

A New Transformation of Thioethers into Ethers Using Thallium(III) Nitrate

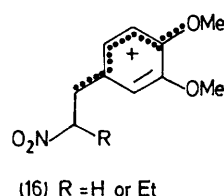
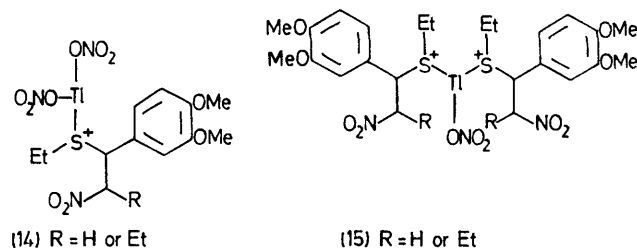
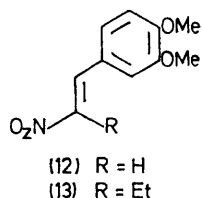
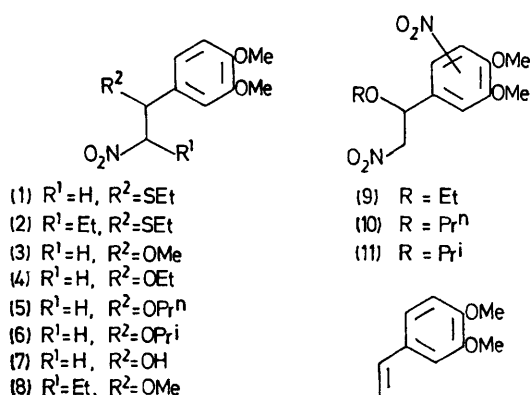
By YOSHIMITSU NAGAO, KIMIYOSHI KANEKO, MASAHITO OCHIAI, and EIICHI FUJITA*

(Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan)

Summary α -(3,4-Dimethoxyphenyl)- β -nitroethylthioethane (1) has been converted into α -(3,4-dimethoxyphenyl)- β -nitroethylthioalkanes in good yield on treatment with 1.2 mol. equiv. of thallium(III) trinitrate (TTN) in several alcohols at room temperature.

RECENTLY, we synthesised α -(3,4-dimethoxyphenyl)- β -nitroethylthioethane (1),[†] m.p. 71–72 °C, in good yield by an effective method. We have now investigated the reactions of this compound with thallium(III) trinitrate

In a typical experiment, a solution of TTN (197 mg, 1.2 mol. equiv.) in methanol (2 ml) was added to a solution of compound (1) (100 mg) in methanol (6 ml), and the mixture was stirred at room temperature for 5 min. The thallium(I) nitrate which precipitated was filtered off and the filtrate was evaporated *in vacuo* to leave a residue, which after addition of water, was extracted with dichloromethane. The extract gave the methyl ether product (3) (87 mg) as white prisms (from methanol).



[$Tl(ONO_2)_3 \cdot 3H_2O$] (TTN) and several alcohols, and also the reaction of the homologue (2)[†] with TTN and methanol. The alkyl ethers (3)–(7) were obtained from (1), and the ether (8) from (2), accompanied by some by-products (Table).

Thallium(III) is expected to be easily and selectively co-ordinated by the sulphur atom in thioethers according to the hard/soft acid/base principle (here a soft-soft co-ordination).¹ Hence, the first step of this reaction must be

TABLE

Thioether (1)	Alcohol MeOH	Mol. equivalent of TTN 0.6 ^b	Reaction time /min 5	Product ^a m.p./°C (3) 109	Yield/% 92
(1)	EtOH	1.2 0.6	5 80	(3) (4) 82 128	98 84, 5 ^c
(1)	Pr ⁿ OH	1.2 0.6	30 60	(4) (5) 143–144 101–102	86, 7 75, 16 ^d
(1)	Pr ⁱ OH	1.2 0.6	10 60	(5) (6) 67–68 89–90	89, trace 69, 16 ^e
(1)	H ₂ O ^f -THF	1.2 1.2	15 30	(6) (7) oil	67, 26 44, 47
(2)	MeOH	1.2	5	(8) oil	98

^a Satisfactory elemental analytical, mass spectral, and ¹H n.m.r. data have been obtained for all new compounds. ^b Using 0.4 mol. equiv. of TTN, the reaction proceeded only to about 60%. ^c 10% Recovery of (1). ^d 9% Recovery of (1). ^e Trace recovery of (1), (checked with n.m.r. spectrum). ^f 6 Mol. equiv. of H₂O were used.

[†] The syntheses of (1) and (2) and their carbon-increasing reactions will be published elsewhere.

the formation of (14) and/or (15). The product ethers can be derived either by a concerted S_N2 -like attack of the alcohols or by stepwise formation of a cation (16) and then nucleophilic attack of the alcohol, the formation of (12) as a by-product is conveniently rationalised by deprotonation from (16).

There is also another possible route where initial elimination from (14) and (15) or (16) gives (12) and (13) and subsequent addition of alcohol to them yields the ethers (3)—(8), but this pathway is denied by the following experimental results. (i) Treatment of the nitro-olefin (12) with TTN (1.2 mol. equiv.) in methanol for 5 h resulted only in

recovery of the starting material. (ii) When (12) is treated with thallium(I) nitrate (1.2 mol. equiv.) in methanol for 2 h,[†] the addition reaction giving the methyl ether (3) occurred only to about 30% [Estimation by n.m.r. indicates the presence of (12) and (3) in a ratio of 3:1 in a mixture of the reaction products]. In the case of (13), m.p. 80—81 °C, the same treatment for 16 h resulted only in recovery of the starting material. (iii) Treatment of (12) in methanol in the presence of 69% nitric acid (5 mol. equiv.) for 2 h only gave the starting material.

(Received, 15th December 1975; Com. 1385.)

[†] In 1 h, all the starting material was recovered.

¹ P. G. Pearson, *J. Amer. Chem. Soc.*, 1963, **85**, 3533; T.-L. Ho, *Chem. Rev.*, 1975, **75**, 1; for the reactions of organic sulphur compounds with Tl^{III} , see, S. Masamune, S. Kamata, and W. Schilling, *J. Amer. Chem. Soc.*, 1975, **97**, 3515; T.-L. Ho and C. M. Wong, *Canad. J. Chem.*, 1972, **50**, 3740.