

$f_x$  and  $\gamma_c$  can be calculated from these values and the relations

$$f_x = x_0/x \text{ and } \gamma_c = \frac{C_0}{C}$$

**Aqueous HNO<sub>3</sub> Solutions.**—The existence of a maximum in the solubility of rubidium iodate in the nitric acid solutions seems surprising. Great care was taken to make sure that this is not due to an analytical error. It may be that one or both of the acid iodates<sup>2</sup> is part of the solid phase.

(2) Mellor, "Comprehensive Treatise on Inorganic Chemistry," Vol. II, Longmans, London, 1927, pp. 337-338, gives the formulas RbIO<sub>3</sub>·HIO<sub>3</sub> and RbIO<sub>3</sub>·2HIO<sub>3</sub>.

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### Reactions of 1-Methylvinyl Acetate

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Marvel<sup>1</sup> reported the formation of 4-acetoxy-2,5-dimethyl-1,3-dioxane by interaction of vinyl acetate and acetaldehyde, pretreated with metallic sodium. The same cyclic acetal apparently was made by Spaeth<sup>2</sup> a few years later by acetylating the adduct of aldol and acetaldehyde. Marvel noted that vinyl acetate was ineffective in the reaction with other aldehydes such as propionaldehyde, *n*- and isobutyraldehyde. A comparable inertness was found in the present work with 1-methylvinyl acetate and acetaldehyde. Aldol was the only product isolated.

Methylvinyl acetate serves as an acetylating agent toward benzene in the presence of aluminum chloride. Acetophenone was the major product.

#### Experimental

1-Methylvinyl acetate, b.p. 96-98°, was prepared by the reaction of ketene with acetone in the presence of sulfuric acid.<sup>3</sup>

**Non-reaction with Acetaldehyde.**—A total of 25 g. of methylvinyl acetate was shaken into 11 g. of acetaldehyde previously treated with a small amount of sodium.<sup>1</sup> Absolute ethanol (25 ml.) was then introduced. After two days at 25°, the alcohol and ester were distilled off under reduced pressure, and 6.35 g. of aldol, b.p. 80-90° (34 mm.), was obtained. On redistillation, it boiled at 94.5-95° (33 mm.), 80.5° (20 mm.),  $n_D^{20}$  1.4532,  $d_4^{20}$  1.090. Analytical figures (C, 55.4; H, 9.01) confirmed the identity of aldol (calcd.: C, 54.5; H, 9.09).

**Reaction with Benzene.** **Run 1.**—To a stirred mixture of 27 g. of anhydrous aluminum chloride in 120 ml. of benzene was added a total of 20 g. of 1-methylvinyl acetate in 40 ml. of benzene over a period of 15 minutes. Some heat was liberated; hence the reaction was moderated by tap cooling. After 20 minutes at 25°, the contents were refluxed for 2 hours, cooled and poured onto ice. From the benzene layer, after washing and drying, were obtained these fractions at 30 mm.: (1) boiling range 94-104°,  $n_D^{20}$  1.5335, 5.75 g.; (2) 117-137°,  $n_D^{20}$  1.5515, 0.75 g. of green oil. Redistillation of (1) yielded colorless acetophenone, b.p. 97-98° (25 mm.). It formed a semicarbazone which after two recrystallizations from aqueous ethanol melted at 203.5-204° (uncor.) and which remained unchanged on admixture with an authentic sample of acetophenone semicarbazone.

(1) C. S. Marvel, J. Harmon and E. H. Riddle, *J. Org. Chem.*, **4**, 252 (1939).

(2) E. Spaeth, R. Lorenz and E. Freund, *Ber.*, **76**, 57 (1943).

(3) B. H. Gwynn and E. F. Degering, *This Journal*, **64**, 2216 (1942).

The absence of ester was ascertained by the saponification test.

**Run 2.**—When 88 g. (0.66 mole) of anhydrous aluminum chloride in 80 ml. of benzene was added to 20 g. of the acetate in 40 ml. of benzene and the mixture refluxed for 15 hours on the steam-bath, the acetophenone fraction at 87-94° (17 mm.) weighed 17.7 g. A small forerun (0.45 g.) was obtained. Of the viscous residue (5.1 g.), 3.2 g. of amber-orange oil boiled at 134-167° (4 mm.).

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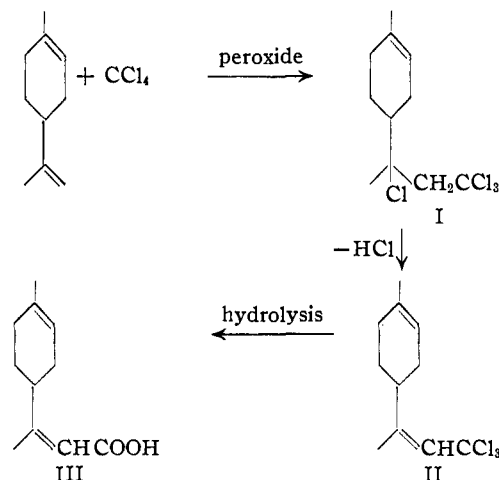
### The Peroxide-catalyzed Addition of Carbon Tetrachloride to *d*-Limonene

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The peroxide-catalyzed addition of polyhalogenated methane to a terminal carbon-carbon double bond has been reported by Kharasch and his co-workers.<sup>1</sup> In the terpene series, it has been shown that the peroxide-catalyzed addition of carbon tetrachloride to  $\beta$ -pinene<sup>2</sup> and nopinene<sup>3</sup> gave good yields of a one-to-one addition product. In this paper we wish to report the applicability of these reactions to *d*-limonene.

We have studied the radical addition reaction of chloroform, bromoform and carbon tetrachloride to *d*-limonene. It was found that *d*-limonene reacts with carbon tetrachloride in the presence of four mole per cent of benzoyl peroxide to give a good yield (60-70%) of a one-to-one addition product, whereas chloroform and bromoform failed to react under the same conditions. However, the addition did not take place readily, even with the relatively large amount of peroxide used. The addition product obtained (II) is optically active  $[\alpha]_D^{25} + 15.8^\circ$ . Bromine titration reveals the presence of two double bonds and according to analysis it contains three chlorine atoms. It is believed that the initial adduct (I) is converted to product (II) by elimination of one molecule of hydrogen chloride from carbon atoms 8 and 9 as



(1) M. S. Kharasch, E. V. Jensen and W. H. Urry, *This Journal*, **69**, 1100 (1947).

(2) D. M. Oldroyd, G. S. Fisher and L. A. Goldblatt, *ibid.*, **72**, 2407 (1950).

(3) G. Dupont, R. Dulou and G. Clement, *Compt. rend.*, **230**, 2027 (1950).