REACTION OF 2-METHYL-2-PHENYL-1,3-DIOXOLANE WITH TRIMETHYLCHLOROSILANE

R. S. Musavirov, Z. F. Mullakhmetova,
E. P. Nedogrei, E. A. Kantor,
and D. L. Rakmankulov

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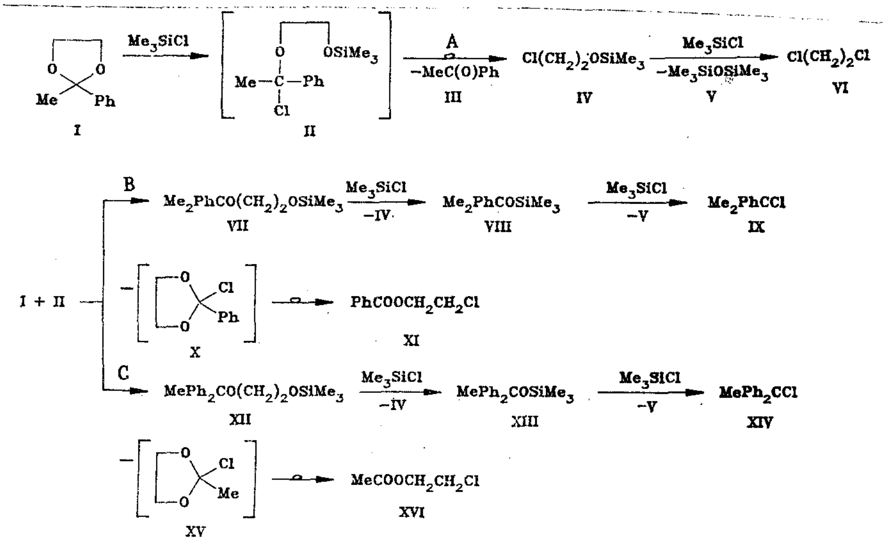
The reaction of 1,3-dioxacyclanes with chlorosilanes is known to involve rupture of the $C_{(2)}$–O bond [1, 2].

We have now found that in the reaction of 2-methyl-2-phenyl-1,3-dioxolane (I) with trimethylchlorosilane cleavage occurs not only at $C_{(2)}$–O, but also at the C–C bond between the heterocyclic moiety of the molecule and the substituent attached thereto.

Presumably, the acyclic chloroether (II) is first formed, intramolecular rearrangement of which (route A) gives the carbonyl compound (III) and 2-(trimethylsilyloxy)-1-chloroethane (IV) and the products of its further chlorosilylation (hexamethyldisiloxane (V) and 1,2-dichloroethane (VI)). Compound (I) reacts with the α-chloroether (II) (routes B and C) to give the unstable cyclic α-chloroethers (X) and (XV), and the ethylene glycol monosilyl ethers (VII) and (XII). Isomerization of the cyclic α-chloroethers (X) and (XV) allows formation of the β-chloroethyl carboxylates (XI) and (XVI) and the ethylene glycol monosilyl ethers (VIII) and (XIII), together with the chlorocompounds (IX) and (XIV).

It is interesting that the C–C bonds between $C_{(2)}$ and the methyl and phenyl substituents are reactive. Furthermore, cleavage of the $C_{(2)}$–phenyl bond is shown by the presence in the reaction products of β-chloroethyl phenylacetate (XVII), which is probably formed by the migration of the phenyl radical in a way similar to that proposed for the reaction of 2-alkyl-2-phenyl-1,3-dioxolanes with iodine monochloride [3].



Compounds (IX), (XI), (XVI), and (XVII) were obtained by heating 0.1 mole of the dioxolane (I) with 0.1 mole of trimethylchlorosilane in the presence of cation exchange resin KU-2 in the H^+-form, in an ampul at 150°C for 6 h.

Compound (XVI): yield 9%, bp 145-147°C (760 mm), n_D^{20} 1.4221, d_4^{20} 1.1360. PMR spectrum (CCl_4): 2.03 (3H, s, CH_3), 4.24 (2H, t, J = 6 Hz, CH_2O), 3.60 ppm (2H, t, J = 6 Hz, CH_2Cl). ^{13}C NMR spectrum: 20.4 (q, J = 120 Hz, CH_3), 170.20 (s, C=O), 64.16 (t, J = 150 Hz, CH_2O), 41.90 ppm (t, J = 150 Hz, CH_2Cl).

Compound (XI): yield 17%, bp 135-138°C (5 mm), n_D^{20} 1.5442, d_4^{20} 1.2581. PMR spectrum (CCl_4): 3.67 (2H, t, J = 6 Hz, CH_2Cl), 4.42 (2H, t, J = 6 Hz, CH_2O), 7.32 ppm (5H, m, C_6H_5).

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^{13}C NMR spectrum: 165.91 (s, C=O), 64.32 (t, J = 149 Hz, CH_2O), 41.91 (t, J = 152 Hz, CH_2Cl), 107.04-102.41 ppm (m, C_6H_5).

Compound (XVII): yield 8%. PMR spectrum (CCl_4): 4.56 (2H, t, J = 6 Hz, CH_2O), 3.77 (2H, t, J = 6 Hz, CH_2Cl), 4.66 (2H, s, CH_2C=O), 7.32 ppm (5H, m, C_6H_5). ^{13}C NMR spectrum: 165.98 (s, C=O), 64.41 (t, J = 149 Hz, CH_2O), 41.28 (t, J = 151 Hz, CH_2Cl), 65.28 (t, J = 149 Hz, CH_2C=O), 107.10-102.44 ppm (m, c_6H_5).

Compound (IX): yield 8%, bp 97-99°C (21 mm).

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REACTION OF TETRANITRODIBENZO-8-CROWN-6 WITH SODIUM ALKOXIDES

É. I. Ivanov, P. B. Terent'ev,
A. A. Polishchuk, K. S. Zakharov,
and B. S. Subbotin

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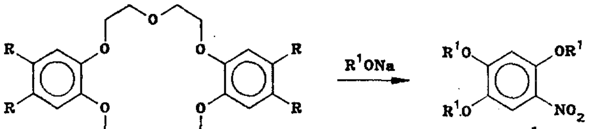
o-Dinitrobenzenes are known to readily undergo nucleophilic substitution. We have found that the reaction between tetranitrobenzo-18-crown-6 (Ib) and an excess of sodium alkoxide in DMSO at room temperature gives, not the expected substitution product, but the 1-nitro-2,4,5-trialkoxybenzene (II). Under these conditions, (Ia) does not undergo cleavage.



IIa,b

I a b

I a R=H; b R=NO_2; II a R^1=CH_3; b R^1=C_2H_5

The reaction products were isolated by chromatography on silica gel. Compound (IIa): yield 56%, mp 112°C. PMR spectrum ($CDCl_3$): 3.87 and 3.93 (9H, s, CH_3), 6.55 and 7.58 ppm (2H, s, =CH). Mass spectrum: m/z 213 (M^+). Compound (IIb): yield 54%, mp 95°C. PMR spectrum ($CDCl_3$): 1.43, 1.47, and 1.49 (9H, t, CH_3), 4.07 and 4.14 (6H, q, CH_2), 6.52 and 7.57 ppm (2H, s, =CH). Mass spectrum: m/z 225 (M^+). The elemental analyses for (IIa, b) were in accordance with the calculated values.

A. V. Bogatskii Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Odessa 270080. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, p. 1573, November, 1985. Original article submitted May 7, 1985.

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