Published on 01 January 1970. Downloaded by Northeastern University on 27/10/2014 18:59:31

The Synthesis of Ethers by the Desulphurisation of Sulphenate Esters

By D. H. R. BARTON,* G. PAGE, and D. A. WIDDOWSON

(Imperial College, London, S.W.7)

Summary Sulphenate esters have been synthesized in good yield by the action of alkoxides on N-t-butylthiophthalimide; desulphurisation of these esters with tri-n-butylphosphine gave the corresponding ethers.

SULPHENATE esters have been synthesized generally by the action of alkoxides on sulphenyl halides.¹ The reversibility of this process and the sensitivity of the sulphenates to hydrolysis and disproportionation² make this an unsatisfactory process. The stable N-alkylthiophthalimides3 offer scope for nucleophilic displacement on sulphur. We have studied such displacements with alkoxides.

N-t-Butylthiophthalimide reacted with sodium methoxide in methanol at 40-45° during 30 min. to give a 46% yield of O-methyl-t-butylsulphenate, b.p. 60°/100 mm, $n_{\rm D}^{24}$ 1·4324, $v_{\rm max}$ (liq) 900 cm^{-1,4} τ 8·7 (9H, s) and 6·27 (3H, s). Similarly prepared were O-ethyl-t-butylsulphenate, (70%) yield) b.p. $60^{\circ}/60 \text{ mm}$, n_D^{24} 1.4280, ν_{max} (liq) 910 cm⁻¹, τ 8.85 (3H, t) 8.78 (9H, s), and 6.25 (2H, q.), O-t-butyl-tbutylsulphenate (28%), b.p. $60^{\circ}/30 \text{ mm}$, n_D^{24} 1.4330, ν_{max} (liq) 905 cm^{-1} . The O-isopropyl analogue was prepared in 80% yield (by g.l.c.) but could not be isolated pure (codistillation with isopropyl alcohol).

As part of a more general study on extrusion reactions,⁵ we have investigated the abstraction of sulphur from these sulphenate esters. In principle, this process should permit the synthesis of hindered ethers under neutral low-temperature conditions. O-Methyl-t-butylsulphenate was treated with tervalent phosphorus compounds in degassed toluene at 35°, under an atmosphere of nitrogen for 48 h, in the dark. The volatile reaction products were assayed by g.l.c., by comparison with authentic standards. The results are presented in the Table. Tri-n-butylphosphine was an efficient abstractor of sulphur, giving quantitative yields of the ether. Triphenylphosphine gave only moderate yields. The sulphenate was inert to triethyl and triphenyl phosphite but hexaethyltriaminophosphine caused fragmentation to isobutene and methanol. This type of fragmentation has recently been observed in the desulphurisation of N-(t-butylthio)phthalimide under similar conditions.⁶

The yields of the abstraction process did not vary with solvent (ethyl acetate, dioxan, and methanol). No products of oxygen abstraction were detected. The abstraction from the other esters was less efficient (see Table).

Sulphur abstraction from ButSOR

R	Reagent (equiv.)	Iso- butene	Bu⁺OR	Recovered Bu ^t SOR
Me	$Bu_{a}^{n}P(1\cdot 0)$	0	98	0
Me	$Ph_{s}P(1\cdot 1)'$	trace	trace	97
Me	$Ph_{3}P(1.66)$	14	54	29
Me	(PhO) P (10.2)	1	2	95
Me	$(Et_2N)_3P(10.0)$	9	0	0
Et	$\dot{B}u^{n}{}_{3}\dot{P}(1\cdot\dot{0})$		47	
Pri a	$\operatorname{Bun}_{3}P(1\cdot 0)$		12	15
But	$Bu^{n}P(1\cdot 0)$		0	0

^a The unpurified isopropyl sulphenate was used.

As a further probe of the nature of the reaction we carried out the desulphurisation of the methyl ester in ethanol. With tri-n-butylphosphine as abstractor, only t-butyl methyl ether was produced. With the less efficient triphenylphosphine, 11% of the ether product was t-butyl ethyl ether. If the reaction is ionic, then a tight ion-pair must be involved, with a rapid re-attack of the alkoxide ion before any appreciable exchange with solvent can occur. The distinction between this and a possible concerted process is the subject of further study.

(Received, September 9th, 1970; Com. 1533.)

¹L. Goodman and N. Kharasch, J. Amer. Chem. Soc., 1955, 77, 6541; T. L. Moore and D. E. O'Connor, Quart. Rep. Sulfur Chem., 1966, 1, 175; I. B. Douglass and D. A. Koop, J. Org. Chem., 1962, 27, 1398; D. R. Hogg, J. H. Smith, and P. N. Vipond, J. Chem. Soc. (C), 1968, 2713.

- ² N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, Chem. Rev., 1946, 39, 269.

- ^a N. Kharasch, S. J. Foteinpa, and H. D. Weinnerster, *Chem. Rev.*, 1940, 39, 209.
 ^a M. Behforouz and J. E. Kerwood, *J. Org. Chem.*, 1969, 34, 51.
 ^a E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, 1968, 90, 4861.
 ⁵ D. H. R. Barton and B. J. Willis, *Chem. Comm.*, 1970, 1225; D. H. R. Barton, E. H. Smith, and B. J. Willis, *ibid.*, p. 1226.
 ⁶ D. N. Harpp and B. A. Orwig, *Tetrahedron Letters*, 1970, 2691.