

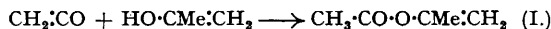
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66. The Behaviour of Keten towards Olefins and Olefinic Peroxides.

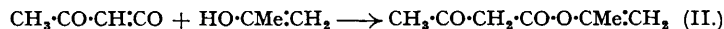
By RALPH F. NAYLOR.

Keten will not react additively with unconjugated olefins such as 1-methylcyclohexene, dihydromyrcene, and rubber. Zinc chloride or sulphuric acid promotes reaction of keten with acetone (carried over from the keten generator), with the formation of a compound $C_7H_{10}O_3$, probably β -propenyl acetoacetate. Keten acetylates olefinic hydroperoxides, but the resultant peracetates are very unstable.

SEVERAL groups of workers have shown that diphenylketen will add to both conjugated and unconjugated olefins, including cyclopentadiene, cyclohexene, cyclohexadiene, 2:3-dimethylbutadiene and $\Delta^{\alpha\gamma}$ -pentadiene, with formation of cyclobutanone derivatives. The only recorded work, however, on the addition of keten to olefins is that of Brooks and Wilbert (*J. Amer. Chem. Soc.*, 1941, **63**, 870), who showed that it reacts under pressure at 100° with an equimolecular quantity of cyclopentadiene to give the bicyclo[0:2:3]heptenone. An attempt has now been made to add keten to representative mono-olefins and unconjugated di- and poly-olefins, in the examples of 1-methylcyclohexene, dihydromyrcene and rubber, at temperatures ranging from 20° to 120° , either under pressure with the olefins alone, or with solutions of the olefins in suitable solvents (chloroform, toluene, and ether). Under these conditions, no action occurred except the formation of diketene; when, however, sulphuric acid or, better, zinc chloride was added as a catalyst, a small quantity of a high-boiling liquid was formed, even when the olefin was omitted from the reaction mixture. This liquid was a compound $C_7H_{10}O_3$, derived apparently by reaction of keten with small quantities of acetone which had been carried over from the keten generator. Keten reacts with acetone in presence of sulphuric acid to give the acetate (I) derived from the enolic form of the ketone (Gwynn and Degering, *J. Amer. Chem. Soc.*, 1942, **64**, 2216) :

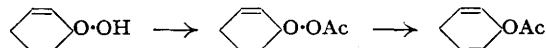


Other products obtained by these authors were diketene and a higher-boiling residue which they did not identify. It was probably the compound $C_7H_{10}O_3$ now isolated. Hurd and Williams (*ibid.*, 1936, **58**, 964) have shown that the dimer of keten can behave as acetylketen and it seems probable that this substance has in the present instance reacted with enolic acetone in the same way as does keten, with the formation of β -propenyl acetoacetate (II) :



Although insufficient ester was separated for complete identification, the above formula is supported by all the available evidence (see experimental part).

To test the possibility that olefinic hydroperoxides might be stabilised by acetylation with keten, the reaction between keten and Δ^2 -cyclohexene hydroperoxide was examined. It proceeded readily at room temperature, but the product was almost entirely Δ^2 -cyclohexenyl acetate. At a lower temperature the acetate was accompanied by some peracetate, which would consequently appear to be the primary product of reaction :



Rubber was not greatly attacked by keten, but when it was treated concurrently with oxygen and keten it broke down oxidatively much more rapidly than when treated with oxygen alone, the percentage of oxygen absorbed after 12 hours being 1.7 and 0.2 respectively. This also would seem to indicate the greater instability of the peracetate groups.

EXPERIMENTAL.

(Microanalyses were carried out by Dr. W. T. Chambers and Miss H. Rhodes.)

Interaction of Keten and Acetone.—Keten (15 g.) as obtained from the generator (Williams and Hurd, *J. Org. Chem.*, 1940, **5**, 122) contained a little acetone; it was passed into dry ether (30 ml.) at -60° . After addition of zinc chloride (0.3 g.) as catalyst, the solution was heated in a sealed tube for 4 hours at 100° . The bulk of the ether and unchanged keten were then removed, benzene (40 ml.) added, and the zinc chloride extracted with water. After removal of solvent, fractionation of the product gave diketene and a liquid (*ca.* 1 g.), b. p. $40^\circ/0.03$ mm., n_D^{18} 1.4632 (Found : C, 59.1; H, 7.2. $C_7H_{10}O_3$ requires C, 59.15; H, 7.0%).

The product dissolved to a slight extent in water, so forming a faintly acid solution which gave a red colour with ferric chloride, and in aqueous alcohol it rapidly reduced alkaline potassium permanganate. The iodine value (Kemp, Bishop, and Lasselle, *Ind. Eng. Chem.*, 1931, **33**, 1445) was 38 after 1 hour and *ca.* 190 after eighteen hours ($C_7H_{10}O_3$ requires I.V. 89.4). Attempted preparation of the oxime gave only an oil, and condensation with dinitrophenylhydrazine in alcoholic sulphuric acid solution gave acetonedinitrophenylhydrazone, the acid conditions of reaction leading to hydrolysis of the ester; this observation corresponds exactly to that of Gwynn and Degering (*loc. cit.*) with the β -propenyl acetate obtained from keten and acetone. The derivative, after chromatography in benzene solution through alumina, crystallised from 95% alcohol in orange plates, m. p. 125° . The dinitrophenylhydrazone prepared from pure acetone and a mixture of the two also melted at 125° (Found : C, 45.5; H, 4.3; N, 23.6. Calc. for $C_9H_{10}O_4N_4$: C, 45.4; H, 4.2; N, 23.5%).

Absorption spectra : In water, a band ($\epsilon = 8500$) at λ 255. In cyclohexane, a band ($\epsilon = 10,000$) at λ 240. The absorption in aqueous solution was unchanged by addition of acid or alkali.

Interaction of Keten and Δ^2 -cyclohexene Hydroperoxide.—To the hydroperoxide (3.7 g.) (Farmer and Sundralingam, *J.*, 1942, 132) in toluene (5 ml.) at -70° was added a solution of keten (2 g.) in toluene (30 ml.) at the same temperature. The mixture was allowed to warm slowly, and the temperature eventually rose to 45° . After removal of the residual keten and toluene, the product (2 g.) was distilled at $27-30^\circ/0.003$ mm. This liquid contained only 0.75%

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of peroxide and consisted almost entirely of an acetic ester, probably Δ^2 -cyclohexenyl acetate (Found : C, 67.8; H, 8.55. $C_8H_{12}O_2$ requires C, 68.6; H, 8.6%).

In an attempt to obtain the undecomposed peracetate the experiment was repeated under carefully controlled conditions. Keten was bubbled through a solution of the peroxide (3 g.) in toluene (40 ml.) at -70° for 30 minutes. The solution was then allowed to warm very slowly to 0° , and the reaction mixture was worked up as before. A peroxide determination at this stage showed that only a third of the original peroxide oxygen remained. The product consisted mainly of the acetate, b. p. $33-34^\circ/0.05$ mm., but a few drops of a liquid, b. p. $55-57^\circ/0.05$ mm., were obtained. This strongly peroxidic material was not pure, but its instability and analysis indicated that it was mainly Δ^2 -cyclohexenyl peracetate (Found : C, 62.4; H, 8.1. $C_8H_{12}O_3$ requires C, 61.5; H, 7.7%).

Keten and Rubber.—(i) Excess of keten was condensed on sol rubber* (1 g.) at -100° in absence of air, and the mixture allowed to warm very slowly to 20° . Swelling of the rubber occurred. Some diketen was formed and was removed under reduced pressure; the product was then washed with acetone and dried in a high vacuum [Found : C, 86.6; H, 11.65; O (diff.), 1.75. Found for the original rubber : C, 87.55; H, 11.8; O (diff.), 0.65%]. Although only 1.1% of oxygen had entered the molecule, the rubber had become insoluble in benzene.

(ii) Oxygen was passed through a 1% solution of sol rubber in methylcyclohexane for 2 hours, and this was followed by the passage for 10 hours of oxygen and keten. Keten, diketen, and the solvent were removed under reduced pressure, and the rubber was dissolved in benzene before precipitation by alcohol [Found : C, 85.9; H, 11.75; O (diff.), 2.35; *M* (viscosity), 31,000. Found for the original rubber : C, 87.55; H, 11.8; O (diff.), 0.65%; *M* (viscosity), 230,000]. Under similar conditions, but with the omission of keten, a product was obtained [Found : C, 87.35; H, 11.75; O (diff.), 0.9. Found for the original rubber : C, 87.4; H, 11.9; O (diff.), 0.7%].

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