

NOTES.

Reactivity of Isoprenic and Analogous Hydrocarbons towards Thiocyanic Acid and Dithiocyanogen.

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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 isobutylene at room temperature to give a mixture of *tert*-butyl thiocyanate and *isothiocyanate*. Under similar conditions in the present work, the only product that was obtained from cyclohexene 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-methylcyclohexene 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 cyclohexene 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-methylcyclohexene 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 cyclohexane 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-Methylcyclohexene.—Lead thiocyanate (40 g.) was stirred as a suspension in chloroform (120 ml.) and methylcyclohexene (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 methylcyclohexene similarly at 13 mm. pressure. 1:2-Dithiocyano-1-methylcyclohexane 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. C₉H₁₂N₂S₂ 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.]

The Oxidation of 1:1-Diphenylethylene with Perbenzoic Acid. By G. T. NEWBOLD and F. S. SPRING.

BRADSHAW (*J. Amer. Chem. Soc.*, 1944, **64**, 45) has reported that treatment of 1-phenyl-1-(2'-diphenyl)ethylene with an excess of perbenzoic acid gives a neutral "dioxide," C₂₀H₁₆O₂, m. p. 111—112°, which, when heated with a variety of reagents, suffers dehydration to give 9-phenylphenanthrene-10-ol: the name "dioxide" does not imply any constitutional significance. We record herewith our experience with the oxidation of 1:1-diphenylethylene with perbenzoic acid, a reaction first studied some years ago by one of us.

Oxidation of 1:1-diphenylethylene with an excess of perbenzoic acid in chloroform gave a 13% yield of a crystalline compound, C₂₁H₁₆O₂, m. p. 154—156°, alkaline hydrolysis of which produced a mixture of 1:1-diphenylethylene glycol and benzoic acid. The compound, m. p. 154—156°, is therefore a monobenzoate of 1:1-diphenylethylene glycol and, since it is recovered unchanged after heating with acetic anhydride, it is characterised as 1-hydroxy-2-benzoyloxy-1:1-diphenylethane. The formation of 1:1-diphenylethylene glycol monobenzoate from 1:1-diphenylethylene is analogous to the preparation of ergostadienetriol monobenzoate by the action of perbenzoic acid on ergosterol (Windaus and Lüttringhaus, *Annalen*, 1930, **481**, 127; see also Böeseken and Elsen, *Rec. Trav. chim.*, 1929, **48**, 363).

Treatment of 1:1-diphenylethylene with perbenzoic acid (1 mol.) in chloroform, followed by distillation of the product, gave diphenylacetaldehyde in a minimum yield of 35%. The monobenzoate, m. p. 154—156°, was not obtained in this experiment, nor was it possible to isolate the intermediate 1:1-diphenylethylene oxide, which according to Klages and Kessler (*Ber.*, 1906, **39**, 1753) has m. p. 59° and is isomerised to give diphenylacetaldehyde on distillation.

1-Hydroxy-2-benzoyloxy-1:1-diphenylethane.—1:1-Diphenylethylene (15 g.) was dissolved in a chloroform solution of perbenzoic acid (1000 c.c. containing 28.3 g. of C₆H₅-CO₂H as estimated by iodine titration) and kept at 0—5° for 16 days; estimation of the perbenzoic acid content of the solution and comparison with a blank then showed that 1.3

atoms of oxygen had been absorbed. The solution was washed with aqueous sodium bicarbonate, largely concentrated, diluted with ether, again washed with sodium bicarbonate solution and with water, and dried (sodium sulphate). After concentration to small bulk, the solution deposited fine needles (3.2 g.), and a further crop (0.25 g.) was obtained from the mother-liquor by concentration and cooling. After four crystallisations from methanol this gave the *monobenzoate* as needles, m. p. 154—156°, insoluble in water and very soluble in chloroform and in ether [Found: C, 78.9, 79.0; H, 5.65, 5.8; M, 319 (Rast); active hydrogen, 0.47%. $C_{21}H_{18}O_3$ requires C, 79.2; H, 5.7%; M, 318; 1 active hydrogen, 0.31%]. The monobenzoate was recovered unchanged after refluxing (a) for 16 hours with alcoholic phenylhydrazine solution, (b) for 24 hours with alcoholic hydroxylamine solution, and (c) for 1 hour with acetic anhydride. It gave a light yellow coloration with concentrated sulphuric acid (according to Zerner and Goldhammer, *Monatsh.*, 1929, 53-54, 485), diphenylhydroxyacetaldehyde gives a red colour).

The monobenzoate (0.25 g.) was refluxed with *n*-methanolic potassium hydroxide (10 c.c.) for 1 hour, the solution diluted with water (4 vols.), and the crystalline solid collected. Recrystallisation from hot water gave 1 : 1-diphenylethylene glycol as fine needles, m. p. 120—121° (Paal and Weidenkaff, *Ber.*, 1906, 39, 2063, give m. p. 121°) (Found: C, 78.8; H, 6.6. Calc. for $C_{14}H_{14}O_2$: C, 78.5; H, 6.5%). The aqueous alkaline filtrate was extracted repeatedly with ether, and the aqueous layer concentrated to a small bulk (reduced pressure); acidification with hydrochloric acid gave benzoic acid, m. p. and mixed m. p. 121°.

Diphenylacetaldehyde.—1 : 1-Diphenylethylene (20 g.), dissolved in a chloroform solution of perbenzoic acid (500 c.c. containing 15.52 g. of $C_6H_5CO_3H$), was kept at 0—5° for 7 days; the solution then gave a negative test for perbenzoic acid. The mixture was treated as described in the previous experiment, but no solid product could be isolated. Distillation of the product (mobile oil) gave the following fractions: (1) b. p. 95—110°/0.6 mm., (2) b. p. 115—123°/0.8 mm., (3) 4.1 g., b. p. 123—127°/0.8 mm., residue (5 g.). Fraction (3), when treated with aqueous-methanolic semicarbazide acetate solution, gave (in very good yield) a semicarbazone which separated as felted needles from light petroleum (b. p. 60—80°), m. p. 160—161° (Found: C, 70.7; H, 5.75; N, 16.6. Calc. for $C_{15}H_{15}ON_3$: C, 71.1; H, 6.0; N, 16.6%), not depressed by diphenylacetaldehyde semicarbazone, m. p. 160°. The authentic diphenylacetaldehyde was prepared by the action of dilute sulphuric acid on hydrobenzoin at 170° (Weise, *Annalen*, 1888, 248, 38) and had b. p. 122—126°/1.7 mm.

Fractions (1) and (2) were combined (10.2 g.) and redistilled, giving two further fractions: (a) b. p. 97—102°/0.5 mm. (5.45 g.) and (b) b. p. 117—121°/0.5 mm. (3.45 g.). Fraction (b) consisted of diphenylacetaldehyde, characterised by the formation of its semicarbazone (felted needles from light petroleum, m. p. and mixed m. p. 160°). Fraction (a) readily decolourised bromine water and was probably mainly unchanged 1 : 1-diphenylethylene.—THE UNIVERSITY, MANCHESTER. [Received, November 28th, 1944.]
