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THE CONVERSION OF 2-DIMETHYLAMINO-1,3-DIOXOLANS INTO ALKENES

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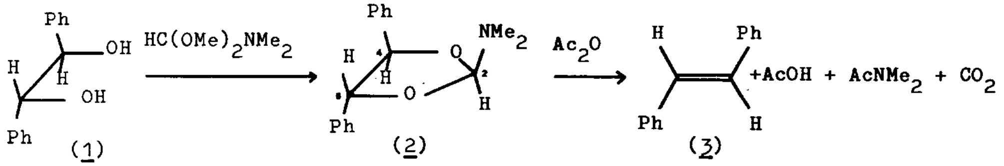
Several methods for the conversion of 1,2-diols into alkenes have been developed in recent years.[1,2] We wish to report a new process that achieves this overall reaction.

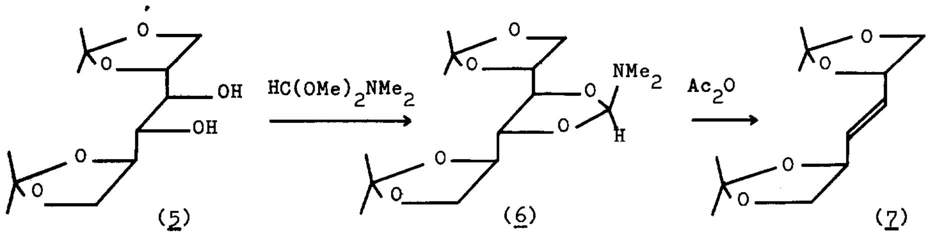
Racemic 1,2-diphenylethane-1,2-diol (1) on heating with N,N-dimethylformamide dimethyl acetal yielded 2-dimethylamino-*trans*-4,5-diphenyl-1,3-dioxolan (2), b.p. 118-120°/0.05 mm., m.p. 40-42°; n.m.r. spectrum (CCl_4): δ 7.18 (m, 10H, aromatic), 5.66 (s, 1H, C_2-H), 4.57 (s, 2H, C_4-H and C_5-H), 2.43 (s, 6H, NMe_2). (When measured in benzene, the C_4-H and C_5-H protons appeared as an AB system, $\Delta\delta$ 0.208, J_{AB} 13.7 Hz). The compound (2) was hydrolysed rapidly by dilute acid to form the starting diol and N,N-dimethylformamide and on treatment with iodomethane in ethanolic solution it formed 2-ethoxy-*trans*-4,5-diphenyl-1,3-dioxolan.[2b] Reaction of (2) with acetic anhydride (1.2 mol. equiv.) at 180° (bath temp.) for 2 hr. or at 165° for 3 hr. yielded *trans*-diphenylethene (3) (80% yield),[3] acetic acid, N,N-dimethylacetamide and carbon dioxide.



meso-1,2-Diphenylethane-1,2-diol on heating with N,N-dimethylformamide dimethyl acetal gave a 1:2 mixture of the *cis* and *trans* isomers of 2-dimethylamino-*cis*-4,5-diphenyl-1,3-dioxolan (4). The mixture of isomers (4) was rapidly hydrolysed by dilute acid to yield the diol and on treatment with iodomethane in ethanolic solution it yielded the known mixture of *cis* and *trans* isomers of 2-ethoxy-*cis*-4,5-diphenyl-1,3-

dioxolan.[2a] Heating (4) at 160° gave *trans*-diphenyloxiran (82% yield) and N,N-dimethylformamide whereas compound (2) was stable under the same conditions. Reaction of (4) with acetic anhydride at 90° for 1.5 hr. gave *cis*-diphenylethene (75% yield) and a trace of *trans*- diphenylethene. The latter isomer was the principal product (76% yield) when the reaction was conducted at 150°.

The process has been shown to be applicable to more complex molecules by reaction of N,N-dimethylformamide dimethyl acetal with 1,2:5,6-di-*O*-isopropylidene-D-mannitol (5) which gave the 2-dimethylamino-1,3-dioxolan (6), m.p. 48° $[\alpha]_D^{20}$ + 6.1 (c 1.1 in chloroform). Treatment of (6) with acetic anhydride (1.4 mol. equiv.) at 130° for 3 hr. gave, after distillation, *trans*-3,4-didehydro-3,4-dideoxy-1,2: 5,6-di-*O*-isopropylidene-D-*threo*-hexitol (7)[1b] in quantitative yield.



(5) (6) (7)

The mechanism of this elimination reaction is unknown but is assumed to be similar to that operating in the acid-catalysed elimination of 2-ethoxy-1,3-dioxolans.[2] The evidence suggests that the reaction is stereospecific but that the resulting alkene may undergo acid-catalysed isomerisation.

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(3) Yields are quoted for purified products.