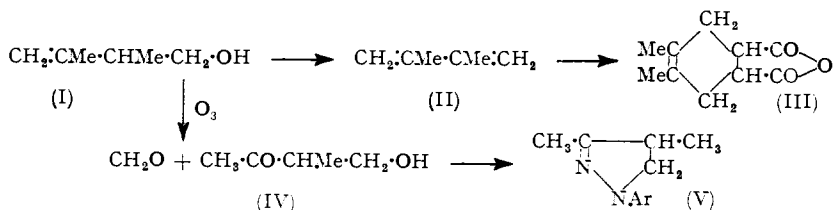


**836.** *Reactions between Trimethylethylene and Formaldehyde catalysed by Stannic Chloride.*

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Contrary to statements in the literature, the simplest product of the stannic chloride-catalysed reaction of trimethylethylene with paraformaldehyde is 2 : 3-dimethylbut-3-en-1-ol (I), the acetate of which is also formed under the conditions of the Prins reaction.

WE have investigated the reaction between trimethylethylene and both paraformaldehyde and trioxan with anhydrous stannic chloride, both with and without solvent, at room temperature, as a possible further example of "aldol"-type olefin addition (Baker, *J.*, 1950, 1302),  $\text{H}-\text{CH}_2\text{:CMe:CHMe} + \text{CH}_2\text{:O} \longrightarrow \text{CH}_2\text{:CMe-CHMe-CH}_2\text{-OH}$  (I). The reaction yields a very complicated mixture of products of varying molecular complexity, from which it is difficult to separate pure compounds, even by repeated fractional distillation through efficient columns. The simplest product, an unsaturated alcohol, b. p. 56°/31 mm., 136°/742 mm., was best obtained by reaction in dry chloroform with a stannic chloride-paraformaldehyde ratio of 0.04 : 1 (mol.). This alcohol reacted readily with phosphorus pentachloride or sodium, and Zerevitinov determination showed the presence of one hydroxyl group in the molecule. It was converted, with some difficulty, into a *p*-nitrobenzoate, m. p. 49.5° (see below). Dehydration with aniline hydrobromide (which was shown not to cause polymerisation of the diene produced) afforded 2 : 3-dimethylbutadiene (II), characterised by its addition product, 4 : 5-dimethyltetrahydrophthalic anhydride (III), m. p. 78.5°, with maleic anhydride. Ozonolysis of the unsaturated alcohol gave



only formaldehyde (with no trace of acetaldehyde or other volatile carbonyl compound) and 2-methyl-3-oxobutan-1-ol (IV), identified by conversion with 2 : 4-dinitrophenylhydrazine into the dihydropyrazole [V; Ar = 2 : 4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], identical with a specimen prepared from an independently synthesised specimen of the keto-alcohol (IV). It is therefore evident that the main constituent of the unsaturated alcohol fraction is 2 : 3-dimethylbut-3-en-1-ol (I). Without evidence, B.P. 545,191/1938 describes the product of this reaction as 3-methylpent-3-en-1-ol.

Similar reaction of trimethylethylene with either trioxan and stannic chloride or with the previously isolated, solid stannic chloride-complex of paraformaldehyde or trioxan occurred much less readily, and yielded formaldehyde-contaminated products. In several

of the more complex, higher-boiling products the presence of the same carbon skeleton C·CMe·CMe·C was established by isolation of (III) or (V) in small yields.

The comparable reaction between the olefin, paraformaldehyde, and 100% acetic acid in the presence of stannic chloride afforded, as the simplest products, a mixture of (I) and its acetate, again contrary to the claim (B.P. 592,838/1940) for formation of 3-methylpent-3-enyl acetate. Under the conditions of the Prins reaction (a mixture of 100% acetic and sulphuric acids) a 22% yield of 2 : 3-dimethylbut-3-enyl acetate was obtained which, on ozonolysis, gave formaldehyde and 2-methyl-3-oxobutyl acetate, characterised as its semicarbazone (Morgan and Holmes, *J.*, 1942, 2667). Hydrolysis of 2 : 3-dimethylbut-3-enyl acetate gave the unsaturated alcohol which afforded a *p*-nitrobenzoate identical with that obtained from (I) (above). The formation of the unsaturated acetate in the Prins reaction with trimethylethylene may be contrasted with the formation of the diacetate of the 1 : 3-diol in the corresponding reaction with propylene (Baker, *J.*, 1944, 296).

#### EXPERIMENTAL

*Preparation of Reference Compounds.—Trimethylethylene.* Prepared by dehydration of *tert.*-amyl alcohol with anhydrous oxalic acid and repeated fractionation, this had b. p. 37.5°/760 mm.,  $n_D^{18}$  1.3880 (Egloff, "Physical Constants of Hydrocarbons," Reinhold Publ. Corp., New York, 1939, Vol. 1, p. 179, gives  $n_D^{20}$  1.3876).

*2-Methyl-3-oxobutan-1-ol.* This, b. p. 90°/12 mm., was prepared by a slight modification of Morgan and Holmes's method (*loc. cit.*). With 2 : 4-dinitrophenylhydrazine in alcoholic 5% hydrochloric acid it gave the dihydropyrazole (V), m. p. 191°, after crystallisation from ethyl acetate (Found : C, 50.1; H, 4.45; N, 21.4. Calc. for  $C_{11}H_{12}O_4N_4$  : C, 50.0; H, 4.55; N, 21.2%). The acetate, b. p. 80—81°/11 mm., gave its semicarbazone, m. p. 138.9°, after crystallisation from benzene (Found : C, 47.8; H, 7.7; N, 20.6. Calc. for  $C_8H_{15}O_3N_3$  : C, 47.8; H, 7.5; N, 20.9%).

*2 : 3-Dimethylbutadiene (Org. Synth., 1942, 22, 39).* This had b. p. 71.5°/753 mm. With maleic anhydride it gave 4 : 5-dimethyltetrahydrophthalic anhydride, m. p. 78.5°, after crystallisation from ligroin (b. p. 60—80°) (Found : C, 66.6; H, 6.5. Calc. for  $C_{10}H_{12}O_3$  : C, 66.67; H, 6.67%).

*Trioxan* (Hamer, Thesis, Leeds, 1948; Frank, U.S.P. 2,304,080/1941). This was dried in ether over sodium and crystallised from ether. Final drying was effected in a sealed vessel in which a tube of phosphoric oxide was suspended. The sample, m. p. 61° (sealed tube), sublimed very readily even at room temperature and was thus introduced into the reaction vessel. Paraformaldehyde was a commercial sample freed from uncombined water by drying over phosphoric oxide. Chloroform (B.P.) was repeatedly washed with water, dried ( $CaCl_2$ ), and fractionated. Final drying was effected by phosphoric oxide in contact with the vapour, and the sample was redistilled immediately before use.

*Trimethylethylene-Formaldehyde Reactions.*—The apparatus and techniques used to exclude moisture were essentially the same as those of Baker and Holdsworth (*J.*, 1945, 724, Figs. 1 and 2), except that the reaction vessel was attached through a suitable adaptor with taps so that it could be isolated and removed for the purpose of mechanical shaking. Many preliminary experiments were carried out to determine the best conditions for obtaining tractable products. In one experiment, dry stannic chloride (0.035 mole) was distilled from phosphoric oxide into a mixture of paraformaldehyde (1 mole), trimethylethylene (1.09 mole) and chloroform (0.63 mole) kept at 0°. The mixture was shaken at room temperature. A clear solution was obtained after 70 hr. It was poured on crushed ice, neutralised with sodium carbonate, and steam-distilled. The distillate was extracted first with the distilled chloroform and then repeatedly with ether. After drying, the solvents were removed through a column and the residue was repeatedly fractionated through an efficient column which was always allowed to attain equilibrium before a small fraction was taken off. Redistillation of the lowest fraction, b. p. 72°/60 mm., 54°/18 mm. (16.7 g.), gave a middle fraction (8 g.), b. p. 56°/31 mm.,  $n_D^{20}$  1.4390 (Found : C, 71.0; H, 12.4. Calc. for  $C_6H_{12}O$  : C, 72.0; H, 12.0%). This was unsaturated to bromine and potassium permanganate, and showed hydroxylic activity towards sodium and phosphorus pentachloride. Zerevitinov determination (Braude and Stern's method, *J.*, 1946, 404) gave active H, 1.12, 1.25 (Calc. for  $C_6H_{12}O$  : 1.0%). Isolation of a *p*-nitrobenzoate was achieved by warming the alcohol with a small quantity of *p*-nitrobenzoyl chloride, without solvent, until the mixture just began to darken. The product was cooled

and stirred with an excess of 20% aqueous sodium hydroxide. The separated ester solidified in ice (scratching). Crystallisation from ligroin (b. p. 40—60°) gave the *p*-nitrobenzoate, m. p. 49.5°, not depressed by a specimen, m. p. 51°, prepared from the acetate (below) (Found: C, 62.2; H, 6.05; N, 5.4.  $C_{13}H_{15}O_4N$  requires C, 62.9; H, 6.05; N, 5.2%). The alcohol (0.66 g.) was ozonised in dry chloroform at 0° for 48 hr. and the ozonide was decomposed by boiling with water and zinc dust under a reflux condenser. No precipitate was obtained in a 2 : 4-dinitrophenylhydrazine trap fitted to the top of the condenser. Ether-extraction of the neutral product afforded a carbonyl compound (iodoform reaction) which, with 2 : 4-dinitrophenylhydrazine in alcoholic hydrochloric acid (Morgan and Holmes, *loc. cit.*), gave the dihydropyrazole (V; 0.83 g.), m. p. and mixed m. p. 191—192° after crystallisation from ethyl acetate. The aqueous liquor from the ozonolysis gave formaldehyde as its dimedone compound (0.4 g.), m. p. and mixed m. p. 189°.

Of the large number of dehydrating agents tried, only aniline hydrobromide and iodine did not cause polymerisation of 2 : 3-dimethylbutadiene, and the former reagent was used to dehydrate the unsaturated alcohol. This was heated with aniline hydrobromide at 120° and the volatile products, escaping from a reflux condenser warmed to 90°, were passed into benzene. After being washed with water, the dried benzene solution was added to a benzene solution of maleic anhydride and was kept at 0° overnight. The benzene was completely removed on a steam-bath with several additions of ligroin (b. p. 60—80°), and the oily residue was extracted with cold ligroin. Concentration of this solution gave 4 : 5-dimethyltetrahydrophthalic anhydride, m. p. and mixed m. p. 78.5°.

*Reaction of Trimethylethylene with Paraformaldehyde-Acetic Acid-Stannic Chloride.*—The reaction vessel, attached to the Baker and Holdsworth apparatus, was fitted with a mercury-sealed stirrer and a reflux condenser closed with a phosphoric oxide drying tube. Dry stannic chloride (0.044 mole) was added dropwise to a stirred mixture of dry paraformaldehyde (0.76 mole) and 100% acetic acid (0.78 mole), the temperature being kept at <10°. When a fine suspension was obtained, dry trimethylethylene (0.77 mole) was added at a rate of 0.5 c.c. per min., the temperature being kept at <10°, at which temperature stirring was continued for a further hour. The temperature was raised to 15° and, finally, to 20° for 3 hr. The mixture was worked up as before. The fraction, b. p. 52.5—53°/12 mm.,  $n_D^{20}$  1.4290, after repeated refractionation, was almost free from hydroxylic activity (initially present due to admixture with the unsaturated alcohol) and consisted mainly of the unsaturated acetate (Found: C, 65.5; H, 10.0.  $C_8H_{14}O_2$  requires C, 67.5; H, 9.85%). Hydrolysis with cold 0.5*N*-sodium hydroxide for 32 hr. (Found: equiv., 135. Calc.: equiv., 142) gave, beside sodium acetate and some formaldehyde, the unsaturated alcohol (I), identified as its *p*-nitrobenzoate, m. p. 51°, not depressed by admixture with the specimen obtained above, and by dehydration to the diene (II), characterised as its maleic anhydride compound, m. p. and mixed m. p. 78.5°.

*Prins Reaction with Trimethylethylene.*—Trimethylethylene (0.66 mole) was added with stirring to a cooled mixture of 100% sulphuric acid (0.36 mole), 100% acetic acid (3.4 moles), and paraformaldehyde (0.83 mole) at such a rate that the temperature was kept at 17° (3 hr.). The mixture was neutralised with crystalline sodium carbonate and extracted with ether. Fractionation of the crude product from the dried ethereal solution gave fractions (i), b. p. 38.5°/44 mm.,  $n_D^{18}$  1.3820 (Found: C, 34.84; H, 7.61%), and (ii), b. p. 51—52.5°/13 mm.,  $n_D^{18}$  1.4299 (20 g.), together with higher-boiling fractions. Fraction (i) appeared to be a loose compound of acetic acid and formaldehyde, possibly of the hydroxymethylene acetate type, and was not further examined. Fraction (ii) is 2 : 3-dimethylbut-3-enyl acetate (Found: C, 67.0; H, 9.9.  $C_8H_{14}O_2$  requires C, 67.5; H, 9.85%). Ozonolysis in dry chloroform gave formaldehyde (dimedone) and 2-methyl-3-oxobutyl acetate, identified as its semicarbazone, m. p. and mixed m. p. 137—138°, after crystallisation from benzene.

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