J. Org. Chem. 1986, 51, 3587–3593

Preparation of *trans*-Myrtanic Acid. *trans*-Myrtanic acid was obtained by permanganate oxidation of *trans*-myrtanol[19] (18) purified by distillation under vacuum [bp 107–110 °C (0.5 mm)]. It was transformed into its methyl ester (by reaction with the diazomethane), and its purity was analyzed by VPC (the methyl *cis*- and *trans*-myrtanoate have different retention times (t_r) in VPC (trans t_r/cis t_r = 1.09 on Silar 5C, 15%, 3.6 min at 150 °C).

Preparation of *cis*- and *trans*-Peroxymyrtanic Acids. *cis*- and *trans*-peroxymyrtanic acids were obtained from the corresponding acids, by a method described in Swern et al.[20] and modified by us.[21] The purity of the peracid (90–95%) was determined by iodometric titration.[22]

Peracid Decomposition. Peracid decomposition, at different concentrations, was done as it has been described previously.[4,21] In a reactor (50 mL) with a condenser was placed the peracid solution (10 mL). The external oil bath temperature was fixed at 100 °C. The reaction is followed by iodiometric measurement. At the end of the reaction the solution was treated by diazomethane in order to transform carboxylic acids into the corresponding methyl esters. The product mixture was analyzed on two types of VPC columns, one polar (Carbowax 20 M, 15%, 2 m, 130 °C) and another one nonpolar (Silar 5C, 15%, 3.6 m, 180 °C). The relative retention times (in min) are as follows: [Carbowax] cyclohexanol, 1; **10** 2.48; **8a**, 2.96; **8b**, 3.47; [Silar 5C] cyclohexanol, 1; **10**, 1.50; **8a**, 1.68; **8b**, 1.92. **8a** and **8b** were identified by comparison of IR and ^{1}H NMR spectra (triplet at τ 4.08 for **8b** and multiplet at τ 4.20 for **8a**[15]) and VPC results with those of authentic samples.

Registry No. **6a**, 103533-22-8; **6b**, 103533-23-9; **7**, 103533-24-0; **8a**, 53767-58-1; **8b**, 51703-63-0; **10**, 90645-55-9; methyl *cis*-myrtanoate, 103617-37-4; methyl *trans*-myrtanoate, 54164-10-2.

---

[19] Collins, J.; McKervey, M. *J. Org. Chem.* **1969**, *34*, 4173.

[20] Silbert, L.; Siegel, E.; Swern, D. *J. Org. Chem.* **1962**, *27*, 1336.

[21] Fossey, J.; Lefort, D.; Massoudi, M.; Nedelec, J. Y.; Sorba, J. *J. Chem. Soc., Perkin Trans. 2* **1986**, 781.

[22] Johnson, R.; Siodiqui, I. *The Determination of Organic Peroxides*; Pergamon: Oxford, 1976.

Product Study of Some One-Electron Oxidations of Bibenzyl and 4-Ethylbibenzyl. Evidence against Carbon–Carbon Bond Cleavage of the Bibenzyl Radical Cation in Solution

Enrico Baciocchi,* Donatella Bartoli, Cesare Rol, Renzo Ruzziconi, and Giovanni V. Sebastiani

Dipartimento di Chimica, Università di Perugia, 06100 Perugia, Italy

Received October 24, 1985

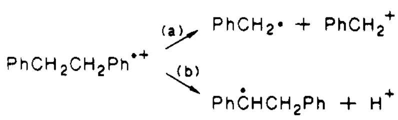
The oxidations of bibenzyl (1) and (or) 4-ethylbibenzyl (2) have been investigated under a variety of conditions, all of which should involve the intermediacy of bibenzyl radical cations: (a) reaction with ceric ammonium nitrate (CAN) in AcOH or CH_3CN-H_2O; (b) anodic oxidation in AcOH–CH_3CN or $(CH_3)_2CO-H_2O$; (c) photochemical oxidation by CAN in CH_3CN; (d) photochemical autoxidation catalyzed by 9,10-dicyanoanthracene or by CAN in CH_3CN. Nearly exclusive formation of side chain substituted products is observed for the chemical and electrochemical oxidations when the reactions are carried out in AcOH, CH_3CN, or AcOH–CH_3CN, whereas extensive formation of C–C bond cleavage products occurs in the same processes when aqueous solvents are used. In the photochemical reactions, autoxidation produces both cleavage and side chain substituted products, whereas only the latter forms in the CAN-induced reaction in the absence of dioxygen. Evidence based on product analysis suggests that in these reactions no significant C–C bond breaking takes place at the state of bibenzyl radical cation. Cleavage products, where observed, nearly certainly derive from first-formed side chain substitution products.

The fragmentation of bibenzyl radical cation through carbon–carbon bond cleavage (Scheme I, path a) is a very important process in the gas phase.[1] A similar process, of course, is in principle possible in solution as well, where, however, it has to compete with deprotonation (Scheme I, path b), which is favored by the extremely high solvation energy of the proton.

Claims in favor of the occurrence of process a in solution have come from studies concerning the oxidation of bibenzyl by one-electron oxidants, i.e., processes suggested to involve the intermediacy of the bibenzyl radical cation. Thus, the observation that the oxidation of bibenzyl induced by cerium(IV) ammonium nitrate (CAN) in aqueous acetonitrile[2] or photochemically in acetonitrile[3] leads exclusively to fragmentation products has been interpreted as an indication that the bibenzyl radical cation undergoes C–C bond cleavage.

However, formation of cleavage products is by no means a general outcome of the oxidations of bibenzyls involving a radical cation intermediate. Accordingly, recent studies have shown that oxidation of bibenzyl by cerium(IV) ammonium nitrate in AcOH[4] or by $S_2O_8^{2-}$ in aqueous acetonitrile[5] leads nearly exclusively to side chain substituted derivatives. Moreover no C–C cleavage occurs when methoxy-substituted bibenzyls are reacted with tris(4-bromophenyl)ammoniumyl hexachloroantimoniate,[6] a process which should lead to bibenzyl radical cations.

Scheme I



In this situation further investigation is desirable, which might rationalize these conflicting results and provide information on the factors influencing the competition between path a and path b for reactions in solution. This is true also in view of the fact that bibenzyl is a coal model[7]

---

[1] Eland, J. H. D.; Danby, C. J. *J. Chem. Soc.* **1965**, 5935–5943.

[2] Trahanovsky, W. S.; Brixius, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 6778–6780.

[3] Reichel, L. W.; Griffin, G. W.; Muller, A. J.; Das, P. K.; Ege, S. N. *Can. J. Chem.* **1984**, *62*, 424–437.

[4] Baciocchi, E.; Ruzziconi, R. *J. Chem. Soc., Chem. Commun.* **1984**, 445–446.

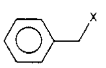
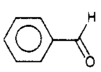
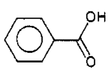
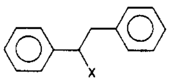
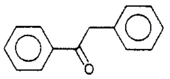
[5] Camaioni, D. M.; Franz, J. A. *J. Org. Chem.* **1984**, *49*, 1607–1613.

[6] Kricke, L. J.; Ledwith, A. *J. Chem. Soc., Perkin Trans. 1* **1973**, 294–297.

[7] See, for example: Poutsma, M. L.; Douglas, E. C.; Leach, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1136–1137 and references therein.

0022-3263/86/1951-3587$01.50/0 © 1986 American Chemical Society

Table I. Product Yields[a] in Some Oxidations of Bibenzyl (1)

			products, %				
entry	reaction conditions	substrate					
1	CAN,[b] AcOH, 80 °C	72		trace		27 (X = OAc)	
2	CAN, MeCN-H_2O, HNO_3, reflux[c]		40 (X = ONO_2) 4 (X = OH)	62			
3	A.O. (2 F mol^{-1}), Me_2CO-H_2O, H_2SO_4[d]	60	6 (X = OH)	14		23 (X = OH)	
4	A.O. (4 F mol^{-1}), Me_2CO-H_2O, H_2SO_4[d]	52	4 (X = OH)	25		20 (X = OH)	
5	CAN,[e] $h\nu$, MeCN (0.2 h)	60	trace (X = ONO_2)	2		38 (X = ONO_2)	
6	CAN,[f] $h\nu$, MeCN, O_2 (0.3 h)	41	6 (X = O_2H)[g]	12	3	35 (X = O_2H)[g] 4 (X = ONO_2)	10
7	CAN,[f] $h\nu$, MeCN, O_2 (1 h)	2	7 (X = O_2H) 3 (X = ONO_2) 2 (X = OH)	28	25	25 (X = O_2H) 8 (X = ONO_2)	15

[a] % of recovered material with respect to the starting substrate. Average of at least two determinations. The error is ±2. To get the material balance, the yield of fragmentation products has to be divided by 2. [b] [CAN] = 4.9×10^{-2} M. [c] 70% aqueous acetonitrile containing 0.36 M HNO_3. Data from ref 2. [d] Anodic oxidation in 97% aqueous acetone containing 0.27 M H_2SO_4. Constant current electrolysis at 20 mA cm^{-2}. The yields of these reactions were determined by ^1H NMR analysis. [e] [CAN] = 8×10^{-2} M. [f] [CAN] = 8×10^{-3} M. [g] Yields calculated by ^1H NMR after conversion to the corresponding alcohols (see Experimental Section).

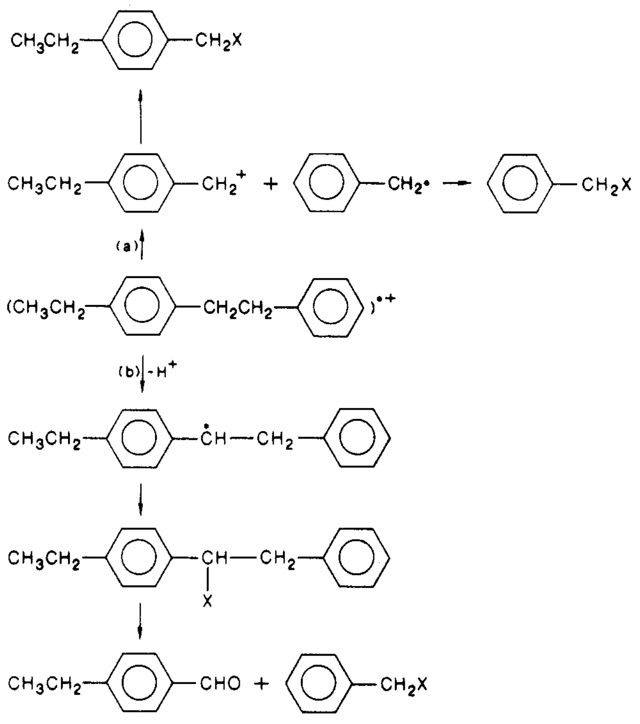
and interest exists for reactions which may break the C–C bridges between the aromatic clusters present in coal under relatively mild conditions.

In this paper we report on the oxidation of bibenzyl (1) and (or) its 4-ethyl-substituted derivative 1-(4-ethylphenyl)-2-phenylethane (2) under a variety of oxidizing conditions: (a) reaction with CAN in AcOH and aqueous CH_3CN; (b) electrochemical oxidation in aqueous acetone and in AcOH–CH_3CN mixed solvent; (c) photochemical autoxidation in the presence of 9,10-dicyanoanthracene (DCA) or CAN in CH_3CN; (d) photochemical oxidation by CAN in CH_3CN. Considerable evidence exists that radical cations should be involved in all these reactions.

As also stated by other authors[5] the mere observation of cleavage products cannot be sufficient evidence in favor of the C–C bond cleavage at the bibenzyl radical cation state. Accordingly, there is the possibility that these products derive by further oxidation, involving C–C bond cleavage, of the first-formed side chain substituted products. The recognition of this possibility can be very difficult when the side chain substituted products are oxidized at a much faster rate than bibenzyl itself.

The parallel study of the reactions of 4-ethylbibenzyl (2) has been planned to overcome this problem. Accordingly, as shown in Scheme II (X = conjugate base of the solvent or another nucleophile in the medium), direct cleavage of the radical cation $2^{\bullet+}$ should lead to the 4-ethylbenzyl carbocation and the benzyl radical (Scheme II, path a)[8] and then to the 4-ethylbenzyl and benzyl derivatives. On the contrary if $2^{\bullet+}$ is first deprotonated, giving side chain substituted products that undergo C–C bond cleavage, 4-ethylbenzaldehyde forms together with benzyl derivatives (Scheme II, path b). This is because deprotonation should mainly involve the hydrogen α to the *p*-ethyl-substituted ring, where most of the positive charge resides. Thus, a very careful search for the presence of 4-ethylbenzyl derivatives can be very informative with regard to the occurrence of C–C bond cleavage at the radical cation state.

Scheme II



In the second place, if C–C bond cleavage is really the predominant decomposition mode of the bibenzyl radical cation, little, if any, substitution reaction at the α-hydrogens of the 4-ethyl group should be observed. Accordingly, if proton loss from the dimethylene bridge cannot compete with C–C bond cleavage, the same should also hold for proton loss from the ethyl group since the two side chain substitutions (therefrom indicated, for the sake of simplicity, as internal and external side chain substitution, respectively) should take place with similar rate. In this respect, it should also be noted that the introduction of a 4-ethyl group in the bibenzyl moiety is expected to favor C–C bond breaking in the radical cation since a 4-ethyl substituent increases the stability of a benzyl carbocation.

Results and Discussion

The yields and distribution of products in the various oxidations of bibenzyl and 4-ethylbibenzyl are reported in Tables I and II, where are also stated the reaction

---

(8) Of course, it cannot be excluded that C–C cleavage in $2^{\bullet+}$ leads to a *p*-ethylbenzyl radical and a benzyl carbocation. However the final products are the same than those predicted for the other way of carbon–carbon bond breaking. Anyway, the *p*-ethylbenzyl carbocation and the benzyl radical should be the favored pair of intermediates since a *p*-alkyl group is expected to stabilize a benzyl carbocation more than a benzyl radical.

conditions. In the majority of cases the oxidant/substrate ratio was 2:1, i.e., the stoichiometric one for a side chain substitution process or for a carbon–carbon bond cleavage leading to benzyl derivatives.

Generally the reaction mixture after usual workup was chromatographed and the various products separated and characterized by spectroscopic methods and (or) by comparison with authentic samples. In the majority of cases, the yields given (Tables I and II) refer to recovered products. Yields were also determined by ^{1}H NMR analysis of the crude products in the presence of an internal standard (1,4-dimethoxybenzene), and there was always an excellent agreement between yields determined in this way and the ones of recovered product. The specific search for the presence of 4-ethylbenzyl derivatives has also been carried out, where possible, by VPC (comparison with authentic specimens). Details are in the Experimental Section.

Oxidations Induced by CAN. The mechanism of the side chain oxidation of alkyl aromatics by CAN is now well established, and there is no doubt that the first step of the reaction is the formation of a radical cation as shown in eq 1.[9] Deprotonation of the radical cation then occurs, leading to a benzylic radical (eq 2), which undergoes further reaction with CAN to give the side chain substituted products.

$$\mathrm{ArCH_3 + Ce^{IV}NO_3 \rightarrow ArCH_3{}^{\bullet+} + Ce^{III}NO_3} \quad (1)$$

$$\mathrm{ArCH_3{}^{\bullet+} \rightarrow ArCH_2{}^{\bullet} + H^+} \quad (2)$$

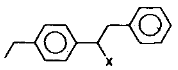
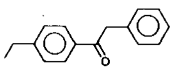
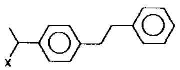
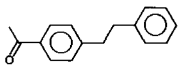
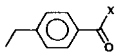
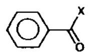
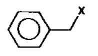
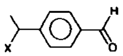
$$\mathrm{ArCH_2{}^{\bullet} + Ce^{IV}NO_3 \rightarrow side\ chain\ substituted\ products} \quad (3)$$

(a) In Acetic Acid. The reaction of 1 with CAN has been carried out at 80 °C, whereas with the more reactive 2 a lower temperature (60 °C) was used. As shown in Table II (entry 1) no C–C bond cleavage occurs with 2, the only products being the side chain substituted acetoxy derivatives. From the product distribution we calculate that the external side chain substitution is 1.8 fold faster than the internal one.[10]

With 1 (Table I, entry 1) the major product is again the side chain acetoxy derivative, however, accompanied by very small amounts of benzaldehyde, a product of C–C bond breaking. In view of the absence of cleavage in the CAN-promoted oxidation of 2 the small amounts of benzaldehyde observed in the reaction of 1 can be ascribed to further oxidation of the first-formed side chain acetoxylated product, probably favored by the higher reaction temperature used in this case.

Few experiments were also carried out with 1,2-bis(4-methoxyphenyl)ethane (3) in order to observe the effect of a strong electron-releasing group. The behavior of 3 appeared similar to the ones of 1 and 2 since in this case too the side chain acetoxylated product 1,2-bis(4-methoxyphenyl)ethyl acetate, accounted for the most part (>90%) of the converted material. However, small but measurable amounts of cleavage products were detected, namely, 4-methoxybenzaldehyde (ca. 4%) and 4-methoxybenzyl acetate (ca. 1%). Probably in the reaction of 3 the first-formed side chain substituted products are more prone to subsequent oxidation than the corresponding products of the reactions of 1 and 2. Interestingly, similar

Table II. Products Yields[a] in Some Oxidations of 4-Ethylbibenzyl (2)

			products, %							
entry	reaction conditions	substrate								
1	CAN,[b] AcOH, 60 °C	24	25 (X = OAc)		41 (X = OAc)	4				
2	CAN, MeCN-H_2O, HNO_3 reflux[c]				12 (X = OH)	36	30 (X = H)	5 (X = H)	18 (X = ONO_2) 3 (X = OH)	7 (X = OH)
3	A.O. (2 F mol^{-1}), AcOH-MeCN, Et_4NBF_4[d]	14	25 (X = OAc)		40 (X = OAc)	15				
4	A.O. (2 F mol^{-1}), Me_2CO-H_2O, H_2SO_4[e]	59	9 (X = OH)		17 (X = OH)	7	7 (X = H)	4 (X = H)	3 (X = OH)	
5	A.O. (4 F mol^{-1}), Me_2CO-H_2O, H_2SO_4[e]	27	7 (X = OH)	6	24 (X = OH)	16	10 (X = H)	14 (X = H)	6 (X = OH)	
6	DCA,[f] $h\nu$, MeCN, O_2	23		8	10 (X = OH)	23	10 (X = H) 13 (X = OH)	11 (X = H) 19 (X = OH)	3 (X = OH)	

[a] % of recovered material with respect to the starting substrate. Average of at least two determinations. The error is ±2. To get the material balance, the yield of fragmentation products has to be deivided by 2. [b] [CAN] = 0.19 M. [c] [CAN] = 0.15 M, 70% aqueous acetonitrile containing 0.36 M HNO_3. [d] Anodic oxidation in AcOH-CH_3CN (3:1) containing 0.07 M Et_4NBF_4. Constant potential electrolysis at 2.2 V (vs. SCE). The products yields of this reaction were determined by ^{1}H NMR analysis. [e] Anodic oxidation in 97% aqueous acetone containing 0.27 M H_2SO_4. Constant current electrolysis at 20 mA cm^{-2}. [f] [DCA] = 2 × 10^{-4} M.

---

[9] Baciocchi, E.; Mandolini, L.; Rol, C. *J. Am. Chem. Soc.* **1980**, *102*, 7597–7598 and references therein.

[10] The reasons for so significant difference between internal and external substitution are not clear at present. Steric effects may be a plausible explanation, but also differences in the hyperconjugation of external and internal benzylic proton might play a role.

results were obtained in the reactions of **1** and **3** with $S_2O_8^{2-}/Ag^{2+}$ and also in that case the greater extent of C–C bond cleavage observed with **3** was attributed to a favorable effect of the 4-methoxy group on the oxidation rate of the side chain substituted products.[5]

On the other hand, since only 4-methoxybenzyl acetate might directly derive from C–C bond cleavage at the radical cation state, this process at most would account for *less* than 1% of the overall process since 4-methoxybenzyl acetate, which is stable under the reaction conditions, can also be formed from cleavage of 1,2-bis(4-methoxyphenyl)ethyl acetate (control experiment).

It is worth noting that the much larger relative yield of 4-methoxybenzaldehyde with respect to 4-methoxybenzyl acetate suggests that most of the cleavage occurs at the state of disubstituted products, the diacetate of 1,2-bis-(4-methoxyphenyl)-1,2-ethanediol; if cleavage would occur at the state of the monosubstituted product approximately equal amounts of aldehyde and acetate should be formed.[11]

(b) In Aqueous Acetonitrile. It has been observed long ago that in refluxing aqueous acetonitrile and in the presence of HNO_3, CAN reacts with bibenzyl to give fragmentation products only.[2] It was, however, observed that, under the reaction conditions, substitution products, if formed, would have been oxidatively cleaved at a much faster rate than bibenzyl.

We have carried out the reaction of **2** under the above reaction conditions, and the results are displayed in Table II, entry 2. It can be seen that as much as 50% of reaction leads to products of substitution at the 4-ethyl group: 1-(4-phenethylphenyl)ethanol and 4-phenethylphenyl methyl ketone. Among the cleavage products (mainly 4-ethylbenzaldehyde and benzyl nitrate) there is also a product that was assigned the structure of 4-(α-hydroxyethyl)benzaldehyde. This product probably derives from further oxidation of 1-(4-phenethylphenyl)ethanol.

Since the ratio between substitution products at the 4-ethyl group and cleavage products (ca. 2.2) is not far from that (1.8) concerning the relative rate of external and internal side chain acetoxylation in acetic acid (see above), it seems reasonable to suggest that the observed fragmentation products derive from further oxidation of the first-formed substitution product at the dimethylene group.

Strong support to this hypothesis comes from the observation that neither 4-ethylbenzyl alcohol nor 4-ethylbenzyl nitrate are among the reaction products, whereas their formation is expected if cleavage occurs at the state of bibenzyl radical cation. Accordingly, as discussed in the introduction (Scheme II), cleavage of $\mathbf{2}^{\bullet+}$ should lead to the 4-ethylbenzyl carbocation, which in the aqueous medium containing nitrate ions gives 4-ethylbenzyl alcohol and 4-ethylbenzyl nitrate. Control experiments have clearly shown that very small amounts of these two products survive under the reaction conditions and can be easily detected in the crude reaction product (see Experimental Section).[12]

Anodic Oxidations. (a) In Acetic Acid–Acetonitrile. Side chain acetoxylation of alkyl aromatics in this mixed solvent is a well-studied reaction that occurs by an ECE mechanism,[13] that is, with the formation of a radical cation in the first electrochemical step.

Oxidation of **2** has been carried out in an undivided cell with Et_4NBF_4 as the electrolyte. After the passage of 2 F mol^{-1} the reaction products are those reported in Table II, entry 3. No C–C bond cleavage occurs, and only side chain acetoxylation is observed. The reactivity ratio between external and internal substitution is ca. 2.2, indicating that the selectivity of the electrochemical process is similar to that of the corresponding CAN-promoted reaction.

(b) In Aqueous Acetone. The choice of this medium is due to a recent report that anodic oxidation of bibenzyl in 97% aqueous acetone (H_2SO_4 as the electrolyte, 8 F mol^{-1}) leads to exclusive formation of cleavage products.[14] We have carried out a similar experiment but analyzed the products after the passage of 2 and 4 F mol^{-1}. As shown in Table I (entries 3 and 4) cleavage products are formed together with products of internal substitution (1,2-diphenylethanol). Moreover the relative amount of cleavage products is significantly larger in the 4 F mol^{-1} than in the 2 F mol^{-1} experiment.

A like situation also holds in the anodic oxidation of **2** under the same experimental conditions (Table II, entries 4 and 5). Moreover in this reaction no evidence for the formation of 4-ethylbenzyl alcohol, which should derive from C–C bond cleavage at the state of $\mathbf{2}^{\bullet+}$ (see above), has been obtained. Control experiments have shown that this compound would have survived under the reaction conditions and would have been detected in amount as small as 1%.

On the basis of these observations it can be concluded that cleavage products observed in the anodic oxidation of **1** and **2** in aqueous acetone derive from first-formed side chain oxidation products.

Light-Induced Oxidations. (a) In the Presence of Organic Sensitizers. The excited states of some organic compounds, i.e., DCA and 1,4-dicyanonaphthalene (DCN), are strong oxidizing species certainly capable, as shown by several workers, to generate alkyl aromatic radical cations.[15] Thus, the observation that light-induced autoxidation of 1-(4-methylphenyl)-1,2-diphenylethane in CH_3CN in the presence of DCN leads to cleavage products (benzaldehydes) was ascribed to C–C bond cleavage of the bibenzyl radical cation.[3]

We have studied the autoxidation of **2** under similar conditions, but using DCA as the sensitizer, and found that cleavage products are accompanied by substantial amounts of both internal and external side chain oxidation products (Table II, entry 6). Benzyl alcohol was found among the cleavage products but not 4-ethylbenzyl alcohol which should instead form if C–C cleavage at the state of $\mathbf{2}^{\bullet+}$ occurs. Again control experiments showed that the latter compound would have survived under the reaction conditions.

Either observations suggest that also in this case the cleavage products derive from the first-formed side chain oxidation products. This conclusion is further supported by the recent observation that no C–C bond cleavage occurs when 1,2-bis(4-methylphenyl)ethane and **3** are subject to sensitized irradiation in the absence of oxygen.[16]

---

[11] In view of the fact that **3** exhibited the same behavior as **1** and **2**, it was considered not worthwhile to extend the study of this compound also under the other reaction conditions.

[12] In ref 2 it is reported that small amounts of 4-methylbenzyl nitrate and 4-methylbenzyl alcohol were detected in the oxidation of 1-(4-methylphenyl)-2-phenylethane by CAN in CH_3CN–H_2O. We have no explanation for the discrepancy between this observation and our own results with **2**. We can only say that in ref 2 the evidence for the presence of the above two compounds is based only on the ^1H NMR analysis of the crude product.

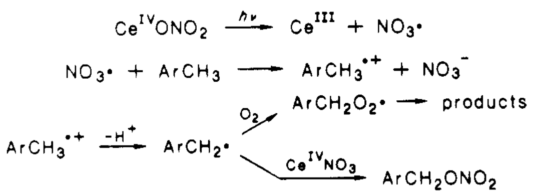
[13] Yoshida, K. "*Electrooxidation in Organic Chemistry*"; Wiley-Interscience: New York, 1984; Chapter 5.

[14] Oberrauch, E.; Mansani, R. *Fuel* **1985**, *64*, 1326–1327.

[15] See, for example: Albini, A.; Fasani, E.; Oberti, R. *Tetrahedron* **1982**, *38*, 1027–1034.

[16] Davis, H. F.; Das, P. K.; Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6968–6973.

Scheme III



(b) In the Presence of CAN. Recently, we have discovered that catalytic amounts of CAN can promote a light-induced autoxidation of alkyl aromatics to give benzaldehydes as the major reaction product.[17] In the absence of oxygen and using stoichiometric amounts of CAN, benzyl nitrates are formed.[18,19]

Evidence exists that both these processes are induced by the nitrate radical, and moreover it seems possible that this radical reacts with alkyl aromatics by an electron-transfer process.[19] The reaction sequences are in Scheme III.

The photochemical reaction of bibenzyl with CAN in CH_3CN has been studied in the absence and in the presence of oxygen and the results are in Table I, entries 5–7.

In the absence of oxygen, with stoichiometric amounts of CAN, side chain nitrooxylation leading to 1,2-diphenylethyl nitrate is the major reaction and only a very small amount of benzaldehyde is detected in the reaction product.

On the contrary in the presence of oxygen, cleavage products are a much more significant fraction of the reaction mixture. However the yield of cleavage products relative to that of substitution products increases by increasing the reaction time (compare entry 6 with entry 7, Table I).

Thus it seems highly probable that in this case too the cleavage products derive from further oxidation of the side chain substituted products.

Conclusions. The results presented in this paper altogether indicate that C–C bond cleavage, to give a benzyl cation and a benzyl radical, is not a significant decay mode of a bibenzyl radical cation in solution, at least under the variety of conditions used. The predominant, if not exclusive, process is α-proton loss, which leads to side chain substitution products.

In this respect bibenzyl radical cations behave in solution differently than in the gas phase. This difference is certainly rationalizable on the basis of the very strong solvation energy of the proton in solution which clearly overcomes the unfavorable factor associated to the stronger energy of the C–H bond with respect to that of the C–C bond.

The fact that under certain experimental conditions substantial amounts of cleavage products can be observed in one electron transfer oxidations of bibenzyl derivatives has nearly certainly to be ascribed to further oxidation of the first-formed substitution products. Thus, the extent of cleavage will depend on the nature of these products as well as on the nature of the oxidizing species.

Accordingly, no fragmentation is observed in both CAN-promoted and electrochemical oxidation of bibenzyl in acetic acid and in AcOH–CH_3CN, which is presumably due to the fair resistance of the side chain substituted acetates toward further oxidation. However, when the above reactions are carried out in aqueous solvents the much more easily oxidizable 1,2-diphenylethanol forms and substantial fragmentation is observed in both processes.

Likewise, in the photochemical CAN-promoted nitrooxylation of bibenzyl there is very little C–C bond cleavage, owing to the stability of benzylic nitrate. However, in the presence of dioxygen the first-formed substitution products, alcohols, ketones, and hydroperoxides, are more prone to undergo further oxidation to cleavage products, which are accordingly found in the reaction product.

The role of the oxidant is illustrated by the oxidation of bibenzyl by CAN and $S_2O_8^{2-}$ in CH_3CN–H_2O. In the former reaction only fragmentation products are observed; in the second there is predominant formation of substitution products. Probably the reactivity of CAN toward 1,2-diphenylethanol is greater than that of $S_2O_8^-$.

Finally, a brief comment with respect to the use of one-electron oxidants to break the dimethylene bridges in coal can be made. Since the present results indicate that α-hydrogen substitution must precede C–C cleavage, one-electron oxidations of coal might not be as successful as those of model compounds if the CH_2CH_2 bridges are not easily accessible to the reactant.

Experimental Section

^{1}H NMR spectra at 90 MHz were registered with a Varian EM 390 spectrometer for solutions in $CDCl_3$. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained on a Varian MAT 311A spectrometer. Elemental analyses were performed on a Carlo Erba Elemental Analyzer M1106. VPC analyses were carried out on a HP 5880A gas chromatograph using a SE-30 capillary column at 40–250 °C. All melting points were uncorrected.

Starting Materials. Ceric ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$], dried at 85 °C for 1 h before use, and 1,2-diphenylethane (**1**) were from a commercial source. 1-(4-Ethylphenyl)-2-phenylethane (**2**) [bp 114–116 °C (0.04 mmHg)] was prepared from reaction of 4-ethylbenzaldehyde with benzylmagnesium chloride, dehydration of the resulting alcohol, and hydrogenation of stilbene using the same procedure described for 1-phenyl-2-(4-tolyl)ethane;[2] the spectroscopic characteristics of **2** were identical with those reported in the literature.[20] 1,2-Bis(4-methoxyphenyl)ethane (**3**) was prepared as described.[2] 9,10-Dicyanoanthracene (DCA) was prepared from 9,10-dibromoanthracene by using the same procedure described for 9-cyanoanthracene.[21]

Chemical Oxidations. (A) Oxidation of Bibenzyl (1) with CAN in Acetic Acid. To a suspension of CAN (5.5 mmol) in acetic acid (65 mL) at 80 °C was added **1** (2.7 mmol). The mixture was allowed to react while being stirred until a pale yellow solution and a white precipitate were observed (17 h). The mixture was poured into cold water and worked up as usual. ^{1}H NMR analysis of the crude product showed the presence of 1,2-diphenylethyl acetate (**4**) as nearly exclusive reaction product [comparison with an authentic specimen prepared by esterification of 1,2-diphenylethanol (**5**), a compound available from a previous work,[22] with acetic anhydride in pyridine]. Moreover, VPC analysis in the presence of diphenyl ether as an internal standard showed the presence of very small amounts of benzaldehyde.

(B) Oxidation of 1-(4-Ethylphenyl)-2-phenylethane (2) with CAN in Acetic Acid. **2** (9.5 mmol) and CAN (19 mmol) were mixed in acetic acid (100 mL), and the mixture was allowed to react at 60 °C while being stirred until a pale yellow solution and a white precipitate were observed. The mixture was poured into cold water (200 mL) and extracted with three 100-mL portions of diethyl ether. The combined organic extracts were washed with water, 5% $NaHCO_3$ solution, and then with water, dried (Na_2SO_4), and concentrated at reduced pressure to yield a yellow oil. Column

---

[17] Baciocchi, E.; Del Giacco, T.; Rol, C.; Sebastiani, G. V. *Tetrahedron Lett.* **1985**, 3353–3356.

[18] Baciocchi, E.; Rol, C.; Sebastiani, G. V.; Serena, B. *Tetrahedron Lett.* **1984**, 1945–1946.

[19] Baciocchi, E.; Del Giacco, T.; Rol, C.; Sebastiani, G. V. *Tetrahedron Lett.* **1985**, 541–544.

[20] Hengelson, R. C.; Cram, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 509–515.

[21] Kenneth, E. W.; Snyder, H. R. *J. Org. Chem.* **1970**, *35*, 30–32.

[22] Baciocchi, E.; Perucci, P.; Rol, C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 329–333.

chromatography of the crude mixture on silica gel, eluting with light petroleum diethyl ether (9:1), afforded, besides starting material, 1-(4-ethylphenyl)-2-phenylethyl acetate (**6**) [by comparison with an authentic specimen prepared by reaction of 4-ethylbenzaldehyde with benzylmagnesium chloride and subsequent esterification of the resulting alcohol with acetic anhydride in pyridine: ^{1}H NMR δ 7.1 (m, 9 H), 6.0–5.8 (4 peaks, X portion of an ABX system, 1 H), 3.3–2.9 (8 peaks, AB portion of an ABX system, 2 H), 2.60 (q, J = 7 Hz, 2 H), 1.93 (s, 3 H), 1.19 (t, J = 7 Hz, 3 H); IR (neat) 3080–2840, 1740, 1370, 1230, 1015, 695 cm^{-1}; MS (70 eV), m/z (relative intensity) 268 (M$^+$, 1), 209 (7), 177 (42), 136 (100), 91 (3), 43 (12)], 1-(4-phenethyl)phenylethyl acetate (**7**) [by comparison with an authentic specimen prepared by esterification of 1-(4-phenethyl)phenylethanol (**8**) (vide infra), with acetic anhydride in pyridine], and 1-(4-acetylphenyl)-2-phenylethane (**9**) [mp 68.5–69 °C (lit.[23] mp 69 °C)].

(C) Oxidation of 1-(4-Ethylphenyl)-2-phenylethane (2) with CAN in Aqueous Acetonitrile. To **2** (4.8 mmol) in 100 mL of 70% aqueous acetonitrile, containing 0.3 M nitric acid, was added CAN (9.0 mmol) in 10 mL of the same solvent. The reaction mixture was refluxed until a pale yellow solution was observed. The mixture was poured into cold water and worked up as above. Column chromatography of the crude product on silica gel by eluting with light petroleum–diethyl ether (4:1) afforded, besides the starting material, the following products: benzyl nitrate (comparison with an authentic specimen available from a previous work[18]), benzaldehyde, benzyl alcohol, 4-ethylbenzaldehyde (comparison with a commercial sample), 1-(4-acetylphenyl)-2-phenylethane (**9**), 1-(4-phenethyl)phenylethanol (**8**) [comparison with an authentic specimen obtained by reduction of **9** with LiAlH$_4$ in anhydrous ether: mp 66–67 °C; ^{1}H NMR δ 7.4–7.0 (m, 9 H), 4.86 (q, J = 7 Hz, 1 H), 2.93 (s, 4 H), 1.83 (br s, 1 H), 1.49 (d, J = 7 Hz, 3 H); IR (CCl$_4$) 3620–3200, 3090–2860, 1455, 1000, 895 cm^{-1}; MS (70 eV), m/z (relative intensity) 226 (M$^+$, 15), 225 (85), 211 (42), 135 (100), 91 (93), 43 (94). Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.88; H, 7.89], and finally a small amount of 1-(4-formylphenyl)ethanol (**10**) (comparison with ^{1}H NMR spectrum reported in the literature[24]). Blank experiments showed that 4-ethylbenzyl alcohol added to the reaction mixture in very small amount (3%) survive in these oxidation condition and can be detected by VPC in an unchanged amount. The same holds for added (7%) 4-ethylbenzyl nitrate, which was detected without loss by ^{1}H NMR spectroscopy. Moreover column chromatography of reaction product on silica gel, eluting with light petroleum–diethyl ether (4:1), allowed a quantitative recovery of this compound.

(D) Oxidation of 1,2-Bis(4-methoxyphenyl)ethane (3) by CAN in Acetic Acid. To a stirred suspension of CAN (2.0 mmol) in 25 mL of acetic acid at 40 °C was added **3** (1.0 mmol). After 20 min the reaction mixture was poured into a cold solution of KI and $Na_2S_2O_3$ and worked up as above. The ^{1}H NMR analysis of the crude product, by using nitromethane as an internal standard, showed the presence of acetate of 1,2-bis(4-methoxyphenyl)ethanol (47%) [the product isolated by column chromatography shows the following spectroscopic characteristics: ^{1}H NMR δ 7.2–6.7 (m, 8 H), 5.9–5.7 (3 peaks, X portion of an ABX system, 1 H), 3.76 (s, 6 H), 3.1–2.9 (7 peaks, AB portion of an ABX system, 2 H), 1.99 (s, 3 H); IR (CCl$_4$) 3100–2900, 2835, 1740, 1615, 1520, 1230, 1180, 1040 cm^{-1}; MS (70 eV), m/z (relative intensity) 300 (M$^+$, 2), 241 (16), 240 (51), 179 (55), 137 (100), 121 (47)]; moreover, 4-methoxybenzaldehyde (~4%), 4-methoxybenzyl acetate (~1%), and unreacted substrate (46%) were detected.

Photochemical Oxidations. (A) Nitrooxylation of Bibenzyl (1). A stirred solution of **1** (4.0 mmol) and CAN (8.0 mmol) in CH_3CN (100 mL) was irradiated at room temperature with an immersion high-pressure mercury lamp (Helios—Italquartz, 125 W) whose emission was filtered through Pyrex. The reaction mixture, poured into water, was extracted with diethyl ether. The combined organic extracts were washed with water and dried. After the solvent was removed, the crude product was chromatographed on silica gel with light petroleum as eluent, affording, besides unreacted **1**, benzaldehyde, benzyl nitrate, and 1,2-diphenylethyl nitrate (**12**) [the structure of **12** was assigned on the basis of (i) ^{1}H NMR spectrum (δ 7.4–7.0 (m, 10 H), 6.0–5.8 (4 peaks, X portion of an ABX system, 1 H), 3.4–2.9 (seven peaks, AB portion of an ABX system, 2 H)), (ii) IR ((neat) 1630 cm^{-1} (characteristic absorption of ONO_2 group)), and (iii) LiAlH$_4$ reduction to alcohol **5**].

(B) Autoxidation of Bibenzyl (1). Into a solution of **1** (4.0 mmol) and CAN (0.8 mmol) in CH_3CN (100 mL) was bubbled dioxygen under irradiation by an immersion high-pressure mercury lamp (125 W, Pyrex filter) at room temperature and the mixture worked up as above. Chromatography of the crude product on silica gel, eluting with 95% light petroleum–diethyl ether, yielded, besides the starting material, **12**, benzyl nitrate, benzaldehyde, benzyl alcohol, benzoic acid, 1,2-diphenylethanone (**13**) (comparison with a commercial sample), and an inseparable mixture of two products, whose ^{1}H NMR spectrum exhibited two singlet at about δ 8 (peroxidic hydrogens). The mixture reacted with KI, giving iodine, 1,2-diphenylethanol (**5**), and benzyl alcohol. Thus, the two products were assigned the structure of 1,2-diphenylethyl hydroperoxide (**14**) and benzyl hydroperoxide (**15**). The yields of **14** and **15** were reasonably assumed to be identical with those determined for **5** and benzyl alcohol, respectively, after reduction of the mixture with KI. The amount of formed iodine was exactly that predicted by the yields of **14** and **15** calculated in this way.

(C) Autoxidation of 4-Ethylbibenzyl (2). A dioxygen bubbled solution of **2** (4.0 mmol) and DCA (0.02 mmol) in CH_3CN (100 mL) was irradiated with an external high-pressure mercury lamp (Helios—Italquartz, 500 W, Pyrex filter) at room temperature, and the mixture was worked up as previously described. Chromatography of the crude product on silica gel by eluting with 95% light petroleum–diethyl ether afforded, besides the starting material, benzaldehyde, benzyl alcohol, benzoic acid, 1-(4-phenethyl)phenylethanol (**8**), 4-acetylbibenzyl (**9**), 4-ethylbenzoic acid [comparison with a commercial sample], and 1-(4-ethylphenyl)-2-phenylethanone (**16**) [^{1}H NMR δ 7.94 (d, J = 8 Hz, 2 H), 7.3–7.0 (m, 7 H), 4.25 (s, 2 H), 2.70 (q, J = 7 Hz, 2 H), 1.26 (t, J = 7 Hz, 3 H); IR (CCl$_4$) 3090–2860, 1680, 1610, 1275, 700 cm^{-1}; MS (50 eV), m/z (relative intensity) 224 (M$^+$, 3), 134 (100), 133 (99), 105 (22), 98 (90), 79 (24), 77 (26). Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.67; H, 7.26]. Blank experiments showed that 4-ethylbenzyl alcohol added (8%) to the reaction mixture survives under the oxidation conditions (^{1}H NMR and VPC analysis).

Anodic Oxidations. The electrochemical experiments were performed in a jacketed microcell thermostated at 25 °C with Pt as anode (4-cm^2 effective electrode area) and cathode. The magnetically stirred solutions were electrolyzed by using an AMEL 552 potentiostat until 2 or 4 F mol^{-1} of charge were passed.

(A) Electrolysis in Aqueous Acetone. The hydrocarbon (2.5 mmol) was dissolved in 100 mL of 98.5% aqueous acetone containing sulfuric acid (0.3 M). The solution was electrolyzed at 20 mA cm^{-2} constant current. The cathodic compartment was separated by a glass frit. The reaction mixture was poured into water and extracted with ether. The combined organic extracts were washed with water, dried, and concentrated. ^{1}H NMR analysis of the crude product from **1** (1,4-dimethoxybenzene as internal standard) indicated the presence of unreacted substrate, benzaldehyde, benzyl alcohol, and 1,2-diphenylethanol (**5**). The crude product from **2** was chromatographed on silica gel by eluting with 95% light petroleum–diethyl ether, affording, besides starting material, benzaldehyde, 4-ethylbenzaldehyde, 1-(4-ethylphenyl)-2-phenylethanol (**18**), 4-acetylbibenzyl (**9**), and 1-(4-phenethyl)-2-phenylethanol (**8**). The yields of the products recovered by column chromatography were similar to those calculated from ^{1}H NMR of the crude mixture with 1,4-dimethoxybenzene as an internal standard. A blank experiment was also performed adding 0.2 mmol of 4-ethylbenzyl alcohol (**17**) to a mixture obtained after 1 F mol^{-1} of charge passed. Then again 1 F mol^{-1} was passed into the solution, and the reaction mixture was worked up as above. ^{1}H NMR and VPC analyses showed the presence of **17** in a practically unchanged amount.

(B) Electrolysis of 4-Ethylbibenzyl (2) in Acetic Acid–Acetonitrile. The hydrocarbon (7.0 mmol) was dissolved in an acetic acid–acetonitrile (3:1, v/v) mixture containing 0.07 M tetraethylammonium tetrafluoroborate. The solution was elec-

---

[23] Buw-Hoi; Royer, R. *Bull. Soc. Chim. Fr.* **1947**, 820–823.

[24] Chihara, T.; Wakabayashi, T.; Taya, K. *Chem. Lett.* **1981**, 1657–1660.

trolyzed at 2.2 V (vs. SCE) constant potential and 20 mA cm^{-2} initial current density. The reaction mixture was worked up as previously described except that the organic layer was washed with 5% $NaHCO_3$. The crude product, analyzed by ^1H NMR, consisted of a mixture of starting material, 4-acetylbibenzyl (**9**), 1-(4-ethylphenyl)-2-phenylethyl acetate (**6**) and 1-(4-phenethyl)phenylethyl acetate (**7**).

Acknowledgment. This work has been supported by "Progetto Finalizzato C.N.R. Energetica II" (Grant 84.02638.59). Thanks are due to Dr. E. Girardi and to Dr. E. Oberrauch (ENIRICERCHE, Milano) for helpful discussion.

Registry No. 1, 103-29-7; 2, 7439-15-8.

Single Electron Transfer in the Meerwein–Ponndorf–Verley Reduction of Benzophenone by Lithium Alkoxides

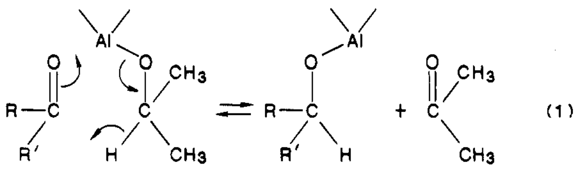
E. C. Ashby* and J. N. Argyropoulos[†]

School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

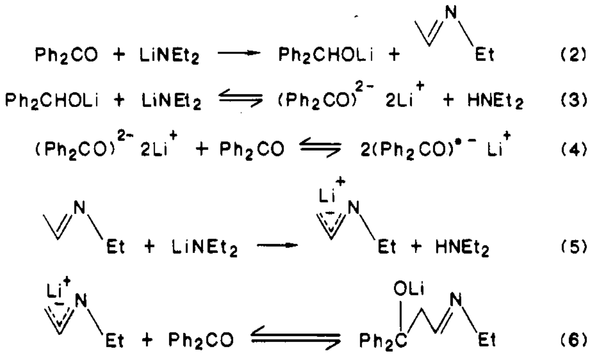
Received October 17, 1985

The Meerwein–Ponndorf–Verley reduction of benzophenone by lithium alkoxides was determined to proceed via a radical intermediate. The radical intermediate was identified as the lithium ketyl of benzophenone and was found to be reduced to lithium benzhydrolate by abstracting a β-hydrogen atom from the lithium alkoxide. The major pathway to benzophenone ketyl appears to be the result of a one-electron transfer from the lithium alkoxide to benzophenone. The formation of benzophenone ketyl from the corresponding dianion, formed in low concentration by deprotonation of lithium benzhydrolate by the alkoxide, provides an alternate pathway to ketyl although it should be a minor one. On the other hand, aluminum isopropoxide gave no indication that it reduces benzophenone via a radical intermediate.

The Meerwein–Ponndorf–Verley reduction of ketones is generally believed to proceed via a polar mechanism[1] involving a cyclic transition state (eq 1).[2] Nevertheless, a single electron transfer (SET) pathway has been proposed for the reduction of benzophenone by lithium, sodium, and potassium alkoxides.[3,4] The basis of the proposed SET mechanism was the appearance of benzophenone ketyl (observed by ESR and visible spectroscopy) as well as the formation of benzophenone ketyl coupling products. In addition, stereochemical evidence for a single electron transfer pathway in the reduction of cyclic ketones with alkoxyaluminum dichlorides has been reported.[5]



The presence of benzophenone ketyl in the reactions of benzophenone with certain nucleophiles has recently been questioned by Newcomb[6] as indication of a SET process. In the reaction of benzophenone with lithium dialkylamides, he proposed an alternate scheme involving fast concerted β-hydride reduction of benzophenone to give lithium benzhydrolate (eq 2), the formation of dilithium benzophenone dianion from the deprotonation of lithium benzhydrolate by the lithium dialkylamide (eq 3), and fast electron transfer from benzophenone dianion to benzophenone to give two molecules of ketyl (eq 4). Benzophenone is provided throughout the reaction by retroaldolization of an aldol-like adduct formed early in the reaction (eq 5 and 6). In support of the pathway depicted in eq 2–6, Newcomb showed that 10% benzophenone dianion was formed when lithium benzhydrolate was treated with a fivefold excess of LDA (eq 3) for 22 h at 22 °C.



Furthermore, the deprotonation of lithium benzhydrolate by LDA in THF at 22 °C occurred with an apparent second-order rate constant which was approximately equal to one-half of the apparent second-order rate constant for ketyl formation when benzophenone was treated with LDA under similar conditions. Lithium diisopropylamide was also found to rapidly reduce benzophenone to give approximately 55% lithium benzhydrolate (after the first few minutes no significant change in the yield of benzhydrol was detected during the next 24 h). Conversely, the ketyl formed slowly and reached a maximum after 30 h, hence indicating that it is not the intermediate in the formation of the reduction product. Based on these results, Newcomb suggested that a similar pathway might be in effect for the reduction of benzophenone by alkoxides.

With this background, a more detailed study of the reaction of lithium alkoxides with benzophenone was carried out in order to determine whether the Meerwein–

[†] Present address: Union Carbide Technical Center, P.O. Box 8361, S. Charleston, WV 25303.

[1] Wilds, A. L. In *Organic Reactions*; Adams, R., Bachmann, W. E., Fieser, L. F., Johnson, J. R., Snyder, H. R., Ed.; Wiley: New York, 1944.

[2] Shiner, V. J.; Whittaker, D. *J. Am. Chem. Soc.* **1963**, *85*, 2337.

[3] Screttas, C. G.; Cazianis, C. T. *Tetrahedron* **1978**, *34*, 933.

[4] Ashby, E. C.; Goel, A. B.; Argyropoulos, J. N. *Tetrahedron Lett.* **1982**, *23*, 2273.

[5] Nasipuri, D.; Gupta, M. D.; Banerjee, S. *Tetrahedron Lett.* **1984**, *25*, 5551.

[6] (a) Newcomb, M.; Burchill, M. T. *J. Am. Chem. Soc.* **1984**, *106*, 2450; (b) 8276.

0022-3263/86/1951-3593$01.50/0