on going from the chloride to the bromide to the iodide in the *m*-nitrobenzyl system–a system which gives only oxygen alkylation. Furthermore, a large spread in rate on going from a chloride to a bromide to an iodide is to be expected for an SN2 displacement in a dipolar aprotic solvent such as DMF.[4]

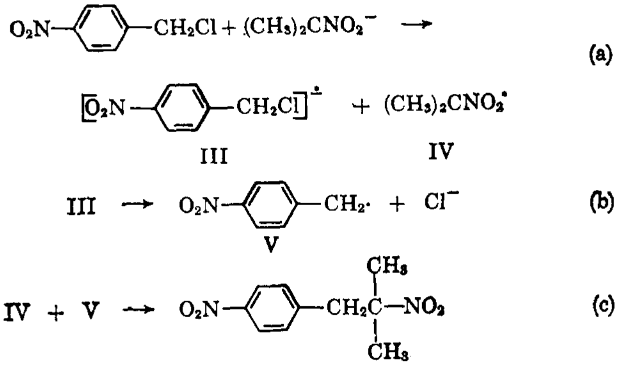
TABLE I

RATES AND PRODUCTS IN THE ALKYLATION OF THE LITHIUM SALT OF 2-NITROPROPANE WITH NITROBENZYL HALIDES[a]

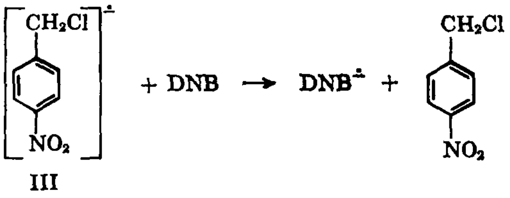
	para					meta
	% yield		Rates[b]			Rate[c]
Halide	C-Alkylate	O-Alkylate	k_{total}	k_{carbon}	k_{oxygen}	k_{total}
Cl	92	6	0.024	0.022	0.002	0.0013
Br	17	57	0.34	0.058	0.28	0.28
I[d]	7	86	1.9	0.13	1.8	1.4

[a] In DMF at 0°. [b] k_{total} in M^{-1} sec.$^{-1}$ as measured by rate of halide ion production; $k_{\text{carbon}} = k_{\text{total}} \times \%$ C-alkylate; $k_{\text{oxygen}} = k_{\text{total}} - k_{\text{carbon}}$. [c] k_{total} in M^{-1} sec.$^{-1}$ as in *b*; here $k_{\text{total}} = k_{\text{oxygen}}$. [d] All iodide rate data extrapolated from −23°

We propose that carbon alkylation, in contrast to oxygen alkylation, is a radical anion process.



This mechanism is supported by the following facts. (1) The lack of sensitivity of the rate of carbon alkylation to the leaving group strongly suggests that here we do not deal with an SN2 displacement. (2) In step a of the proposed mechanism it is postulated that the anion derived from 2-nitropropane transfers one electron to a nitroaromatic system. Actually, direct evidence for this view has been obtained. A solution of the lithium salt of 2-nitropropane in DMF converts nitrobenzene into its radical anion as shown by the production of a well resolved ten-line e.p.r. spectrum.[5] *p*-Nitrobenzyl methyl ether also gives an e.p.r. spectrum when treated with a DMF solution of the lithium salt of 2-nitropropane; and, most directly, a study of the reaction of *p*-nitrobenzyl chloride with the lithium salt of 2-nitropropane in DMF at −50° reveals an unambiguous, albeit unresolved, resonance of about 30-gauss width. (3) Radical anions derived from nitroaromatics are long-lived radicals.[6] Furthermore, electron transfer from nitroaromatic radical anions to nitroaromatics is often very rapid.[7] Consequently, it appeared possible that an easily reduced nitroaromatic such as a dinitrobenzene (DNB) might be able to take an electron away from the radical anion (III) before loss of chloride occurred (b) and, thereby, prevent carbon alkylation.



The net effect of such interception would be to retard carbon alkylation without affecting oxygen alkylation and, hence, the proportion of oxygen alkylate should rise even as that of carbon alkylate falls. As can be seen from Table II, carbon alkylation is, indeed, suppressed by aromatic nitro compounds. It is especially noteworthy that the efficiency with which the nitroaromatics suppress carbon alkylation completely parallels the ease with which they undergo one-electron reduction.[8] It is also significant that with much less than a stoichiometric amount of *p*-DNB the major product is the oxygen alkylate.

TABLE II

THE INFLUENCE OF NITROAROMATICS ON THE REACTION OF *p*-NITROBENZYL CHLORIDE WITH THE LITHIUM SALT OF 2-NITROPROPANE[a]

Added nitroaromatic (mmoles)	% yield C-Alkylate	O-Alkylate
None	92	6
$PhNO_2$ (40)	84	7
m-DNB (10)	61	29
m-DNB (20)	40	48
p-DNB (2)	29	57
p-DNB (10)	2	72

[a] In DMF at 0° using 10 mmoles of chloride and 21 mmoles of lithium salt.

It will be seen that a radical anion such as III has the special property that by loss of a stable anion it is readily transformed into the corresponding free radical V. Extension of these ideas to the reactions of other nucleophiles is in progress.

Acknowledgment.—This work was supported by a grant from the Explosives Department of the Du Pont Company to whom our sincere thanks are due.

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(4) A. J. Parker, *J. Chem. Soc.*, 1332 (1961).

(5) G. A. Russell, E. G. Janzen, and E. T. Strom [*J. Am. Chem. Soc.*, **86**, 1807 (1964)] have very recently shown that the nitrobenzene radical anion is formed on treating nitrobenzene with nitroparaffin salts in *t*-butyl alcohol–DMSO. Although our spectrum is less well resolved than theirs there is no doubt that it is produced by the same radical anion.

(6) D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960); L. H. Piette, P. Ludwig, and R. N. Adams, *ibid.*, **84**, 4212 (1962); P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 609 (1963).

(7) S. I. Weissman, *Z. Elektrochem.*, **64**, 47 (1960); R. L. Ward, *J. Chem. Phys.*, **32**, 410 (1960); M. T. Jones and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 4269 (1962).

(8) A. H. Maki and D. H. Geske, *ibid.*, **83**, 1852 (1961).

(9) National Science Foundation Cooperative Graduate Fellow.

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GRANT W. URRY
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RECEIVED JULY 31, 1964

A New Insertion Reaction of Cationic Oxygen

Sir:

It has been reported that 1,3,3-trimethylcyclohexyl hydroperoxide (I, X = OH), when treated with *p*-nitrobenzenesulfonyl chloride in pyridine, forms the bicyclic ether II in 5–10% yield.[1] It was suggested that the reaction proceeds by decomposition of an intermediate persulfonate *via* an ion-paired transition state involving C–H insertion of cationic oxygen. We

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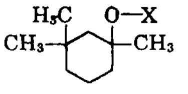
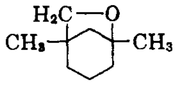
(1) E. J. Corey and R. W. White, *J. Am. Chem. Soc.*, **80**, 6686 (1958).

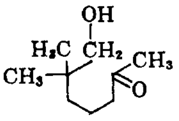
have confirmed that the bicyclic ether II is formed under these conditions and in addition have identified the major products of the reaction as the keto alcohols III and IV, the products to be expected by analogy with the solvolysis products of 9-decalyl *p*-nitroperbenzoate[2] and formed indeed on solvolysis of 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate (I, X = $O_2CC_6H_4NO_2$).[3]



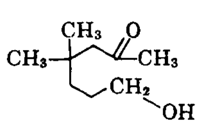
I



II



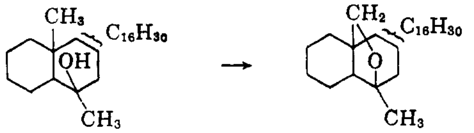
III



IV

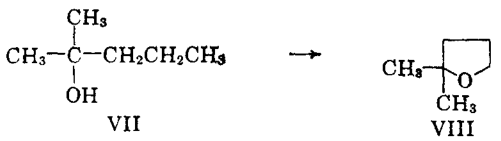
We wish to report here a related reaction of both synthetic and mechanistic interest which gives oxygen insertion products in far better yields and which proceeds by a process, almost certainly heterolytic in nature, involving a non-ion-paired cationic transition state. We have found that, when certain tertiary alcohols are treated with bromine in the presence of silver salts (nitrate, acetate, oxide) and in the absence of light, ring closure occurs directly to give cyclic ethers. Thus a pentane solution of 1,3,3-trimethylcyclohexanol (I, X = H), when treated with bromine and silver oxide at room temperature and in the absence of light, furnished the bicyclic ether II in 75% yield (based on recovered starting material).[4] Detectable amounts of the keto alcohols III and IV were not formed.

The reaction appears to be quite general for tertiary alcohols. Thus 6α-methylcholestan-6β-ol (V)[5] [m.p. 105–106.5°, $[\alpha]^{32}\mathrm{D}$ +25.1° (chloroform). *Anal.* Found: C, 83.38; H, 12.52] gives in 55% yield by the same procedure 6α-methyl-6,19-oxidocholestane (VI), m.p. 83–84°, $[\alpha]^{28}\mathrm{D}$ +14.7° (chloroform). *Anal.* Found: C, 83.84; H, 12.16.



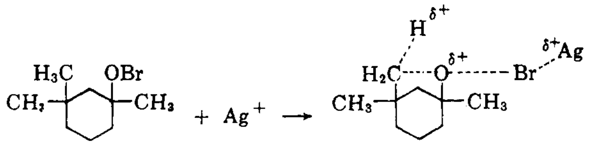
V VI

Even the straight-chain tertiary alcohol, 2-methyl-2-pentanol (VII), undergoes the reaction, furnishing 2,2-dimethyltetrahydrofuran (VIII) in 50% yield (by v.p.c.).



VII VIII

Our experiments indicate that the reaction takes place by way of an intermediate hypobromite[8] whose decomposition is silver ion catalyzed.[9]



Mechanistically the decomposition of the hypobromite is similar to the reaction reported by Corey and White[1] in that a form of cationic oxygen is involved, but it differs in that the leaving group is effectively neutral silver bromide rather than sulfonate anion. To what extent the developing positive charge in the transition state is resident upon oxygen is a question requiring further experimentation.

Extensions of this new reaction to primary and secondary systems are currently under active investigation as are questions of any implications which it may have for the mechanism of the Hunsdiecker reaction.

Acknowledgment.—This work was supported in part by the Army Research Office (Durham) and by the Purdue Research Foundation.

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(2) R. Criegee and W. Schnorrenberg, *Ann.*, **560**, 141 (1948).

(3) N. P. Matheny, Ph.D. Thesis, Purdue University, 1964.

(4) A heterogeneous mixture of the alcohol I (2.75 g.), silver oxide (8.0 g.), and bromine (1.0 ml., 3.1 g.) in pentane (100 ml.) was stirred in the absence of light and at room temperature for 30 min. Chromatography on alumina furnished 1.50 g. of bicyclic ether II and 0.76 g. of recovered alcohol I.

(5) Prepared by the addition of the methyl Grignard reagent to cholestan-6-one. Note that the success of the ring closure reation confirms the 6β orientation assigned to the alcohol function in V and, by analogy, that the configurations tentatively assigned by R. A. S. to the products of addition of various Grignard reagents to cholestan-3β-ol-6-one acetate are incorrect.[6] These adducts should be formulated as 6α-(*R*)-3β,6β-cholestandiols.[7]

(6) R. A. Sneen, *J. Am. Chem. Soc.*, **80**, 3971, 3982 (1958).

(7) This conclusion had earlier been reached by others: M. Davis and G. H. R. Summers, *J. Chem. Soc.*, 4707 (1960), and M. Shiota, *Chem. Abstr.*, **51**, 17,969 (1957).

(8) 1,3,3-Trimethylcyclohexyl hypobromite, prepared *in situ* by the action of bromine and mercuric oxide on a pentane solution of the alcohol I in the absence of light, gave rise to the cyclic ether II when treated with silver oxide.

(9) The heterolytic nature of the reaction is evidenced by our observations that it takes place readily in the absence of light and is unaffected by the addition of known free-radical inhibitors.

DEPARTMENT OF CHEMISTRY RICHARD A. SNEEN
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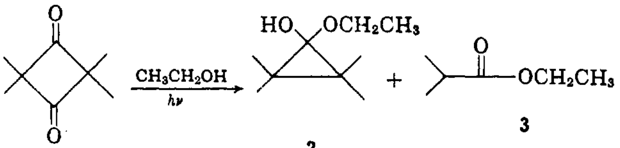
RECEIVED JULY 30, 1964

Isolation of Tetramethylcyclopropanone Ethyl Hemiketal from Photolysis of Tetramethylcyclobutanedione

Sir:

Tetramethylcyclopropanone ethyl hemiketal (**2**) has been prepared by photolytic decarbonylation of tetramethylcyclobutanedione (**1**). Solutions of 5–15%



1 **2** **3**

by weight of **1** in absolute ethanol were irradiated at 40–75° with a Hanau PL 321 immersion mercury lamp until little starting material remained. After removal of most of the solvent at reduced pressure, yields of up to 35% of **2**, m.p. 20–26°, were obtained by crystallization and yields of up to 55% were isolated by gas-liquid chromatography (g.l.c.). The other major product was ethyl isobutyrate (**3**), obtained from the photolysis solutions by g.l.c. in yields[1] of 20–25%.

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(1) Calculated on the assumption that one molecule of **1** furnished two molecules of **3**.