Tetrahedron. Vol. 34, pp. 933 to 940. Pergamon Press 1978. Printed in Great Britain

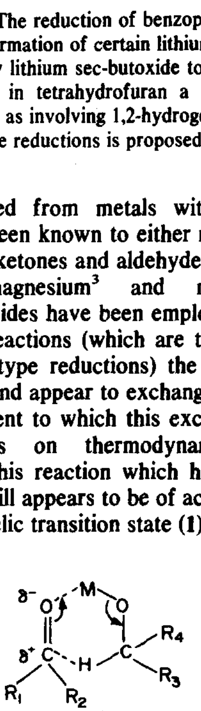
MECHANISM OF MEERWEIN-PONDORF-VERLEY TYPE REDUCTIONS

CONSTANTINOS G. SCRETTAS* and CONSTANTINE T. CAZIANIS
The National Hellenic Research Foundation, Athens 501/1, Greece

(*Received in the UK* 14 *July* 1977; *Accepted for publication* 20 *July* 1977)

Abstract—The reduction of benzophenone by lithium and chloromagnesium alkoxides has been studied as well as the transformation of certain lithium alkoxides to the corresponding ketones by electron transfer. Fluorenone was reduced by lithium sec-butoxide to the corresponding lithium ketyl to the extent of 65%. Lithium 9-fluoroenolate underwent in tetrahydrofuran a spontaneous transformation to lithium fluorenone ketyl. This process was interpreted as involving 1,2-hydrogen shift in an oxygen-centred radical. A mechanism for the Meerwein-Pondorf-Verley-type reductions is proposed, invoking single electron as well as 1,2-hydrogen shift steps.

Alkoxides derived from metals with low ionization potentials have been known to either reduce or catalyse the reduction of ketones and aldehydes. Sodium,[1] potassium,[2] bromomagnesium[3] and more commonly aluminium[4] alkoxides have been employed in such reactions. In these reactions (which are termed Meerwein-Pondorf-Verley type reductions) the alkoxide and the carbonyl compound appear to exchange their functionalities and the extent to which this exchange takes place usually depends on thermodynamic factors. A mechanism for this reaction which has been proposed long ago[1,5] and still appears to be of acceptance[3] invokes a six-member cyclic transition state (**1**) for a hydride-like transfer reaction



(**1**)

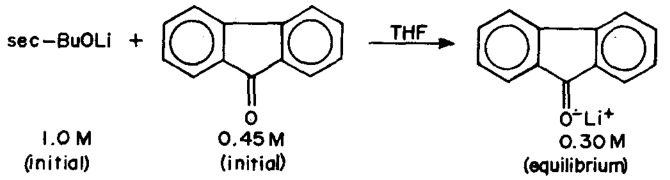
The purpose of this paper is to report the identification of some intermediates derived from both the alkoxide and the substrate and to propose a new mechanism for the Meerwein-Pondorf-Verley type (MPV-type), reaction which can accomodate the new as well as the old experimental evidence.

Lithium sec-butoxide alone or in the presence of sec-butanol was found to reduce benzophenone to benzhydrol in refluxing tetrahydrofuran (THF) under an atmosphere of argon. Similar results were obtained with lithium isoamyl alkoxide and chloromagnesium sec-butoxide. In the latter case a bluish-purple coloration was observed in the initial stages of the reaction. When the reduction of fluorenone was attempted with lithium sec-butoxide the reaction stopped in the stage of lithium fluorenenone ketyl and it did not seem to go any further. The lithium ketyl survived even after adding a large excess of sec-butanol and the mixture was refluxed for several hours. The results are summarized in Table 1.

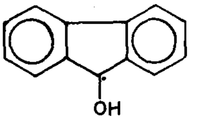
By measuring the bulk paramagnetism of the solution, before adding butanol, we were able to estimate the extent to which the reduction to ketyl took place, eqn 2.

Thus, although Russell *et al.* have generated fluorenone ketyl by electron transfer from tert-butoxide to fluorenone,[6] this extent of ketyl production by electron transfer from alkoxide could be a record. The slowness with which lithium fluorenone ketyl is protonated can be accounted for on considering the pK_a values of the two acids, namely sec-butanol and **2a**, ~18 and 6.3,[7] respectively. Secondary butanol is too weak of an acid to protonate the conjugate base of another acid which is 12 orders of magnitude more acidic.

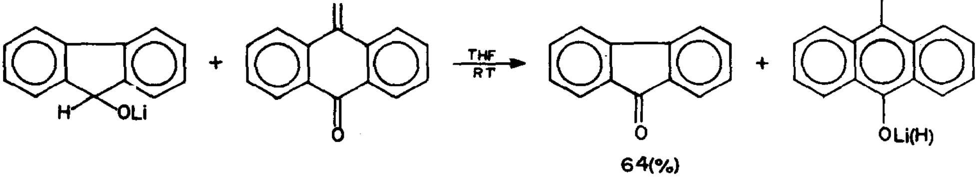
Lithium 9-fluorenolate underwent electron loss to 9,10-anthraquinone and it was transformed to fluorenone in



(2)

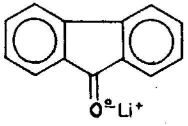
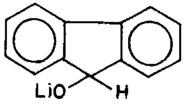
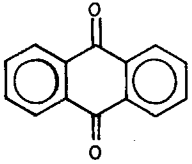
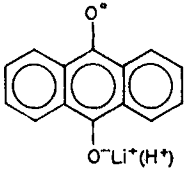
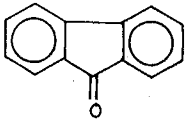
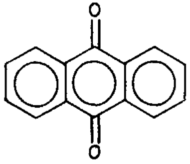
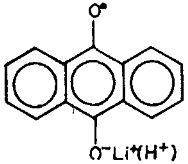


(**2a**)



(3)

Table 1. Reduction of benzophenone by certain metal alkoxides, and some other relevant reactions

Metal alkoxide (mmole)	Alcohol (mmole)	Ketone or electron acceptor (mmole)	Recovered material (%)	Reduced ketone (%)	Solvent THF–C_6H_6 (ml)	Reaction time (h)	Ketone derived from alkoxide (%)	Remarks
sec-BuOLI (10)	—	$Ph_2C{=}O$ (10)	80†	Ph_2CHOH (70)	15–6	28‡	+‖	Faint bluish color
sec-BuOLi (10)	sec-BuOH (10)	$Ph_2C{=}O$ (10)	96	Ph_2CHOH (73)	15–6	28‡	+	
sec-BuOLi (5.2)	sec-BuOH (22)	$Ph_2C{=}O$ (22)	90	Ph_2CHOH (62.5)	10–3	24‡	Not checked	
i-AmOLi (10)	i-AmOH (35)	$Ph_2C{=}O$ (27.5)	100	Ph_2CHOH (41)	10–6	24‡	Not checked	
sec-BuOMgCl (14.8)	sec-BuOH (55)	$Ph_2C{=}O$ (27.5)	71†	Ph_2CHOH (67.5)	10–0	42.5‡	Not checked	Bluish-purple (faint)
sec-BuOLi (10)	—	Fluorenone (4.5)	—	 (65)	8–0	7§	Not checked	
 (10)	—	 (20)	—		25–0	38§	 (64)	
Ph_2CHOLi (10)	—	 (20)			25–0	24‡	$Ph_2C{=}O$ (58)	

†The low recovery could be due to cleavage of $Ph_2C{=}O$ to $PhCO_2M$, see G. A. Swan, *J. Chem. Soc.*, 1408 (1948).

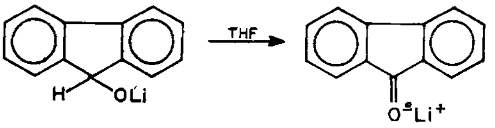
‡At the reflux temperature.

§At room temp.

‖Positive qualit. test.

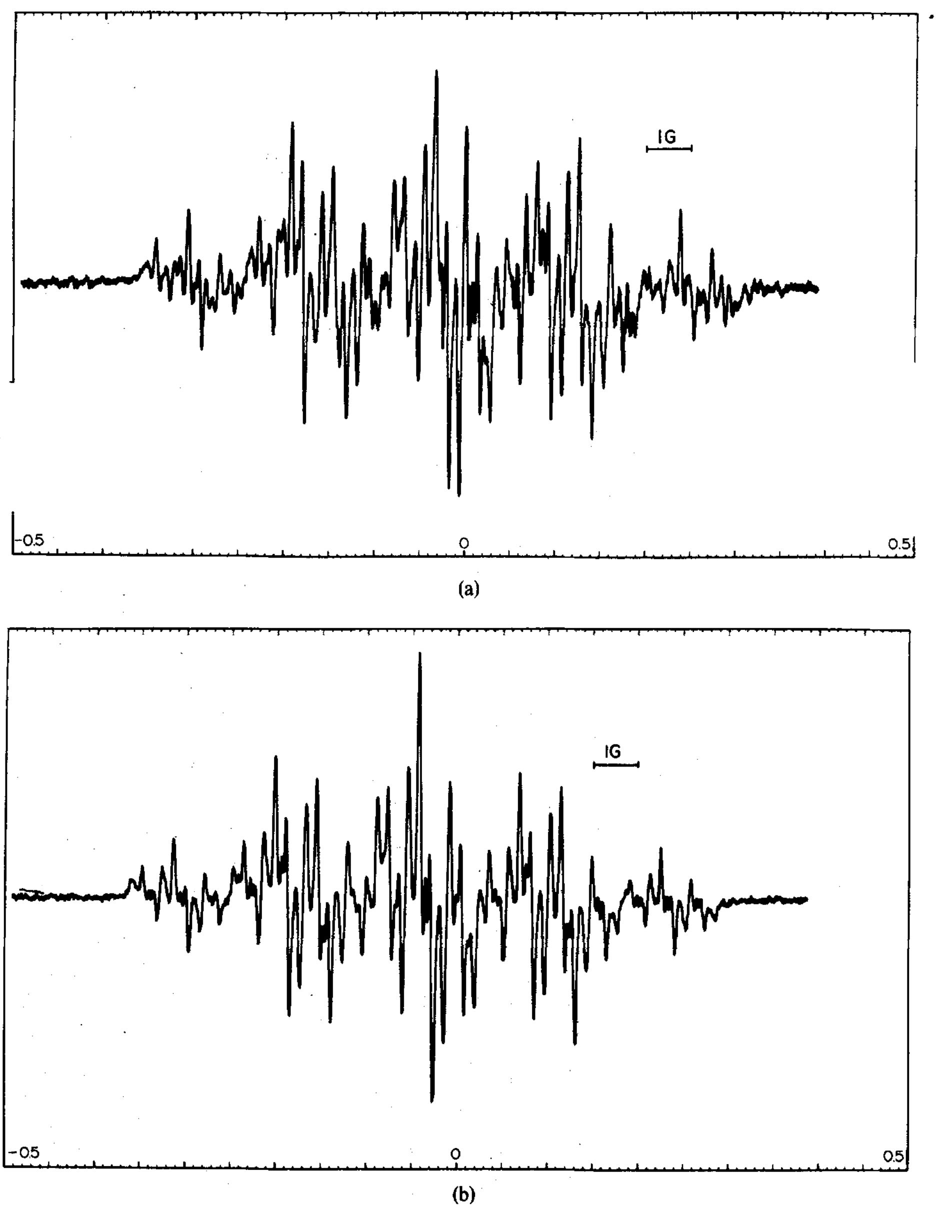
64% yield. The reaction takes place at room temperature in THF under an atmosphere of argon. The transformation is accompanied by color changes: initially a red solution is produced and at the later stages a green precipitate forms, which most probably is the semiquinone radical anion dimer.[8]. Less ready was the transformation of lithium benzhydrolate to benzophenone by anthraquinone. This system required long heating at the reflux temperature, eqn (3)

Addition of THF to solid lithium fluorenolate under argon, resulted to a green solution exhibiting bulk paramagnetism and the ESR spectrum shown in Fig. 1.[a] This spectrum is identical to the ESR spectrum of lithium fluorenone ketyl prepared by a conventional method (Fig. 1),[b] and both having been equilibrated. Following the rate of the increase of paramagnetism in a solution which was initially 0.88 M in lithium fluorenolate we measured an initial rate for the formation of lithium fluorenone ketyl of 6.3×10^{-4} ml^{-1} min^{-1} at 38°C. The equilibrium paramagnetism in the same solution corresponded to a concentration of 0.12 M of lithium ketyl. Thus over 13% of the alcoholate was transformed to the corresponding ketyl by some thermal reaction, most probably with the solvent (eqn 4).



(4)

Actually our first indication of the transformation (eqn 4) was during our early attempt to prepare lithium fluorenolate in THF-benzene solution. Addition of an equivalent amount of butyllithium to a solution of fluorenol produced green paramagnetic solutions which

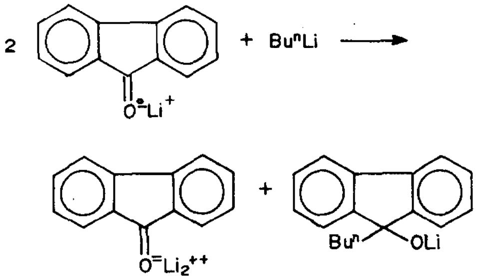


(a)

(b)

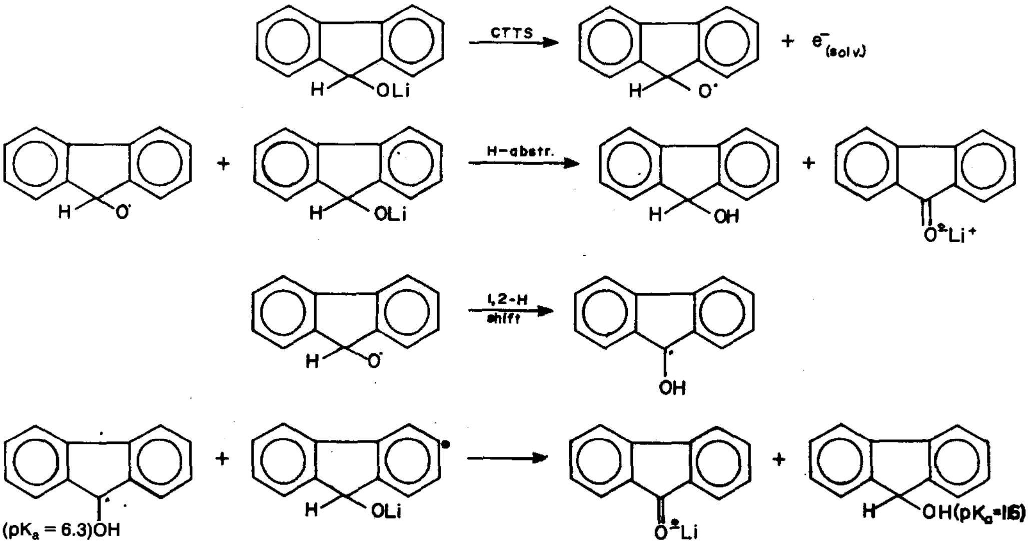
Fig. 1. (a) ESR spectrum of lithium fluorenone ketyl produced by dissolution of lithium 9-fluorenolate in THF. (b) ESR spectrum of lithium fluorenone ketyl prepared by lithium metal reduction of fluorenone in THF.

attacked the teflon of the magnetic stirring bar. In excess of butyllithium fluorenone dianion and some 9-butyl-9-fluorenol were also identified in the reaction products. On the basis of the known[9] reaction (5), lithium fluorenone ketyl appeared to be responsible for all these observations.



(5)

We interpret the "spontaneous" transformation of lithium fluorenolate to lithium fluorenone ketyl as involving thermal electron ejection from the anion to THF solvent and the original alkoxide is converted to the corresponding oxygen-centred radical[10] (eqn 6).



(6)

(A)

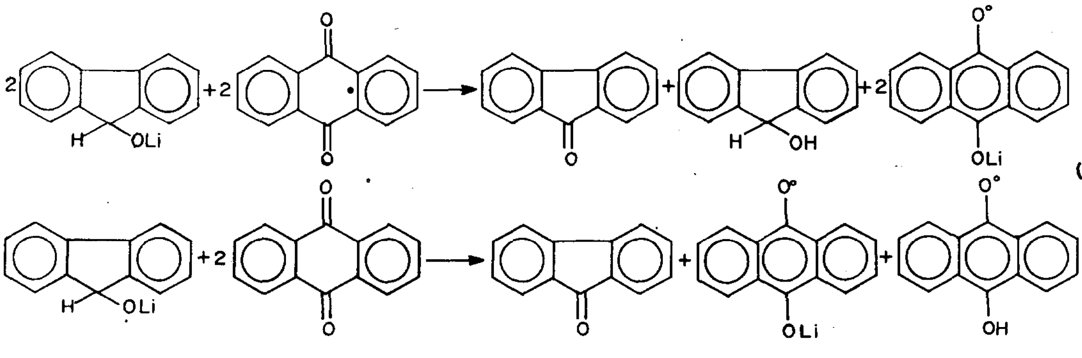
(B)

Such a process could be possible if there existed very strong coupling between vibrational and electronic (CTTS) energy levels in the solvated fluorenolate anion. The observed lithium ketyl then can be derived from the oxygen centred radical by a number of possible mechanisms two of which are given in eqn (6) A and B.

Let us now try to explain the conversion of lithium fluorenolate to fluorenone, by its reaction with anthraquinone. There is no doubt that single electron transfer is the initial step. Assuming then that the oxygen-centred radical can react by the two mechanisms (6) A and B, we are led to the over-all reaction: (eqn (7); A, B)

The first mechanism predicts a 50% maximal yield of fluorenone and the second 100% one, in accord with experiment.[11] Scheme A in order to survive one has to make the assumption that hydrogen abstraction from lithium fluorenolate by anthrasemiquinone radical anion is feasible. An atom transfer (electron plus proton) mechanism rather than a hydrogen atom abstraction one, appears to be more probable. Support for this is given by the result of the following experiment. We generated fluorenone ketyl radical by decomposing fluorenone pinacol with a catalytic amo of base, and subsequently we added anthraquinone to the stable [11a] solution of the ketyl in THF. A 72% yield of fluorenone was isolated, far in excess of the theoretical 50%, indicating that hydrogen atom transfer from the ketyl to anthraquinone is feasible (eqn 8).

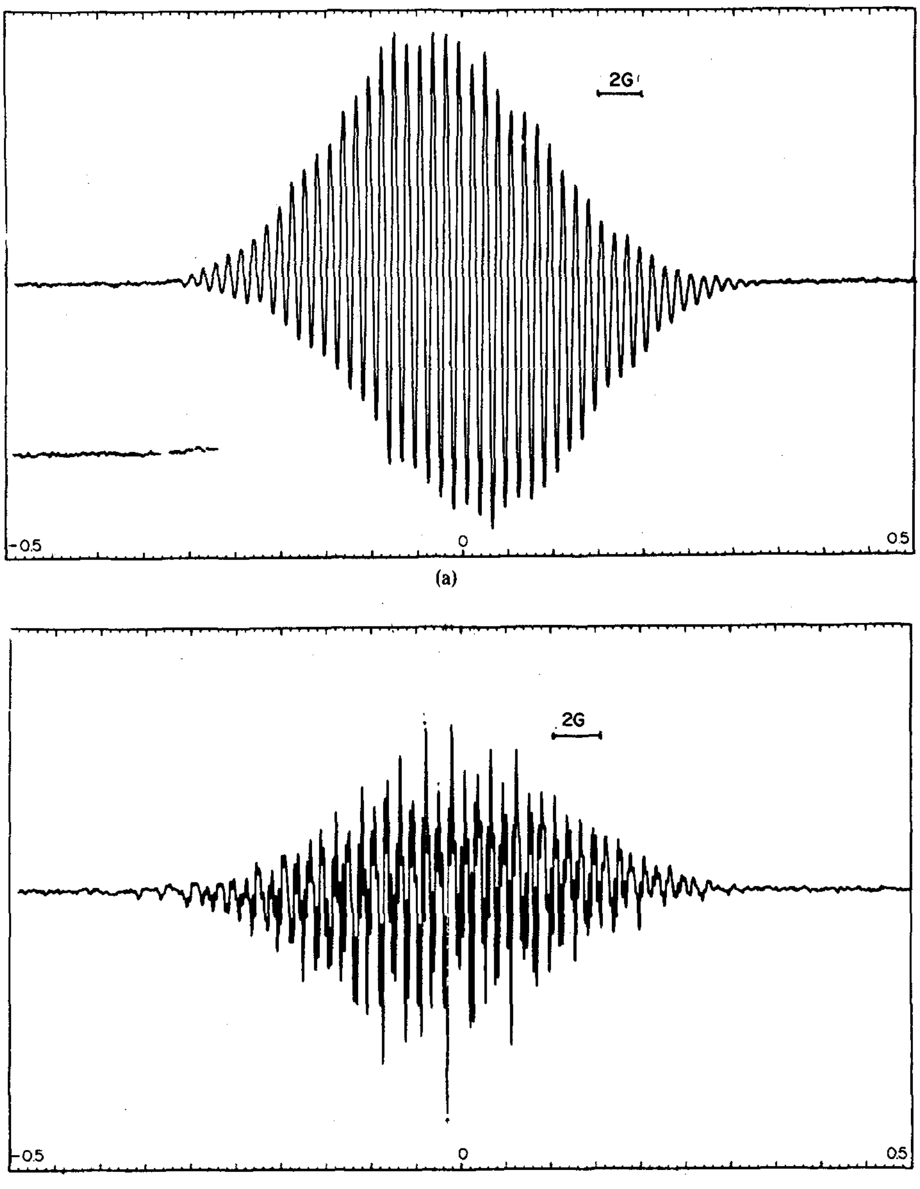
It is felt that 1,2-hydrogen shift[12] in oxygen centred radicals is not an improbable process for mainly thermochemical reasons. The transformation (eqn 9), is certainly accompanied by considerable gain in stability due to the resulting π-system of the carbonyl group in the "protonated" ketyl, $R_1R_2\dot{C}$–OH.[14] One can also argue that hydrogen abstraction cannot be the sole pathway by



(A)

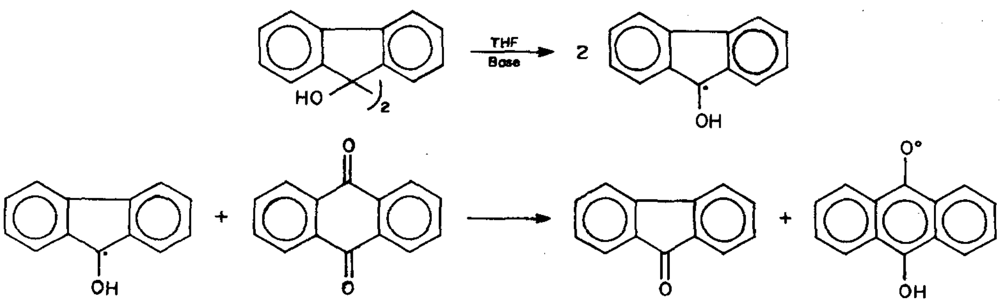
(7)

(B)



(b)

Fig. 2. (a) ESR spectrum of $Ph_2C=O^-Li^+$ produced by photolysis of Ph_2CHOLi in THF. (b) ESR spectrum of $Ph_2C=O^-Li^+$ produced by photolysis of Ph_2CHOLi in DME.



(8)

which an oxygen centred radical can be transfromed into stabler products; otherwise the phenomenon of β-scission would be unknown.

$$R_1R_2CHO^{\cdot} \rightleftharpoons R_1R_2\dot{C}\text{—}OH \qquad (9)$$

We propose that reaction (9) represents an actual tautomeric system, and that it is involved in the mechanism of the reduction of carbonyl compounds by metal alkoxides. The proposed mechanism is as follows: The alkoxide donates a single electron to the substrate carbonyl compound. This results to an oxygen centred radical and a ketyl anion. The oxygen-centred radical tautomerizes to the corresponding carbon-centred (ketyl) radical. The ketyl donates a proton to the conjugate ketyl anion which by virtue of the tautomerism is converted to the corresponding oxygen radical. Finally the ketyl anion derived from the original alkoxide donates an electron to the oxygen-centred radical. Schematically the proposed mechanism is summarized as follows:

$$\mathrm{Me_2CHO^- + R_2C{=}O \overset{A}{\rightleftharpoons} (Me_2CHO^{\cdot} + R_2C{=}\dot{O}^{-}) \overset{B}{\rightleftharpoons}}$$

$$\mathrm{(Me_2\dot{C}{-}OH + R_2C{=}\dot{O}^{-}) \overset{C}{\rightleftharpoons} (Me_2C{=}\dot{O}^{-} + R_2\dot{C}{-}OH) \overset{D}{\rightleftharpoons}}$$

$$\mathrm{(Me_2C{=}\dot{O}^{-} + R_2CHO^{\cdot}) \overset{E}{\rightleftharpoons} Me_2C{=}O + R_2CHO^{-}.}$$

This mechanism makes obvious the main feature of the MPV-type reaction namely of being an equilibrium process. It is also consistant with the experimental fact that the transferred hydrogen originates from a position geminal to the oxygen of the alkoxide.[1] It can accommodate the experimental evidence reported in this paper and elsewhere.[6] Namely, the reduction of a ketone to the relevant ketyl by the alkoxide. Moreover it can explain the results reported[3] recently on the reduction of phenyltrifluoromethyl ketone by bromomagnesium methylphenyl methanolate. The observed lack of reversibility in this case could be readily accounted for on considering the reversibility of step E. The ability of the alkoxide in step E to function as an efficient electron donor, or not, is a decisive factor for the reversibility of the reaction. Comparing the relative ability for single electron donation between $\mathrm{Ph(CF_3)CHO^-}$ and $\mathrm{Ph(CH_3)CHO^-}$ it can be said rather confidently that the alkoxide derived from the alcohol with the larger $\mathrm{p}K_a$ value will be a better single electron donor.[13] Obviously, $\mathrm{Ph(CF_3)CHOH}$ is more acidic than $\mathrm{Ph(CH_3)CHOH}$ and the equilibrium is shifted towards the $\mathrm{Ph(CF_3)CHO^-}$. The lack of reversibility can be accounted for, also, on consideration of the relative electron affinities of the ketones $\mathrm{PhCOCF_3}$ and $\mathrm{PhCOCH_3}$. Although, redox potentials are not available for both ketones, an idea about the differences in electron affinity could be obtained from the $\mathrm{p}K_a$ values of the related, acetone and hexafluoroacetone ketyl radicals, $\mathrm{(CH_3)_2\dot{C}{-}OH}$ and $\mathrm{(CF_3)_2\dot{C}{-}OH}$, 12.2 and 1.7, respectively.[14a] Through the well-known correlation,[14b] between redox potential of a ketone and the $\mathrm{p}K_a$ value of the corresponding ketyl radical, can be decided that the ketyl with the lower $\mathrm{p}K_a$ value is derived from the ketone with the higher electron affinity. Thus it is reasonable to expect that the ketone $\mathrm{PhCOCF_3}$ is a better electron acceptor than acetophenone by several orders of magnitude.

Lastly, there should be mentioned that our mechanism bears some similarities to the one proposed recently by Bard *et al.*[15] for the oxidation of alcohols by 1,1'-dimethyl-4,4'-bipyridylium dichloride (Paraquat, $\mathrm{PQ^{2+}}$). In their mechanism a 1,2-hydrogen shift-step is implied, by which an oxygen-centred radical is reversibly converted to the corresponding ketyl, step (ii), below:

$$\mathrm{PQ^{2+} + CH_3O^- \rightleftharpoons PQ^{\cdot+} + CH_3O^{\cdot}} \qquad \text{(i)}$$

$$\mathrm{CH_3O^{\cdot} + OH^- \rightleftharpoons CH_2O^{\cdot-} + H_2O} \qquad \text{(ii)}$$

$$\mathrm{CH_2{=}O^{\cdot-} + PQ^{2+} \longrightarrow CH_2{=}O + PQ^{\cdot+}} \qquad \text{(iii)}$$

EXPERIMENTAL

NMR analysis was performed with a Varian A60A NMR spectrometer. ESR spectra were recorded on a Varian E-4 ESR spectrometer, using Fremy's salt for field calibration ($a_N = 13$ G). Concentrations of paramagnetic compounds were measured with the NMR spectrometer according to the method of Evans[16] as it was adapted [17] to the study of radical ions. Cyclohexane, 20% v/v in carbon tetrachloride served as the external marker. A working curve for shift ($\Delta\nu$) versus lithium fluorenone ketyl concentration was employed. It has the form:

$$\Delta\nu = -5.5 + 97C \quad (\Delta\nu \text{ in Hz})$$

where $\Delta\nu$ is the position of the high field band of THF in the solution of the paramagnetic compound referred to external 20% v/v cyclohexane in $\mathrm{CCl_4}$, and C the concentration of lithium fluorenone ketyl, in $\mathrm{ml^{-1}}$.

9-Fluorenol was prepared by sodium borohydride reduction of fluorenone and it was recrystallized from benzene–hexane, m.p. 152–4°, lit.[18] 154°. All the other chemicals were commercial products, usually 99% pure and they were used without further purification. Tetrahydrofuran and 1,2-dimethoxyethane were purified as follows: The solvent was stored for at least one week over sodium hydroxide pellets. Refluxed under nitrogen for several hours over fresh NaOH pellets, distilled under nitrogen, the distillate was refluxed with sodium metal under nitrogen and finally it was distilled from lithium aluminum hydride containing triphenyl methane indicator, under argon. In absolutely anhydrous THF (dimethoxyethane) lithium aluminum hydride metalates $\mathrm{Ph_3CH}$ rapidly and therefore the final distillation was done after the appearance of the red coloration due to $\mathrm{Ph_3CLi}$.

The following procedure illustrates the reduction of benzophenone by alkoxides:

Reduction by sec-butanol and catalytic amount of lithium sec-butoxide

The reaction system was a 100-ml three-necked flask equiped with a magnetic stirring bar, a thermometer, a reflux condenser and a rubber septum and connected through the upper end of the condenser to a vacuum argon line. Under an atmosphere of argon was injected 4.0 ml of sec-butanol followed by 3.25 ml of 1.60 M butyllithium in benzene (cooling). A solution of 4.0 g of benzophenone in 10 ml of dry, freshly distilled THF was introduced into the flask and the resulting mixture was refluxed for 24 hr. After hydrolysis with 5 ml of water the volume of the mixture was reduced in a rotary evaporator, the product was extracted with benzene. The dried ($\mathrm{MgSO_4}$) benzene extract was evaporated to constant weight, 3.62 g. Analysis of this material by NMR indicated a mixture of benzhydrol and benzophenone in the molar ratio 1.67 : 1.0. This amounts to an extent of reduction of 62.5% on the recovered (90%) material. Taking the amount of sec-butoxide equivalent to butyllithium used, 5.2 mmole, the catalyst efficiency is 2.4 mole of benzhydrol per mole of sec-BuOLi. In a separate experiment solvents and volatile products were removed from the reaction mixture by freeze-drying and a test was made for ethyl methyl ketone with 2,4-dinitrophenylhydrazine in the volatile fraction. The test was positive.

Results from similar reactions are summarized in Table 1.

Lithium 9-fluorenolate

Fluorenol, 1.82 g, 10 mmole, was placed in a 100-ml, two-necked flask equipped with magnetic stirring bar (glass coated), a rubber septum in the side neck and connected through the other neck to a vacuum-argon line. The air inside the flask was replaced by pure argon and 10 ml of anhydrous, argon-saturated benzene was introduced into the flask. The resulting solution was cooled on an ice-water bath and butyllithium, 6.4 ml of 1.56 M in benzene was added with a syringe to the stirred fluorenol solution. During this operation the flask was protected from the diffuse daylight. Upon contact of the two solutions a purple coloration was produced which fainted initially rapidly and at the later stages of the addition less so. Finally, a pale greenish suspension was formed. The mixture on freeze-drying gave an off-white powder. Hydrolysis of this material gave unchanged fluorenol in quantitative yield.

Reaction of lithium 9-fluorenolate with 9,10-*anthraquinone*

To 10 mmole of solid lithium fluorenolate was added under a blancket of argon 4.2 g of powdered anthraquinone, followed by 25 ml of absolute THF. The mixture turned rapidly red and on further stirring at room temperature it became thicker and a green suspension appeared to have been formed. After stirring the mixture for 38 hr at room temp. it was subjected to steam distillation. Extraction of the distillate with methylene chloride gave 1.15 g, 64% of fluorenone (m.p. IR).

Transformation of lithium 9-fluorenolate to lithium fluorenone ketyl

Lithium fluorenolate solid, prepared from 10 mmole of fluorenol was dissolved in THF by standard vacuum-line techniques and an aliquot was transferred in an NMR tube containing a capillary with cyclohexane as an external marker. The tube was sealed and kept in liquid nitrogen. A second aliquot was taken for analysis which on the basis of total alkalinity was found to 0.88 M in lithium fluorenolate. The THF solution of lithium fluorenolate was found to be paramagnetic. That is, the NMR signals of THF in the solution lost their fine structure and were shifted to higher fields with time. Following the increase of paramagnetism (shift) the initial rate of the production of the paramagnetic species was found to be $6.3 \times 10^{-4}\,ml^{-1}\,min^{-1}$, at 38°C, assuming that the paramagnetic species was lithium benzophenone ketyl (see below). The equilibrium paramagnetism corresponded to 0.12 M in lithium fluorenone ketyl. In an identical experiment a sample was transferred in an ESR tube and after dilution was sealed for ESR analysis. The ESR spectrum after equilibration for about one week was identical to the ESR spectrum of lithium fluorenone ketyl prepared by lithium reduction of fluorenone in THF, and equilibrated for the same length of time.

Reaction of fluorenopinacol with base and anthraquinone

Fluorenopinacol, 0.91 g, 2.5 mmole, was dissolved under argon in 15 ml of THF and decomposed by adding 0.5 ml of 1.0 M lithium sec-butoxide in THF. The mixture was stirred at 10° for 2 min. and 2.0 g of powdered anthraquinone was added under a blanket of argon. The mixture turned originally red then green. After stirring for over night at room temp. the mixture was subjected to steam distillation. The volatile product was extracted with benzene to give, after drying the benzene extracts and removal of benzene, 0.75 g of crude fluorenone which after recrystallization from benzene–hexane gave 0.66 g, 72%, of fluorenone m.p. 80–82°, lit.[19] 84°.

Reduction of fluorenone to lithium fluorenone ketyl by lithium sec-butoxide

To solid lithium sec-butoxide, prepared from 10 mmole of sec-butanol and an equivalent amount of butyllithium according to the procedure for making lithium fluorenolate (protection from light unnecessary) was added 9.0 ml of 0.5 M fluorenone in absolute THF. The mixture turned greenish rapidly. A sample of this solution was sealed in an NMR tube containing a capillary with cyclohexane external marker. The paramagnetism of the solution increased slowly with time and in about 7 hr reached its equilibrium. At this stage the shift was 23.5 Hz or 0.30 M in lithium fluorenone ketyl, or 65% reduction to ketyl. Addition of sec-butanol did not cause destruction of the green color, which survived even after refluxing the solution for 2 hr.

Acknowledgement—We thank Mrs M. Voyadji and Miss M. Avgerinou for technical assistance.

REFERENCES

[1] E. P. Dar'eva, G. P. Miklukhin and A. F. Rekasheva, *J. Gen. Chem. U.S.S.R.* **29**, 273 (1959).

[2] D. C. Kleinfelter, *J. Org. Chem.* **32**, 840 (1967). In this report KOH in ethylene glycol was used. However, the reducing species most probably was $KOCH_2CH_2OH$.

[3] J. D. Morrisson and R. W. Ridgway, *J. Org. Chem.* **39**, 3107 (1974).

[4] A. L. Wilds, *Org. React.* **2**, 178 (1944).

[5] L. M. Jackman and J. A. Mills, *Nature* **164**, 789 (1949).

[6] G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.* **84**, 4163 (1962); G. A. Russell, E. G. Janzen and E. T. Strom, *Ibid.* **86**, 1807 (1964).

[7] E. Hayon, T. Ibata, N. N. Lichtin and M. Simic, *J. Phys. Chem.* **76**, 2072 (1972).

[8] N. Hirota, Metal ketyls and related radicals. In *Radical Ions* (Edited E. T. Kaiser and L. Kevan), p. 55. Wiley, New York (1968).

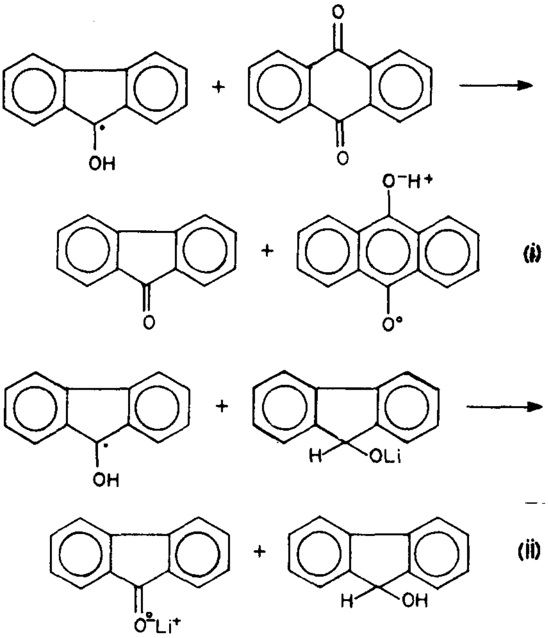
[9] C. G. Screttas, Abstracts of Papers (No. 26), *6th Int. Conf. Organomet. Chem.*, (Aug. 13–17) 1973, Amherst Mass.

[10] In support to the idea of electron ejection we performed the following experiment: A solution of lithium benzhydrolate in THF or 1,2-dimethoxyethane under argon, in a sealed ESR tube was irradiated with a medium pressure mercury lamp. A bluish solution was obtained which exhibited the ESR spectra shown in Fig. 2. The spectrum (2a) is assigned to lithium benzophenone ketyl with the following parameters:

$$a_o : a_m : a_p : a_{Li} \simeq 3:1:4:0.5, \text{ where } a_{Li} \simeq 0.5_5\ \text{G}.$$

The ejected electron in reaction (6) is presumed to reduce solvent molecules.

[11] The lack of quantitative yield can be accounted for on the basis of the competing reactions (i) and (ii):



The experiment has been repeated several times. In no case the yield of fluorenone was lower than 61%.

[11a] Addition of a catalytic amount of base such as lithium sec-butoxide to a solution of fluorenone pinacol in THF causes fragmentation of the pinacol to fluorenone ketyl radical and the paramagnetism of the solution decays slowly. D. G. Georgiou and C. G. Screttas, unpublished results.

[12] Although 1,2-hydrogen shifts are considered to be processes of high activation energy, see e.g. J. W. Wilt, Free radical rearrangements. In *Free Radicals* (Edited by J. K. Kochi), Vol. 1, pp. 332–502. Wiley, New York (1973), examples of this process can be located in the most recent bibliography, e.g. A. S. Gordon, D. C. Tardy and R. Ireton, *J. Phys. Chem.* **80**, 1400 (1976). The absence of 1,2-hydrogen shift in oxygen-centred radicals has been decided on the basis of improperly designed experiments. For example, N. Kornblum and H. E. de la Mare, *J. Am. Chem. Soc.* **74**, 3079 (1949), thermolysed on optically active peroxide in the presence of thiophenol and obtained an optically active alcohol.

$$\underset{\text{optically active}}{Ph(CH_3)CHOOC(CH_3)_3} \xrightarrow[125°C]{PhSH} \underset{\text{optically active}}{Ph(CH_3)CHOH}$$

Hydrogen abstraction from thiophenol and the production of the radical $PhS^{\cdot}$ is certainly a process of low activation energy as is the abstraction of acidic hydrogen atoms, in general. For correlations between activation energies for hydrogen abstraction and pK_a values (see Ref. 13). Thus there was not left any alternative pathway for the $Ph(CH_3)CHO^{\cdot}$ to be transformed to a stable product.

[13] C. G. Screttas, *J. C. S. Perkin II*, 165 (1975).

[14] That a radical such as $R_1R_2\dot{C}{-}OH$ can be considered as a protonated ketyl, $R_1R_2C{=}O^{\dot{-}}H^+$, agrees with the observed restricted rotation in the radical $Ph\dot{C}H{-}OH$, relative to CHOH and Ph groups; R. Wilson, *J. Chem. Soc.* (*B*) 84 (1968). It also agrees with its relatively low pK_a, usually around 11. See for example: [a] P. Neta, In *Advances in Physical Organic Chemistry*, **12**, 223 (1976); [b] E. Hayon and M. Simic, *Accounts Chem. Res.* **7**, 114 (1974).

[15] A. J. Bard, A. Ledwith and H. J. Shine, *Adv. Phys. Org. Chem.* **13**, 256 (1976).

[16] D. F. Evans, *Proc. Chem. Soc.* 115 (1958); *J. Chem. Soc.* 2003 (1959).

[17] C. G. Screttas, *J. C. S. Chem. Comm.* 869 (1972); *J. C. S. Perkin II* 745 (1974).

[18] *Handbook of Chemistry and Physics*, 54th Edn, CRC Press (1973–74), Section C-301.

[19] Ref. 18, Section C-302.