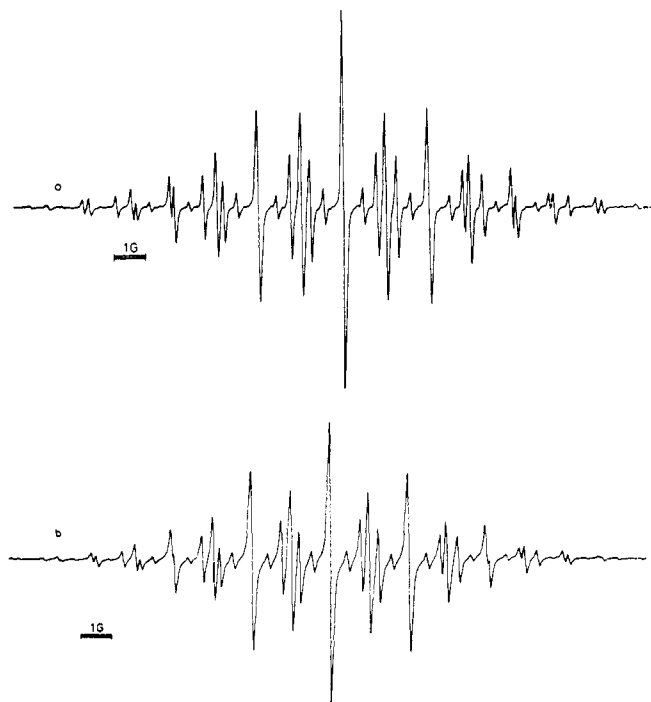
Figure 1. First-derivative esr spectrum observed in the air oxidation of *p*-ethylacetophenone in NaOMe–HMPA solutions. The structure is attributed to the cis and trans isomers of diacetylbenzene radical anions: a, experimental spectrum; b, computed spectrum for Lorentzian line width of 0.10 G with equal proportions in cis and trans forms.
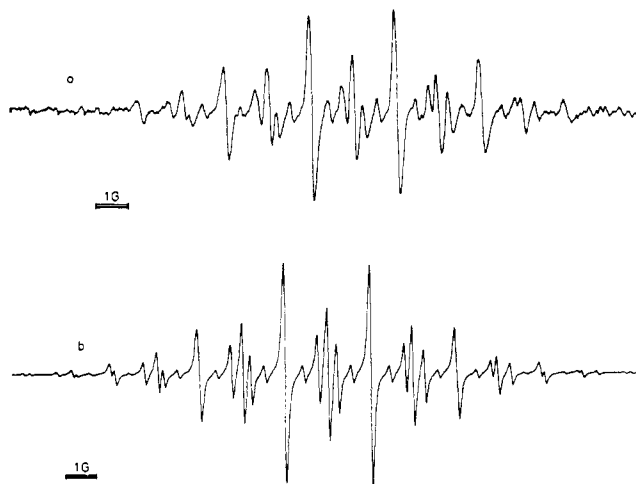

Figure 2. First-derivative esr spectrum observed in the air oxidation of *p*-*n*-propylacetophenone in NaOMe–HMPA solutions. The structure is attributed to the cis and trans isomers of CH_3CH_2CO-$C_6H_4COCH_3$ radical anions: a, experimental spectrum; b, computed spectrum for Lorentzian line width of 0.12 G with equal proportions in the cis and trans forms.

range of temperatures (Figure 1); the signal is stable toward an excess of oxygen. Temperature variations induce some slight modifications of the splittings; the total spectrum width is about 20 G. The spectrum must be interpreted in terms of a superposition of two resonance signals, having the same *g* factor, which we will refer to as T and C. Spectrum T is assumed to be due to the interaction of the unpaired electron with a set of six equivalent protons (hfs = 2.7 G at −5°), a set of two equivalent protons (hfs = 1.66 G at −5°), and a set of two protons (hfs = 1.05 G at −5°). Spectrum C is assigned to a structure consisting of two sets of protons (6 protons with a splitting of 2.65 G and 4 protons with a splitting of 1.31 G at −5°). The ratio T/C is equal to unity. The overall T + C spectrum *computed* from the above-mentioned hyperfine splitting values, with T/C = 1, is identical with the experimental spectrum. Unambiguous assignment of the composite spectrum will be attempted on the basis of the following arguments. Firstly, the attribution of the T and C spectra to the $EtC_6H_4COCO\cdot^-H$ semidione radical anions must be excluded as shown by the symmetries of the signals as well as by their total widths. The spectra show some relevant features which will be helpful in the following discussion: the overall splittings of the T and C spectra are equivalent; the coupling constants of the two sets of six equivalent protons differ only slightly; consequently, the *total splitting* from the four remaining protons is the same in T and C but the contribution from the various atomic sites differs from one structure to the other; this suggests a modification of the spin densities on the four hydrogen atoms by a cis–trans isomerization process. We postulate that the T and C spectra are attributable to the trans and

cis isomers of diacetylbenzene radical anions, respectively;[4] the hfs values are consistent with those previously reported.[5,6]

p-*n*-**Propylacetophenone.** When 10^{-3} mol of *p*-*n*-propylacetophenone is added to 0.15 mol of NaOMe in partially deoxygenated HMPA (20 ml), a weak esr spectrum is observed. Ketone concentration must be raised to 0.02 mol to observe an intense, stable esr signal (Figure 2); the signal only becomes observable a short time after mixing, and it is stable to an excess of oxygen. The total width of the spectrum is about 19 G. As above, the signal must be attributed to the superposition of two distinct spectra (T and C) having the same *g* factor. The hfs values are approximately the same as those measured for *cis*- and *trans*-diacetylbenzene radical anions; however, the number of lines and the symmetry of the spectrum are different. Spectrum T is attributable to the unpaired electron interaction with three sets of protons: 5 protons (hfs = 2.7 at −5°), 2 protons (1.65 G), and 2 protons (1.05 G). Spectrum C is assigned to a structure consisting of two sets of protons: 5 protons (2.65 G) and 4 protons (1.30 G). The computed T + C spectrum, with equal contributions from the two structures, is identical with that observed experimentally. For the reasons previously stated, the T and C spectra are attributed to the trans and cis isomers of $CH_3CH_2COC_6H_4COCH_3$

(4) (a) We have excluded the occurrence of the cis–trans equilibrium between ion pairs of Na benzoquinone radical anions[4b] which might have formed eventually from the starting ketones; ion pairs are not likely to form in HMPA and the esr spectrum we observed when *p*-benzoquinone was allowed to react with the NaOMe–HMPA system was that of the free ion (five lines with relative intensities of 1, 4, 6, 4, 1 split by 2.4 G). (b) E. A. C. Lucken, *J. Chem. Soc.*, 4234 (1964).

(5) P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 37, 2811 (1962).

(6) The formation of $R'COC_6H_4COR$ radical anions could be misleading in an attempt to prepare the ketyls of $R'CH_2C_6H_4COR$ by reduction with Na in HMPA; when a partially evacuated blue Na HMPA solution is added to $R'CH_2C_6H_4COR$ (R' = H, CH_3, C_2H_5; R = CH_3, C_2H_5), the observed esr spectra are those attributed to $R'CO$-C_6H_4COR radical anions. The decomposed Na HMPA solutions (yellow) lead to the same observation. We have not, so far, investigated the nature of the strong base formed when sodium reacts with HMPA; according to H. Normant [*Angew. Chem., Int. Ed. Engl.*, 6, 1046 (1967)] the base might be Me_2N^-.
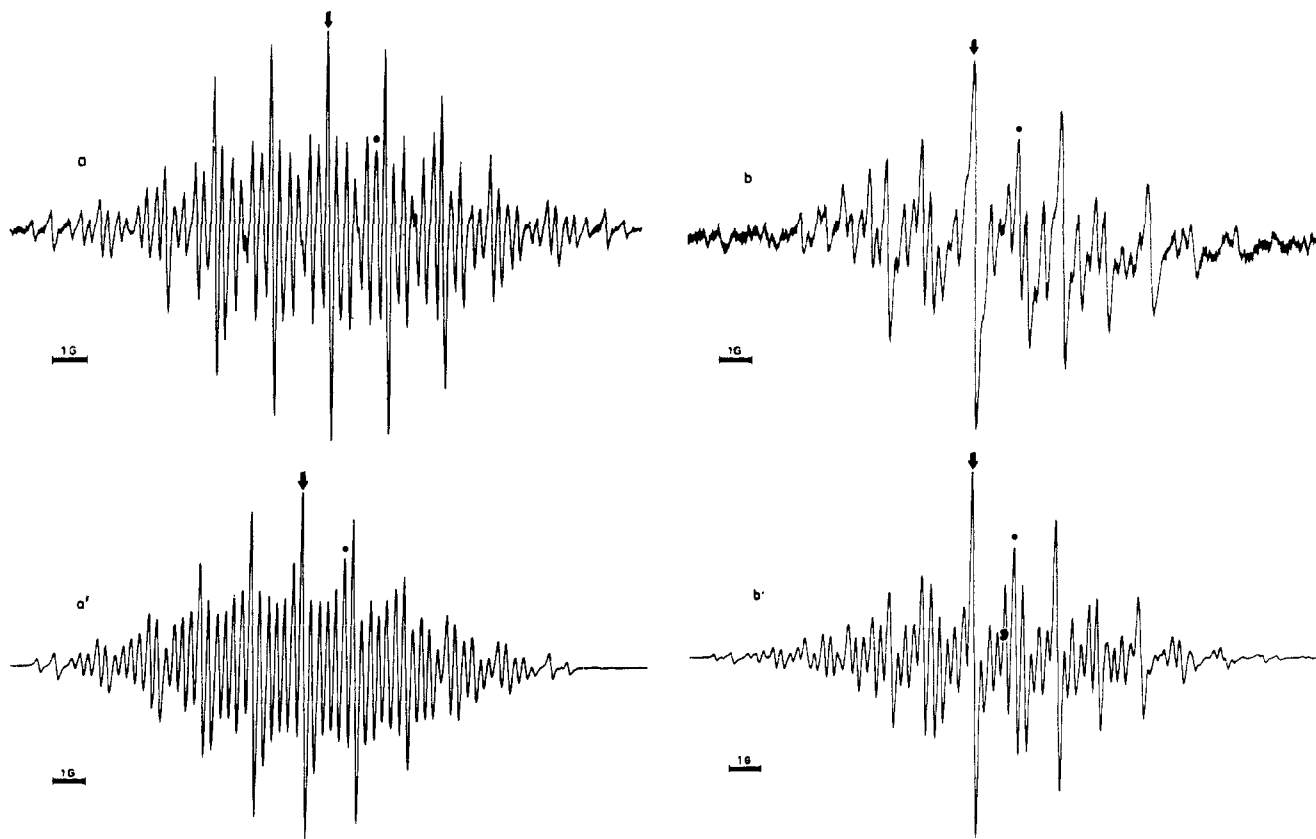
Figure 3. First-derivative esr spectrum observed in the air oxidation of p-ethylpropiophenone in NaOMe–HMPA solutions: a, experimental spectrum attributed to a mixture of $CH_3CH_2C_6H_4COCO^-CH_3$ and $CH_3COC_6H_4CO^-CH_2CH_3$ (cis + trans) with a concentration ratio semidione:para diketone = 30; a', computed spectrum with Lorentzian line width of 0.12 G; b, spectrum observed after reaction with an excess of oxygen (6 hr; b', computed spectrum (semidione:para diketone = 3). The arrow and the closed circle refer to the centers of semidione and para diketone radical anion spectra, respectively.

radical anions, respectively; no hyperfine splitting is observed for the β'-methyl group.

p-**Ethylpropiophenone.** p-Ethylpropiophenone (10^{-3} mol) is added to the base–solvent system. An intense, well-resolved spectrum is observed which can be recognized as the signal of $C_2H_5C_6H_4COC-OCH_3 \cdot^-$ semidione radical anion.[2] The splittings are independent of temperature in the range of -5 to $+30°$ (Figure 3). The spectrum computed from the preceding hfs values appears to be slightly different from the experimental one insofar as the intensities of the lines are concerned; this led us to assume some contribution to the overall spectrum from another paramagnetic species. When air is allowed to enter the sample tube, the esr signal evolves slowly. After approximately 6 hr the signal from $C_2H_5C_6H_4COCO \cdot^-$-CH_3 has decreased and the spectrum from the other paramagnetic entity becomes clearly observable; this signal is shifted toward low magnetic fields by 1.35 G with respect to the semidione spectrum. The signal appears to be quite identical with that previously attributed to the radical anions of $C_2H_5COC_6H_4COCH_3$ cis and trans isomers. After about 12 hr, the signal from 1-p-ethylphenylpropane-1,2-dione radical has totally vanished while the spectra of the p-dicarbonyl radicals remain unchanged.

p-**Methylacetophenone.** Quantities of p-methylacetophenone ranging from 10^{-3} to 10^{-2} mol are added to the partially deoxygenated NaOMe–HMPA mixture. Several runs were needed for the detection of a weak

paramagnetic signal which we have not yet been able to interpret. The spectrum evolves slowly and after 2 hr a weak but stable signal is recorded. The signal is broadened and differs from that initially observed; its total width is approximately 16 G. The splittings are of the same order of magnitude as those previously attributed to the various atomic sites of $RCOC_6H_4COR'$ radical anion cis and trans isomers. Tentatively, the spectrum is interpreted in terms of the superposition of the signals from $HCOC_6H_4COCH_3$ cis and trans isomer radical anions [trans structure: 4 protons (2.7 G), 2 protons (1.63 G), 2 protons (1 G); and cis structure: 4 protons (2.65 G), 4 protons (1.30 G)]. These results may appear somewhat unexpected since they assume the equivalence of the aldehydic and methyl proton couplings. The following molecular orbital calculations will help to clarify this point.

p-**Tolunitrile.** p-Tolunitrile (10^{-3} N) in the solvent–base system leads to an esr signal (Figure 4) which is attributed to the $HCO \cdot^-C_6H_4CN$ radical anion (see Table V).

p-**Tolualdehyde.** p-Tolualdehyde (10^{-3} N) in the solvent–base system leads to a mixture of the cis and trans isomers of terephthalaldehyde radical anions (Figure 5, Table V). The ratio of the trans and cis isomers, trans–cis, is 1.35.

Para-Substituted Nitrobenzenes. p-Nitrotoluene (10^{-3} N) and p-ethylnitrobenzene (10^{-3} N) lead to esr signals attributed to p-nitrotoluene and p-ethylnitrobenzene radical anions, respectively. When the con-
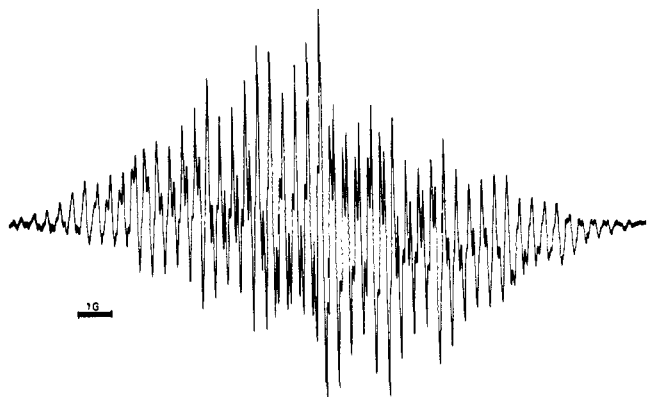
Figure 4. First-derivative esr spectrum observed in the air oxidation of p-methylbenzonitrile (10^{-3} N) in HMPA–NaOMe solutions. The spectrum is attributed to the radical anion of $HCOC_6H_4CN$.

centrations are lowered to 10^{-4} N, the esr signals of $HCOC_6H_4NO_2$ and $CH_3COC_6H_4NO_2$ radical anions are observed (Figure 6, Table V).

Molecular Orbital Calculations

Calculations were performed in order to assign the experimental hyperfine splitting constants to the various groups of nuclei.

Spin Densitites and Coupling Constant Assignments. Hyperfine splittings were calculated (a) by the INDO (OS) method[7] and (b) from the atomic coefficients of the first unoccupied molecular orbital, computed by INDO (CS), using the simple McConnell relation (without taking into account the contribution from β' pro-

Chart I

R = R' = Me   R = Me; R' = H

R = Me; R' = Et
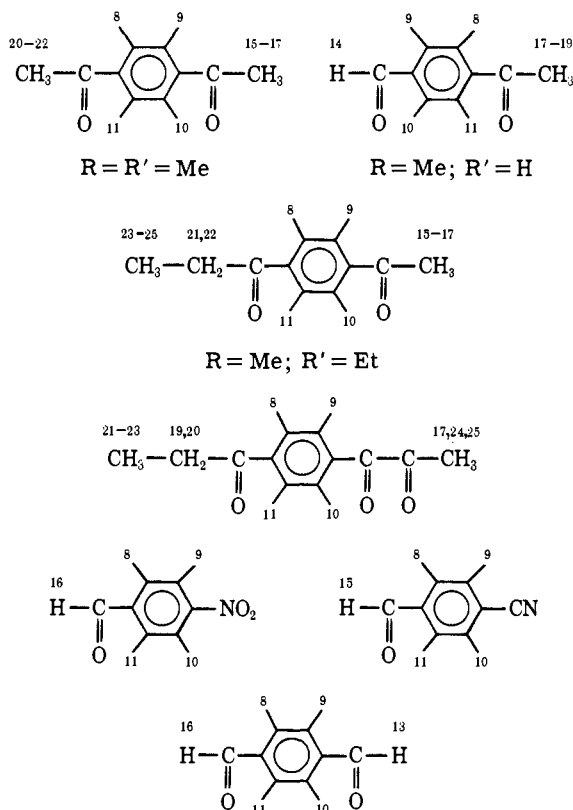
(7) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970, and references cited therein.
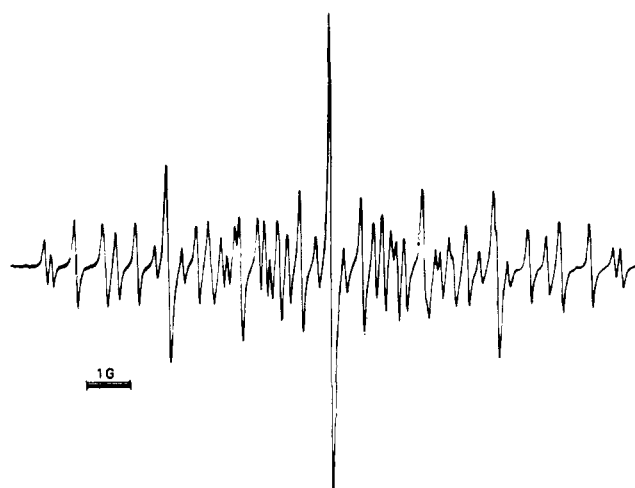

Figure 5. First-derivative esr spectrum observed in the air oxidation of p-methylbenzaldehyde (10^{-3} N) in HMPA–NaOMe solutions. The spectrum is attributed to a mixture of the *trans-* and *cis-*terephthalaldehyde radical anions (trans:cis = 1.35).

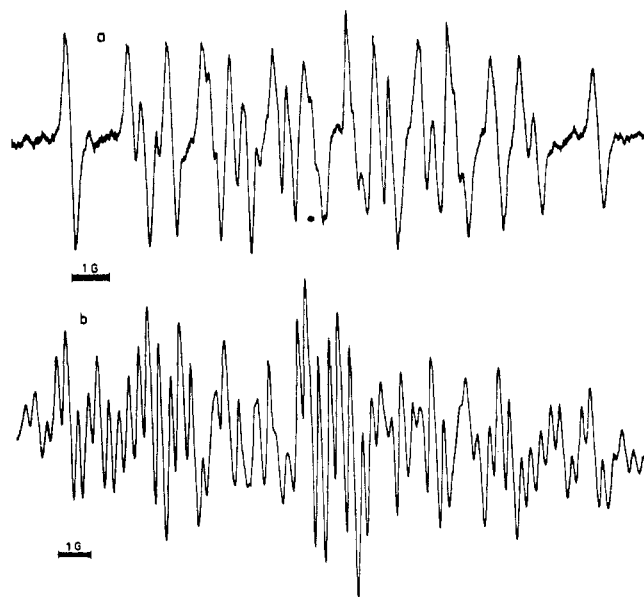Figure 6. First-derivative esr spectrum observed in the air oxidation of p-nitrotoluene and p-ethylnitrobenzene (10^{-4} N) in HMPA–NaOMe solutions. Spectrum a is attributed to the radical anion of $HCOC_6H_4NO_2$. Spectrum b is attributed to the radical anion of $CH_3COC_6H_4NO_2$.

tons). Since no geometrical data are available for the diketone nor for the diketone radical anions, bond lengths and angle values were chosen by comparison with known parent molecules (Tables I and II).

The carbonyl groups are assumed to be locked in the plane of the aromatic ring;[8] the numbering of the ketones is shown in Chart I.

The INDO (OS) method is the most satisfactory for the calculation of hyperfine splittings from a theoretical viewpoint, since it includes spin polarization accounting for negative spin densities. The differences observed between INDO (OS) calculated and experimental split-

(8) Though determination of the conformation of $R'COC_6H_4COR$ molecules is beyond the purpose of this work, it seems that a good quantitative fitting between experimental and INDO calculated hfs is observed when COR groups are twisted out of the ring plane.

Table I. Estimated Bond Lengths (Å) and Angle Values (deg) in RCH$_2$C$_6$H$_4$COCH$_3$ and RCOC$_6$H$_4$COCH$_3$

Bond lengths	C-C$_{ring}$	C-H$_{ring}$	C$_{ring}$-CO	C-O	CO-CH$_3$	C-H$_{carbonyl}$	C-CH$_3$	C-C$_{chain}$	C-H$_{alkyl}$
	1.397	1.084	1.47	1.215	1.50	1.086	1.51	1.537	1.11
Angle values		C-C-C$_{ring}$		C-C$_{ring}$-H		C$_{ring}$-CO		C$_{ring}$-CO-CH$_3$	H-C-H$_{alkyl}$
		120		120		113° 6'		123	109° 28'

Table II. Estimated Bond Lengths (Å)^a and Angle Values (deg) in R'C$_6$H$_4$R (R = Me, Et; R' = NO$_2$, CHO, CN)

Bond lengths	C-CN	C-N$_{nitrile}$	C-N$_{nitro}$	N-O	C-O	C-H$_{ald}$
	1.419	1.158	1.47	1.21	1.215	1.08
Angle values		C-C-CN	O-N-O		H-C-O	
		120	132		127	

^{a} Ring bond lengths and angle values are the same as in Table I.

ting values are of little consequence since we are ultimately interested in estimating the ratio of coupling constants corresponding to the different positions. However, the INDO (OS) method fails to account for the equivalence of the protons bound to the C=O groups in the diketones. Values calculated by the McConnell relation (with $Q = -22.5$ G for the ring carbon atoms and $Q' = -30$ G for the carbon atoms extranuclear) are, both qualitatively and quantitatively, in good agreement with the experimental values (Tables III and IV).

The calculated hyperfine splittings in para-substituted benzaldehyde radical anions differ from the experimental values but assignments to the various nuclei can be achieved (Table V).[9]

Isomerization Barrier and Isomerization Enthalpy. Energy calculations are effected by the INDO (CS) method for neutral molecules with the assumption that the results remain valid for the radical anion species; the molecular geometries are the same as previously. We must emphasize that too much importance should not be placed upon the absolute magnitude of the calculated values. The cis–trans equilibrium may be understood in terms of a four-step equilibrium model (Table VI).
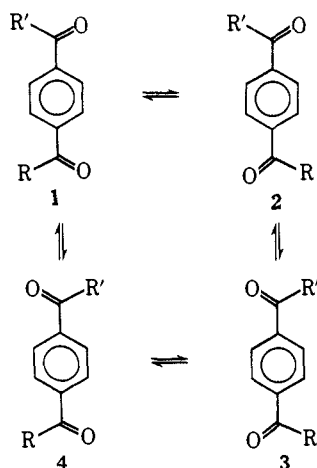
The differences between the total energies of the cis and trans isomers are obviously independent of the reaction pathway. If we accept, to a first approximation, that entropy variation in the isomerization process is equal to zero, the total energy variation is related to the cis–trans equilibrium constants by the equation $K_{cis-trans} = \exp(-\Delta H/RT)$ (Table VII).

(9) The experimental hyperfine splitting values are similar to those reported in the literature for radical anions in aprotic media (see K. W. Bowers, "Advances in Magnetic Resonance," Vol. 1, Academic Press, New York and London, 1965, and references cited therein).

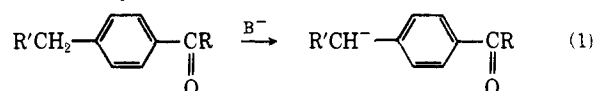**Table III.** Observed and Calculated Hyperfine Splitting Constants for CH$_3$CH$_2$C$_6$H$_4$CO · $^-$COCH$_3$ Semidione

Position	8	9	10	11	17,24,25	19,20
Obsd^a	0.55	1.6	1.6	0.55	3.2^c	1.35
Calcd^b	0.7	1.61	1.4	0.8	0.4	3.5

^{a} Values are in gauss. ^{b} By INDO (OS). ^{c} hfs values for the hydrogen atoms out of the ring fail to fit the experimental results.
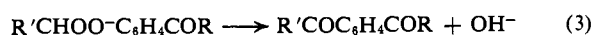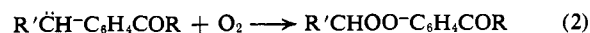
On the other hand, rotational barriers are strongly dependent on the isomerization pathway; for R and R' = CH$_3$ or C$_2$H$_5$ the two pathways are equally probable, while for R or R' = H isomerization through 1 → 2 will be greatly favored due to the low relative value of the barrier. This might explain the broadening of the esr spectrum in that case.

Mechanism of Phenone Oxidation

We have not, so far, carried out quantitative kinetic studies of p-alkyl-substituted phenone oxidation. However, we can formulate a working hypothesis from the above mentioned qualitative features of the reaction. We will assume that the reaction scheme is similar to that proposed by Russell[10] to account for the oxidation of aromatic hydrocarbons.

The following resonance forms may stabilize the carbanion.

$$R'\ddot{C}H^-C_6H_4COR + O_2 \longrightarrow R'CHOO^-C_6H_4COR \quad (2)$$

$$R'CHOO^-C_6H_4COR \longrightarrow R'COC_6H_4COR + OH^- \quad (3)$$
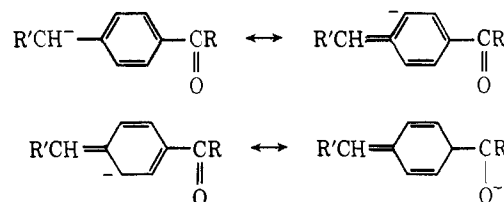
The reduction of the diketone would be effected by the carbanion formed in step 1.

$$R'COC_6H_4COR + R'\ddot{C}H^-C_6H_4COR \longrightarrow$$
$$R'COC_6H_4C\dot{O}^-R + R'CHC_6H_4C\dot{O}R \quad (4)$$
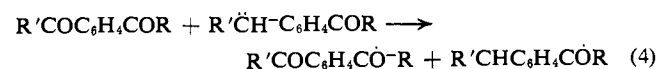
We did not observe paramagnetic compounds from β' oxidation. The α-oxidation rate is assumed to be negligible compared to that of α' in p-ethylacetophenone

(10) G. A. Russell, A. G. Bemis, E. J. Goels, E. G. Jansen, and A. J. Moye, *Advan. Chem. Ser.*, No. 75, 174 (1968).

Table IV. Observed and Calculated Hyperfine Splitting Constants[a] for RCOC₆H₄COR' Radical Anions at −5°

			R = H; R' = Me			
Position	8	9	10	11	14	17,18,19
Obsd cis	1.3	1.3	1.3	1.3	2.65	2.65
trans	1	1.65	1.65	1	2.7	2.7
Calcd[b] cis	1.3	1.34	1.38	1.31	2.61	2.77
trans	1.27	1.41	1.32	1.34	2.61	2.77
Calcd[c] cis	0.8	0.5	0.63	0.78	0.17	0.8
trans	0.82	0.55	0.62	0.76	0.17	0.8

			R = Me; R' = Me			
Position	8	9	10	11	15,16,17	20,21,22
Obsd cis	1.31	1.31	1.31	1.31	2.65	2.65
trans	1.05	1.66	1.05	1.66	2.7	2.7
Calcd[b] cis	1.32	1.32	1.29	1.29	2.63	2.63
trans	1.26	1.36	1.26	1.36	2.63	2.63
Calcd[c] cis	0.60	0.60	0.70	0.70	1.07	1.07
trans	0.48	0.83	0.48	0.83	1.1	1.1

			R = Et; R' = Me				
Position	8	9	10	11	15,16,17	21,22	23,24,25
Obsd cis	1.30	1.30	1.30	1.30	2.63	2.63	Not obsd
trans	1.05	1.65	1.05	1.65	2.7	2.7	Not obsd
Calcd[b] cis	1.35	1.33	1.30	1.30	2.58	2.63	0.02
trans	1.26	1.39	1.27	1.37	2.58	2.63	0.02
Calcd[c] cis	0.69	0.61	0.71	0.73	0.98	0.9	0.01
trans	0.79	0.58	0.74	0.64	0.99	0.9	0.01

[a] All values are in gauss. [b] Using the McConnell relation with $Q = -22.5$ G for the ring protons and $Q' = -30$ G for the protons of the substituents. [c] Using INDO (OS).

Table V. Observed and Calculated Hyperfine Splitting Constants[a] for RC(=O)C₆H₄R' Radical Anions at Room Temperature

			R = H; R' = NO₂			
Position	8	9	10	11	12	16
Obsd	2.75	3.05	3.05	2.75	4.7	1.65
Calcd[b]	1.13	1.7	1.7	1.13	3.2	1.9
Calcd[c]	0.3	2.0	1.96	9.3	1.4	0.38

			R = H; R' = CN			
Position	8	9	10	11	13	15
Obsd	3.15	0.25	0.74	2.87	1.5	5.5
Calcd[b]	2.18	0.90	0.9	2.12	2	5
Calcd[c]	2.32	0.54	0.53	2.27	1.47	1.58

			R = R' = H			
Position	8	9	10	11	13	16
Obsd cis	1.47	1.47	1.16	1.16	3.6	3.6
trans	2.05	0.67	2.05	0.67	3.7	3.7
Calcd[b] cis	1.34	1.34	1.36	1.36	2.81	2.81
trans	1.38	1.31	1.38	1.31	2.83	2.83
Calcd[c] cis	0.72	0.72	0.77	0.77	0.358	0.35
trans	0.75	0.74	0.75	0.74	0.36	0.36

[a] In gauss. [b] Using the McConnell relation with $Q = -22.5$ G for the ring protons, $Q' = -30$ G for the extranuclear protons, and $Q_N = -25$ G for nitrogen. [c] Using INDO (OS).

less stable than the radical of the para diketone and evolves slowly, probably through reaction with oxygen). Semidione or para diketone radical anion formation will depend on which kind of carbanion is formed in the first step and, obviously, on the relative acidic character of the α and α' hydrogen atoms. INDO calculations of C–H bonding energies in RCO-C₆H₄COR' (Table VIII) confirm the preceding assumptions and suggest that α'-proton labilities increase in acetophenones when R' is successively Me, Et, H.

Since para diketone radical anion observation is increasingly facile for the preceding R' substituent order, we will assume that ketyl formation rates vary in the same manner as the acidity of the α' protons. By analogy with the conclusions reported in the case of aromatic hydrocarbon oxidations, the stability toward oxygen of the carbanion formed by α' proton abstraction in acetophenones (step 1) would normally increase with the acidity of the starting ketone. Step 2 would be rate determining and, hence, reaction rates would decrease when α' proton acidities increase. We must as-

Table VI. INDO (CS) Calculated Isomerization Energies of R'COC₆H₄COR[a]

Pathway	1cis → 2trans	1cis → 4trans	2trans → 1cis	4trans → 1cis
R' = H; R = CH₃	−1.614	−3.66	−1.549	−3.595
R' = R = CH₃	−3.63	−3.63	−3.52	−3.52
R' = C₂H₅; R = CH₃	−3.69	−3.99	−3.58	−3.89
R = R' = H	−1.24	−1.24	−1.205	−1.205

[a] All energy values are in kilocalories per mole.

and propylacetophenone[11] and greater in propiophenone (the semidione preferentially formed is, however,

(11) The α oxidation may occur in substituted acetophenones as can be assumed from the observation of phenylglyoxal radical anion formation in the air oxidation of acetophenone. INDO calculations suggest that, in p-methylacetophenone, α-proton lability is slightly greater than that of α' protons; since radicals from α' oxidation are observable (through at low rate) one may therefore assume that α

sume, consequently, that carbanion consumption is accelerated by the neutral diketone (formed in step 3)

oxidation also takes place. This might account for the unassigned esr spectrum, observed a short time after addition of the p-methylacetophenone to the solvent-base system, which may result from the overlap of semidione and para diketone radical signals with the semidione spectra evolving slowly.

Table VII. INDO (CS) Calculated Difference of the Total Energy of $R'COC_6H_4COR$ Cis and Trans Isomers.[a]
Calculated Constants of the Cis ↔ Trans Equilibrium at Room Temperature

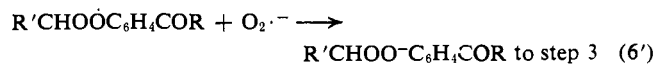| Substituent	$R = CH_3$; $R' = H$	$R = R' = CH_3$	$R = CH_3$; $R' = C_2H_5$	$R = R' = H$
$E_{cis-trans}$	−0.065	−0.109	−0.108	−0.035
$K_{cis-trans}$	1.12	1.2	1.2	1.06

[a] Energy values are in kilocalories per mole.

Table VIII. INDO (CS) Calculated C–H Bond Energies in $R'CH_2C_6H_4COR$[a]

Bond energy	$C-H_\alpha$[b]	$C-H_{\alpha'}$[b]	$C-H_{\beta'}$[b]	$C-H_{\gamma'}$[b]
$R' = H$; $R = Me$	−467.10	−468.14		
$R' = Me$; $R = Me$	−467.14	−460.66	−471.80	
$R' = Et$; $R = Me$	−467.13	−461.36	−464.27	−472.03
$R' = Et$; $R = Et$	−460.247	−460.667	−471.84	

[a] Energies are in kilocalories per mole. [b] Subscripts α, α', β', and γ' refer to the positions from the ring of the substituent carbon atoms.

acting as an electron acceptor (step 4) until step 1 becomes rate determining. One may expect that the consequence of this autocatalyzed mechanism would be the occurrence of an inductive phase until neutral diketone concentration becomes high enough. After step 4 the reaction would proceed as follows.

$$R'\dot{C}HC_6H_4COR + O_2 \longrightarrow R'CHOO\dot{}C_6H_4COR \quad (4')$$

$$R'\dot{C}O^-C_6H_4COR + O_2 \longrightarrow R'COC_6H_4COR + O_2\cdot^- \quad (5')$$

$$R'CHOOC_6H_4COR + O_2\cdot^- \longrightarrow$$
$$R'CHOO^-C_6H_4COR \text{ to step 3} \quad (6')$$

Mechanism of p-Tolunitrile, p-Tolualdehyde, and Para-Substituted Nitrobenzene Oxidation

Russell's mechanism will also apply to the oxidation of p-tolunitrile, p-tolualdehyde, and para-substituted

nitrobenzenes. The fact that the oxidation of the methyl group occurs readily for these compounds, while it was difficult in p-methylacetophenone, must be understood in terms of the σ^- values of NO_2, CN, and CHO groups being greater than $\sigma^-_{COCH_3}$.

p-Methylnitrobenzene and p-ethylnitrobenzene radical anions from 10^{-3} N solutions may be formed either by direct reduction of the nitrobenzenes by the strong base[12] or by reaction (step 4) with the carbanion formed in step 1, the nitrobenzenes acting as catalyst. This reaction would compete with that of the carbanion with the neutral ketone formed in step 3.

In conclusion, alkylbenzenes which are substituted in the para position by strong electron-attracting groups behave as acidic hydrocarbons and lead to carbanions which can autoxidize to ketones. We are at present investigating the extension of the autoxidation reaction to other series of organic compounds. Quantitative studies of the reaction kinetics and application to ketone synthesis will be discussed in following papers.

(12) Nitrobenzene (10^{-3} N) in HMPA–NaOMe leads to the formation of the nitrobenzene radical anion.

Electrochemical Studies of the Formation and Decomposition of Halogenated Benzonitrile Anion Radicals

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Abstract: The electrochemical reduction of a series of bromo-, chloro-, and iodobenzonitriles in N,N-dimethylformamide has been shown to be an overall two-electron process which gives benzonitrile as the principal product. Since reduction of one of these halogenated benzonitriles (4-chlorobenzonitrile) in the presence of cyanide ion gives rise to a small amount of terephthalonitrile anion radical, the intermediacy of cyanophenyl radicals is suggested. A reaction pathway consistent with these data involves the initial one-electron reduction of the halogenated benzonitrile, rapid loss of halide ion from the anion radical to give the corresponding cyanophenyl radical, and subsequent reduction of the cyanophenyl radical at the electrode surface to cyanophenyl anion. Abstraction of a proton from the solvent system by the cyanophenyl anion yields benzonitrile and completes the reaction pathway. The results obtained here are contrasted with previously reported decomposition pathways of the anion radicals of 4-fluoro- and 4-aminobenzonitrile.

Electrochemical and electron spin resonance studies of numerous substituted aromatic nitrile radicals in N,N-dimethylformamide (DMF) have been reported by Rieger, et al.[1] Although reduction of the cyano and

nitro derivatives of benzonitrile gave very stable anion radicals, the anion radicals of 4-amino- and 4-

(1) P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 683 (1963).