Communications

See Editorial, *J. Org. Chem.*, **38**, No. 19, 4A (1972)

The Disproportionation of Trityl Alkyl Ethers. The Synthesis of Aldehydes and Ketones in a Cationic Chain Reaction Involving Hydride Transfer

Summary: Trityl alkyl ethers undergo disproportionation in acetonitrile or methylene chloride, catalyzed by salts of the triphenylmethyl cation, to give aldehydes or ketones and triphenylmethane in good yields.

Sir: Alkyl ethers have been reported to be good hydride donors to carbenium ions.[1,2] Representative ethers have been oxidized to aldehydes or ketones by the triphenylmethyl cation with production of triphenylmethane.[3] These oxidations are, however, inefficient in that only one of the alkyl groups of dialkyl ethers undergoes oxidation, and have only recently received serious consideration in synthetic applications.[4] Ethers also undergo disproportionation to carbonyl compounds and hydrocarbons in related hydride transfer reactions.[1] However, in previous reports of ether disproportionation reactions, studied in strongly acidic media with ethers that form relatively stable carbenium ions, hydrogen transfer was described as occurring from an alcohol to a carbenium ion (Scheme I).[5] A similar mechanism has been proposed for those reactions in which an alcohol serves simultaneously as a hydride donor and hydride acceptor.[6]

Scheme I

$$(R_2CH)_2O + H^+ \rightleftharpoons (R_2CH)_2OH^+ \qquad (1)$$

$$(R_2CH)_2OH^+ \rightleftharpoons R_2CH^+ + R_2CHOH \qquad (2)$$

$$R_2CH^+ + R_2CHOH \longrightarrow R_2CH_2 + R_2C{=}OH^+ \qquad (3)$$

We have observed that trityl alkyl ethers undergo disproportionation to triphenylmethane and aldehydes or ketones when small amounts of the triphenylmethyl cation, as the PF_6^-, SbF_6^-, and AsF_6^- salts,[7] are employed (eq 4). In a typical experiment trityl benzyl

$$(C_6H_5)_3COCHR_2 \xrightarrow{(C_6H_5)_3C^+X^-} (C_6H_5)_3CH + R_2C{=}O \qquad (4)$$

ether (5.0 mmol) was added as a solid to a stirred solution of triphenylmethyl hexafluorophosphate (0.50 mmol) in 10 ml of anhydrous acetonitrile. The progress of the reaction was followed by observing the increase in the benzaldehyde and triphenylmethane absorptions as well as the simultaneous decrease in the ether signals by pmr spectroscopy. After 4 hr at room temperature water was added, and the products were isolated and analyzed. In separate reactions with 0.50, 0.25, 0.10, and 0.05 equiv of triphenylmethyl hexafluorophosphate (based on trityl benzyl ether used) quantitative yields of benzaldehyde and triphenylmethane were obtained.[8] The same amount of trityl salt as that initially added could be recovered quantitatively, either as triphenylmethanol or trityl butyl ether (quenching with butanol). Both dipolar aprotic solvents, acetonitrile and nitromethane, and chlorinated hydrocarbon solvents, chloroform and methylene chloride, have been employed. The PF_6^- and SbF_6^- salts are soluble in the dipolar aprotic solvents, while trityl hexafluoroarsenate is conveniently soluble in the chlorinated hydrocarbon solvents; the trityl ethers are usually more soluble in chloroform and methylene chloride than in nitromethane or acetonitrile. Results from the disproportionation of several representative trityl ethers are given in Table I. Although no attempt was made to maximize product yields for each ether studied, the results obtained indicate that the disproportionation of trityl ethers may provide a general method for oxidation of alcohols[9] to aldehydes or ketones.[10]

Table I

Disproportionation of Trityl Alkyl Ethers in Anhydrous Solvents Using Various Salts of the Triphenylmethyl Cation[a]

$(C_6H_5)_3COCHR_2$, R_2CH	Equiv $(C_6H_5)_3C^+X^-$	Solvent	% yield[b] R_2CO
Benzyl	0.10[c]	CH_3CN	100
p-Chlorobenzyl	0.30	CH_2Cl_2	100
p-Methylbenzyl	0.10	CH_2Cl_2	100
p-Nitrobenzyl	1.00	CH_2Cl_2	100[d]
1-Phenylethyl	0.25	CH_2Cl_2	76[e]
Cyclohexyl	0.25	CH_2Cl_2	97
Octyl	0.25	CH_2Cl_2	56[f]

[a] Reactions were run at room temperature (25 ± 3°). Ether (5.0 mmol) was added to the trityl salt; unless noted otherwise, the hexafluoroarsenate salt was used. Reaction times were generally less than 4 hr. [b] Based on pmr spectroscopy and glpc analysis by reference to an internal standard. The yield of triphenylmethane was equal to that of the carbonyl compound. [c] The PF_6^- and SbF_6^- salts were used and gave identical results. [d] Required a reaction time of 90 hr in refluxing CH_2Cl_2. [e] 24% of the symmetrical 1-phenylethyl ether was also formed. [f] The yield of triphenylmethane was 82%.

---

(1) C. D. Nenitzescu in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer Ed., Wiley-Interscience, New York, N. Y., 1970, Vol. 2, Chapter 13.

(2) N. C. Deno, H. J. Peterson, and G. S. Saines, *Chem. Rev.*, **60**, 7 (1960).

(3) P. D. Bartlett and J. D. McCollum, *J. Amer. Chem. Soc.*, **78**, 1441 (1956); N. C. Deno, G. Saines, and M. Spangler, *ibid.*, **84**, 3295 (1962).

(4) D. H. R. Barton, P. D. Magnus, G. Smith, G. Streckert, and D. Zurr, *J. Chem. Soc. C*, 542 (1972).

(5) (a) G. Baddeley and P. G. Nield, *J. Chem. Soc.*, 4684 (1954); (b) H. Burton and G. W. H. Chesseman, *ibid.*, 986 (1953); (c) A. Rieche and E. Schmitz, *Chem. Ber.*, **90**, 531 (1957); (d) F. G. Kny-Jones and A. M. Ward, *J. Chem. Soc.*, 535 (1930).

(6) M. P. Balfe, J. Kenyon, and E. M. Thain, *ibid.*, 790 (1952).

(7) These salts were obtained from the Ozark Mahoning Co. and were dried and purified, if necessary, to a minimum analysis of 99% trityl salt.

(8) Determined by pmr spectroscopy and glpc analysis through reference to an internal standard.

(9) Trityl ethers are conveniently prepared in high yields from trityl chloride and alcohols.

(10) Procedures for the preparation and disproportionation of trityl ethers will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-73-625. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Since ether disproportionation should be characterized by first-order kinetics (rate = k_{obsd}[ether]), where the observed rate constant is dependent on the concentration of trityl salt ($k_{\text{obsd}} = k[(C_6H_5)_3C^+X^-]_0$), we undertook a kinetic study of the disproportionation of trityl benzyl ether. These results, given in Table II, demonstrate the expected rate law and show that the rate-limiting step is also the chain-propagating step (eq 5). The rate of appearance of benzaldehyde was

$$(C_6H_5)_3COCH_2C_6H_5 + (C_6H_5)_3C^+ \xrightarrow{k} (C_6H_5)_3C^+ + C_6H_5CHO + (C_6H_5)_3CH \quad (5)$$

observed to be equal to the rate of disappearance of ether, while the concentration of the triphenylmethyl cation remained constant. Although cationic chain reactions involving hydride transfer have been recognized in a number of reactions involving alkanes and alkyl cations,[1] the present study represents the first reported example of a similar chain-transfer reaction involving ethers.

TABLE II

DISPROPORTIONATION OF TRITYL BENZYL ETHER IN METHYLENE CHLORIDE AT 23.5° IN THE PRESENCE OF TRIPHENYLMETHYL HEXAFLUOROARSENATE[a]

[Ether], M	$[(C_6H_5)_3C^+AsF_6^-]$, M	$10^4\ k_{\text{obsd}}$,[b] sec^{-1}	$10^3\ k$,[c] $M^{-1}\ \text{sec}^{-1}$
0.371	0.0945	1.23	1.31
0.463	0.192	2.52	1.31
0.463	0.0960	1.16	1.22
0.467	0.0192	0.268	1.41

[a] Kinetic determinations were made by following the increase in benzaldehyde concentration and the decrease in ether concentration by pmr spectroscopy using an internal standard. Analyses were identical with those determined by glpc analysis. Temperature control was ±0.1°. [b] Good first-order plots were observed through more than one half-life. [c] Duplicate runs give the precision as $\pm 0.08 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$.

Previous studies of ether disproportionation reactions have represented hydride transfer as occurring from an alcohol to an alkyl cation (Scheme I); our observations of hydride abstraction reactions with trityl ethers suggest that the accumulated data[5] can be equally well explained by a chain reaction involving hydride transfer from the ether. Under reaction conditions identical with those given in Table III, the rate of benzyl alcohol oxidation by an equivalent amount of triphenylmethyl hexafluoroarsenate is at least ten times as slow as that of the corresponding trityl ether.

We are continuing investigations concerning the synthetic utility of this oxidative method and examining the general characteristics of hydrogen abstraction reactions from trityl ethers and related systems.

Acknowledgment.—Support of this work by the National Science Foundation (GP-27587) is gratefully acknowledged. We wish to thank Dr. N. C. Deno for his helpful comments on this study.

---

[11] National Science Foundation Undergraduate Research Participant, summer 1972.

DEPARTMENT OF CHEMISTRY
HOPE COLLEGE
HOLLAND, MICHIGAN 49423

MICHAEL P. DOYLE*
DONALD J. DEBRUYN[11]
DONALD J. SCHOLTEN[11]

RECEIVED NOVEMBER 10, 1972