Carbonium Ions from Oxidation of Organic Radicals by Transition-metal Salts

By ANTHONY B. EVNIN* and ANNA Y. LAM

(*Union Carbide Research Institute, P.O. Box 278, Tarrytown, New York 10591*)

CARBONIUM ions have been invoked as intermediates in certain oxidations of free radicals by transition-metal salts.[1,2] The relationship of these species to the organic cations generated in other systems (Friedel–Crafts reactions, deaminations, *etc.*) has not, however, been defined.

We have found that toluene reacts with t-butyl peroxide and di(phenylsulphonyl)amine in the presence of catalytic amounts of cuprous chloride to afford the phenyltolylmethanes (I) as the major product.[3] These must be the result of an electrophilic benzylation of toluene. Free-radical benzylation is ruled out as a route to (I) since addition of benzyl radicals to mononuclear aromatics is apparently not observed.[4] Evidence on the mechanism of formation of (I) comes from comparison of the isomer distribution with those obtained by reaction of toluene with $PhCH_2Cl$–$AlCl_3$ (ref. 5) or with $PhCH_2NH_2$–$NO^+PF_6^-$ (ref. 6) (see Table 1).

$$PhMe + (Bu^tO)_2 + (PhSO_2)_2NH \xrightarrow[110°;\ 2hr.]{CuCl} \underset{(I)\ 21\%}{PhCH_2{\cdot}C_6H_4Me} + \underset{(II)\ 2{\cdot}3\%}{PhCH_2{\cdot}OBu^t} + \underset{(III)\ 7{\cdot}3\%}{PhCH_2N(SO_2Ph)_2} + Bu^tOH \qquad (1)$$

The relative reactivities of various added aromatic substrates towards benzylation in this reaction are very similar to those obtained in typical electrophilic benzylations (see Table 2). The slight dependence of the relative reactivities on the solvent composition (toluene : benzene) could arise from variations in the reaction temperature, although minor changes in the media could be important in determining the reactivity of a tight ion-pair.[7]

TABLE 1

Benzylation of toluene; distribution of isomers

	o-	*m*-[d]	*p*-
This study (110°)[a]	35	9	56
$PhCH_2Cl$–$AlCl_3$/CH_3NO_2 (25°)[b]	43·5	4·5	52
$PhCH_2NH_2$–$NO^+PF_6^-$/CH_3CN (25°)[c]	47·5	8·6	43·9

[a] Reaction carried out at 100° ± 10° with 55 mmole of peroxide and di(phenylsulphonyl)amine, 0·5–0·8 mole of toluene and 0·5 mmole of cuprous chloride. Isomer ratios were determined by g.l.c. and n.m.r. Samples of each isomer were prepared independently. [b] Ref. 5. [c] Ref. 6. [d] Under equilibrating conditions >50% of the *m*-isomer is obtained: G. A. Olah and J. A. Olah, *J. Org. Chem.*, 1967, **32**, 1612.

Benzyl t-butyl ether (II) must also be the product of a benzyl cation (reaction with the t-butyl alcohol formed from t-butyl peroxide). Addition of two equivalents of t-butyl alcohol at the start of the reaction changes the ratio of (II) : (I) from 1 : 10 to 3 : 1. Interaction of a benzyl radical with cupric t-butoxylate[8] is ruled out as a major route to (II) by the variations in yield caused by changes in the concentration of t-butyl alcohol or in the structure of the amides.

TABLE 2

Relative reactivity of aromatic substrates towards benzylation

Substrate	Relative reactivity This study[a]	Lit.
Anisole	21	
Toluene	4·5 ± 0·5	3·5[c]
Benzene	1·0	1·0[c]
Chlorobenzene	0·15	0·24[d]

[a] Conditions were those described in Table 1. Ratios were determined by g.l.c. and n.m.r.; substituted diphenylmethanes were prepared independently for comparison. [b] Ratio of substrates varied over a four-fold range. [c] Ref. 4. [d] G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, 1962, **84**, 1695.

Yields of the solvolysis products [(I) and (II)] decrease and yields of amidation products [*e.g.* (III)] increase as di(phenylsulphonyl)amine is replaced in (I) by increasingly less acidic amides. With saccharin the amidation (both *N*- and *O*-) and solvolysis products are present in the ratio of 1·25 : 1, while with benzenesulphonamide the ratio is 15 : 1. Carboximides and amides afford only traces of (I) and (II) but good yields (50—80% based on peroxide) of amidation products. In these last cases reaction (I) is useful for the synthesis of novel amides and for conversion of C–H into C–N bonds.[9]

A variety of molecules with benzylic and allylic hydrogens have been studied under these conditions and behave analogously to toluene. Simple hydrocarbons or ethers, however, afford only analogues of (III) and olefins.

The data above indicate that the intermediate formed in reaction (1) is entirely analogous in behaviour to the carbonium ions obtained from an organic halide and a Lewis acid or from nitrosation of an amide. In the aprotic nonpolar media utilized in (1), this cation most likely exists as part of a tight ion-pair involving the cuprous salt. The formation and fate of this species are accounted for by the following mechanism. Steps (2) and (3) of the mechanism have been well established in closely analogous reaction systems by other workers in the field.[1,2] Evidence for radicals in this system is the formation of bibenzyl in cases where the co-reagent forms a less efficient oxidant with Cu^{II} than does di(phenylsulphonyl)amine.† The results obtained with various substrates, amides, and peroxides suggest that the relative rates of collapse (6) and solvolysis [(7) and (8)] of an intermediate such as (IV) depend on the structure of the carbonium ion and anion; with resonance-stabilized cations and stable amide anions solvolysis predominates even when the solvent is a poor nucleophile. Di(phenylsulphonyl)amine is a particularly valuable co-reagent since it drives equilibrium (4) far to the right and affords an unreactive counterion which permits observation of the chemistry of the carbonium ion.

$$(\mathrm{Bu^tO})_2 + \mathrm{Cu^IX} \rightarrow \mathrm{Bu^tO\cdot} + \mathrm{Bu^tO{-}Cu^{II}X} \tag{2}$$

$$\mathrm{Bu^tO\cdot} + \mathrm{PhMe} \rightarrow \mathrm{PhCH_2\cdot} + \mathrm{Bu^tOH} \tag{3}$$

$$\mathrm{Bu^tO{-}Cu^{II}X} + (\mathrm{PhSO_2})_2\mathrm{NH} \rightleftarrows (\mathrm{PhSO_2})_2\mathrm{N{-}Cu^{II}X} + \mathrm{Bu^tOH} \tag{4}$$

$$\mathrm{PhCH_2\cdot} + (\mathrm{PhSO_2})_2\mathrm{N{-}Cu^{II}X} \rightleftarrows [\mathrm{PhCH_2{}^+Cu^IX{-}N(SO_2Ph)_2}]\ (\mathrm{IV}) \tag{5}$$

$$(\mathrm{IV}) \rightarrow \mathrm{PhCH_2N(SO_2Ph)_2} + \mathrm{Cu^IX} \tag{6}$$

$$(\mathrm{IV}) + \mathrm{PhMe} \rightarrow \mathrm{PhCH_2{\cdot}C_6H_4Me} + (\mathrm{PhSO_2})_2\mathrm{NH} + \mathrm{Cu^IX} \tag{7}$$

$$(\mathrm{IV}) + \mathrm{Bu^tOH} \rightarrow \mathrm{PhCH_2{\cdot}OBu^t} + (\mathrm{PhSO_2})_2\mathrm{NH} + \mathrm{Cu^IX} \tag{8}$$

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† The efficiency of radical oxidation by Cu^{II} salts is strongly dependent on both the radical and on the environment of the metal. In favourable cases second-order rate constants of 10^{-9} l. mole^{-1} sec.$^{-1}$ are observed (ref. 1) which explains why radical dimerization, which is second order in radical, becomes unimportant.

[1] For reviews see J. K. Kochi, *Rec. Chem. Prog.*, 1966, **27**, 207; *Science*, 1967, **155**, 415.

[2] C. Walling and G. Zavitsas, *J. Amer. Chem. Soc.*, 1963, **85**, 2084.

[3] Diphenylmethane was recently reported as a minor product of the decarboxylation of phenylacetic acid with Pb(OAc)$_4$; no comment on its origin was made, J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, 1968, **33**, 83.

[4] R. A. Jackson, *J. Chem. Soc.*, 1963, 5284.

[5] G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, 1962, **84**, 1688.

[6] G. A. Olah, N. A. Overchuk, and J. C. Lapierre, *J. Amer. Chem. Soc.* 1965, **87**, 5788.

[7] A somewhat analogous effect has been reported in the isopropylation of benzene–toluene mixtures: A. T. Jurewicz, J. H. Bayless, and L. Friedman, *J. Amer. Chem. Soc.*, 1965, **87**, 5788.

[8] J. R. Shelton and A. Camp, *J. Org. Chem.*, 1962, **28**, 1393.

[9] Fragmentary results on this amidation reaction have been reported: A. Fono, *Chem. and Ind.*, 1958, 414.