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THE BEHAVIOUR OF KETEN TOWARDS OLEFINS AND OLEFINIC PEROXIDES.

By RALPH F. NAYLOR.

REACTIVITY OF ISOPRENIC AND ANALOGOUS HYDROCARBONS TOWARDS THIOCYANIC ACID AND DITHIOCYANOGEN.

By RALPH F. NAYLOR.

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

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Keten will not react additively with unconjugated olefins such as 1-methyl*cyclo*hexene, 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 *cyclo*pentadiene, *cyclo*hexene, *cyclo*hexadiene, 2 : 3-dimethylbutadiene and $\Delta^{\alpha\gamma}$-pentadiene, with formation of *cyclo*butanone 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 *cyclo*pentadiene 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-methyl*cyclo*hexene, 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 diketen; 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) :

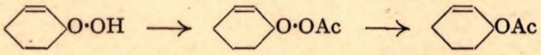
$$CH_2{:}CO + HO{\cdot}CMe{:}CH_2 \longrightarrow CH_3{\cdot}CO{\cdot}O{\cdot}CMe{:}CH_2 \quad \text{(I.)}$$

Other products obtained by these authors were diketen 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) :

$$CH_3{\cdot}CO{\cdot}CH{:}CO + HO{\cdot}CMe{:}CH_2 \longrightarrow CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CMe{:}CH_2 \quad \text{(II.)}$$

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-*cyclo*hexene hydroperoxide was examined. It proceeded readily at room temperature, but the product was almost entirely Δ^2-*cyclo*hexenyl 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 diketen and a liquid (*ca.* 1 g.), b. p. 40°/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 (ε = 8500) at λ 255. In *cyclo*hexane, a band (ε = 10,000) at λ 240. The absorption in aqueous solution was unchanged by addition of acid or alkali.

*Interaction of Keten and Δ^2-*cyclo*Hexene 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°/0·003 mm. This liquid contained only 0·75%

of peroxide and consisted almost entirely of an acetic *ester*, probably Δ^2-*cyclo*hexenyl 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°/0·05 mm., but a few drops of a liquid, b. p. 55—57°/0·05 mm., were obtained. This strongly peroxidic material was not pure, but its instability and analysis indicated that it was mainly Δ^2-*cyclo*hexenyl 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 methyl*cyclo*hexane 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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Reactivity of Isoprenic and Analogous Hydrocarbons towards Thiocyanic Acid and Dithiocyanogen.

By Ralph F. Naylor.

By analogy with hydrogen halides and hydrogen sulphide (Duffey, Snow, and Keyes, *Ind. Eng. Chem.*, 1934, **26**, 91; Ipatieff and Friedman, *J. Amer. Chem. Soc.*, 1939, **61**, 71; Vaughan and Rust, *J. Org. Chem.*, 1942, **7**, 472) it is reasonable to expect thiocyanic acid to react with olefins, and it has been reported by Kharasch, May, and Mayo (*J. Amer. Chem. Soc.*, 1937, **59**, 1580) that it will add to *iso*butylene at room temperature to give a mixture of *tert.*-butyl thiocyanate and *iso*thiocyanate. Under similar conditions in the present work, the only product that was obtained from *cyclo*hexene and thiocyanic acid was a small quantity of an amorphous powder, probably mainly a perthiocyanic acid, formed by elimination of hydrogen cyanide from three molecules of thiocyanic acid. This tendency towards decomposition of the reagent prevented the use of elevated temperatures, and when methyl thiocyanate (a potential source of SCN and Me radicals by thermal decomposition) was heated at 170° with 1-methyl*cyclo*hexene and a little benzoyl peroxide (as catalyst), it underwent but slight reaction, the drop or two of product giving analytical values which suggested that it might be an impure adduct. Attempts to catalyse the addition of thiocyanic acid to rubber included the use of ultra-violet irradiation, and of aluminium chloride or ferric chloride as catalyst. The most successful of these attempts was with ultra-violet light, but even then the product contained only 1·95% of sulphur, which represented 6% addition to the double bonds of rubber.

Although dithiocyanogen is known to add readily to many unsaturated compounds (Kaufmann, *Ber. deut. pharm. Ges.*, 1923, **33**, 139; Kaufmann and Liepe, *Ber.*, 1923, **56**, 2514), the only reference to its reaction with *cyclo*hexene indicated that addition was very slow, and no product was isolated (Oda, Tamura, and Imai, *Sci. Papers Inst. Phys. Chem. Research, Tokyo*, 1938, **34**, 610). It has now been established that 1-methyl*cyclo*hexene reacts very readily with nascent dithiocyanogen in chloroform. With rubber the reaction proceeds readily with pre-prepared dithiocyanogen, as has been observed by several workers, and by varying the quantities used products were prepared in which 7—100% of the unsaturation was destroyed. In every case gelling started after about 1 hour, increased concurrently with addition of dithiocyanogen, and was not complete for several hours. With nascent dithiocyanogen, however, reaction was complete within a few minutes.

Addition of Thiocyanic Acid to Rubber.—A 10% ethereal solution of thiocyanic acid was prepared from sodium thiocyanate by the method of Klason (*J. pr. Chem.*, 1887, **35**, 407). Treatment of a 10% carbon tetrachloride solution of milled crepe with this solution in daylight at 15° gave products containing, after 24 hours 0·07% of sulphur, and after 120 hours 0·245%. A similar experiment in *cyclo*hexane solution at 0° in the dark gave values of 0·32% and 0·25% respectively.

When a mixture of a 10% carbon tetrachloride solution of milled crepe (50 ml.) and 10% ethereal thiocyanic acid (100 ml.) contained in a quartz flask was irradiated with ultra-violet light for 1½ hours, only 0·05% of sulphur entered the rubber. The experiment was repeated, acetone being added as a photosensitiser and the mixture sealed under nitrogen (at 360 mm.) in a Pyrex tube. After 16 hours' irradiation at 25—30° the product contained 1·95% of sulphur.

With ferric chloride and aluminium chloride as catalyst after 3 days in daylight at 15° products were obtained containing 0·6% and 0·85% of sulphur respectively.

Addition of Dithiocyanogen to 1-*Methyl*cyclo*hexene.*—Lead thiocyanate (40 g.) was stirred as a suspension in chloroform (120 ml.) and methyl*cyclo*hexene (10 g.) at 0°, and phenyl iodochloride (29 g.) added in small quantities. The mixture was stirred at 0° for 5 hours and then kept overnight at that temperature. The lead chloride was filtered off, and excess of dithiocyanogen destroyed by shaking the solution with sodium thiosulphate solution (40 g. in 120 ml. of water). From the dried solution, chloroform was removed by distillation at atmospheric pressure, and iodobenzene and unchanged methyl*cyclo*hexene similarly at 13 mm. pressure. 1 : 2-*Dithiocyano*-1-*methyl*cyclo*hexane* distilled at 100—106°/0·1 mm. as a heavy, viscous, yellow oil, which solidified on cooling to 0° (Found : C, 50·8; H, 5·9; N, 12·9; S, 30·4. $C_9H_{12}N_2S_2$ requires C, 50·9; H, 5·7; N, 13·2; S, 30·2%).

Addition of Dithiocyanogen to Rubber.—Dithiocyanogen was prepared by reaction of lead thiocyanate (8 g.) with bromine (3·2 g.) in carbon tetrachloride or disulphide (100 ml.) at 0°. To 25 ml. of this solution were added 100 ml. of a 1% carbon disulphide solution of milled acetone-extracted crepe. After 40 minutes some of the product was separated by precipitation with alcohol (Found : S, 1·6%), and the remainder, which started gelling after about 1½ hours, was separated by washing with alcohol at the end of 20 hours (Found : S, 14·85%). The time of initiation of gelling was not changed by the substitution of carbon tetrachloride as solvent; with 10% rubber solutions in either solvent, gelling commenced after 30 minutes.—The British Rubber Producers' Research Association, 48, Tewin Road, Welwyn Garden City, Herts. [*Received, November 24th*, **1944**.]

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