f_x and γ_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_3 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[2] is part of the solid phase.

[2] Mellor, "Comprehensive Treatise on Inorganic Chemistry," Vol. II, Longmans, London, 1927, pp. 337–338, gives the formulas $RbIO_3 \cdot HIO_3$ and $RbIO_3 \cdot 2HIO_3$.

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Reactions of 1-Methylvinyl Acetate

BY CHARLES D. HURD AND LEON L. GERSHBEIN

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Marvel[1] 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[2] 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.[3]

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.[1] 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.), $n^{20}D$ 1.4532, d^{20}_{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°, $n^{20}D$ 1.5335, 5.75 g.; (2) 117–137°, $n^{20}D$ 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. 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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[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 Peroxide-catalyzed Addition of Carbon Tetrachloride to *d*-Limonene

BY SHALOM ISRAELASHVILI AND ERICH DIAMANT

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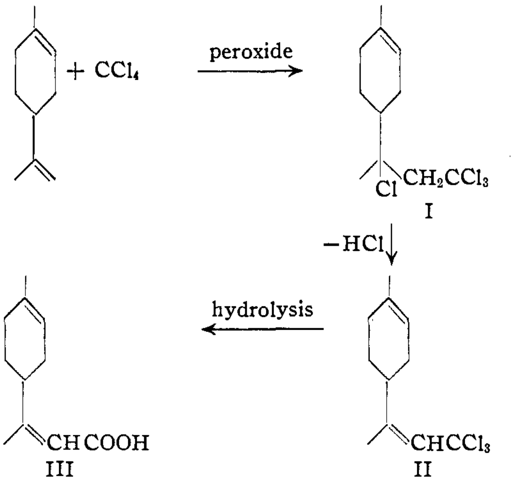
The peroxide-catalyzed addition of polyhalogenated methane to a terminal carbon–carbon double bond has been reported by Kharasch and his co-workers.[1] In the terpene series, it has been shown that the peroxide-catalyzed addition of carbon tetrachloride to *β*-pinene[2] and nopinene[3] gave good yields 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 $[\alpha]^{13}D$ + 15.8°. 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



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[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).

The alternate elimination of hydrogen chloride from carbon atoms 8 and 4 would have given an optically inactive product. The structure of (II) receives additional support from the properties of the carboxylic acid (III) obtained by alkaline hydrolysis of (II). In ultraviolet absorption spectrum (Fig. 1) the carboxylic acid (III) shows a peak at 248–250 mμ, which is indicative of a chromophore involving a conjugation of the carboxylic group with a double bond between carbon atoms.[4]

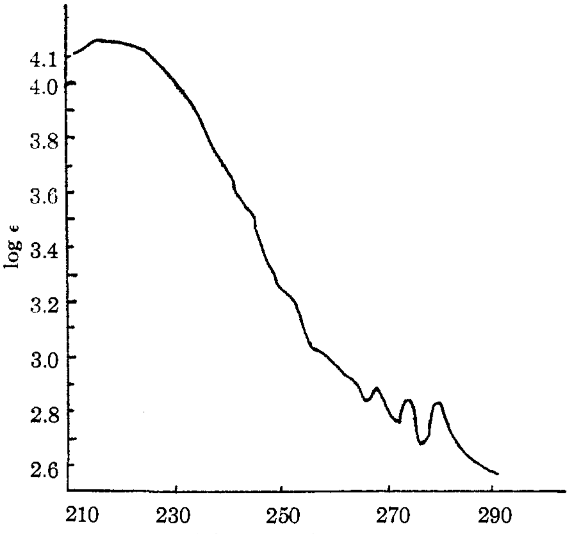

Fig. 1.—Ultraviolet absorption spectrum of 9-carboxy-1,8-(9)-*p*-menthadiene in 95% ethanol.

Experimental[5]

***d*-Limonene.**—*d*-Limonene was obtained by fractional distillation of commercial *d*-limonene. The fraction used had the following constants: b.p. 171–172° (680 mm.), d^{20}_{4} 0.8404, $n^{20}_{\rm D}$ 1.4407, $[\alpha]^{20}_{\rm D}$ +124°.

Addition of Carbon Tetrachloride to *d*-Limonene.—In a three-necked, 500-cc. flask fitted with a reflux condenser, thermometer, dropping funnel and gas inlet-tube, a mixture of *d*-limonene (14 g., 0.1 mole) and C.P. carbon tetrachloride (154 g., 1.0 mole) was refluxed for 24 hours in a continuous stream of dry nitrogen. Benzoyl peroxide (1 g., 0.004 mole) in carbon tetrachloride (20 cc.) was added in four equal portions at intervals of six hours. During refluxing the temperature gradually rose to 88°. The brown reaction product was then washed with 10% sodium carbonate solution and with water, and dried over anhyd. sodium sulfate. From the sodium carbonate washings 0.6 g. of benzoic acid was obtained upon acidification. From the dry reaction mixture, the excess of unreacted carbon tetrachloride was removed by distillation at atmospheric pressure. The residue obtained weighed 19 g., and gave upon fractional distillation at reduced pressure 7 g. of unreacted *d*-limonene, 1.1 g. of intermediate and 8.7 g. of yellow oil (II), b.p. 165–170° (19 mm.), $n^{20}_{\rm D}$ 1.5260, $[\alpha]^{13}_{\rm D}$ +15.8° (*ca.* 10% in ethanol).

The adduct (II) represents a yield of about 30% on the basis of the *d*-limonene used or 60% on the basis of the *d*-limonene consumed.

Anal. of adduct. Calcd. for $C_{11}H_{15}Cl_3$: C, 52.4; H, 5.95; Cl, 41.6. Found: C, 51.9; H, 6.1; Cl, 41.2.

A higher yield of adduct (70% on the basis of *d*-limonene consumed) is obtained when the same mixture is heated in a sealed tube at 120–130° for 12 hours.

Hydrolysis of (II).—The adduct (II) is not readily hydrolyzed by aqueous, methanolic or ethanolic alkali. However, it is hydrolyzed by aqueous alcoholic alkali when heated in a sealed tube at 140°. For the preparation of the carboxylic acid (III), a mixture of 7 g. of (II), 50 cc. of ethanol and 6.5 g. of potassium hydroxide dissolved in 15 cc. of water was heated for 15 hours at 140–150° in a sealed tube. The reaction mixture was diluted with 100 cc. of water, the ethanol removed by distillation and the alkaline residue extracted with ether. The alkaline solution was acidified with dilute sulfuric acid and again extracted with ether. After removal of the ether, 2 g. of crude acid was obtained. Recrystallization from dilute acetic acid yielded 1.5 g. (30%) of colorless long prismatic rods, m.p. 94–95°. The acid absorbs two moles of bromine (titration with 0.1 *N* solution of KBr–$KBrO_3$[6]).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 8.9; neut. equiv., 180. Found: C, 73.2; H, 9.0; neut. equiv., 179.8.

The same yield of the saponification product was obtained, when a mixture of 20 g. of (II) and 10 g. of potassium hydroxide dissolved in 75 cc. of dry ethanol was heated for 24 hours at 150–160° in a sealed tube (see, Gätzki and Stammbach,[7] Grummitt, *et al.*[8]).

Ethyl Ester of (III).—The ethyl ester of (III) was obtained when 1 g. of the acid was dissolved in absolute ethanol, saturated with dry hydrogen chloride, and refluxed for two hours. The ethanol was removed by distillation, and the residue was washed with water, dried and distilled at reduced pressure. A colorless oil of very pleasant odor was obtained; b.p. 125° (25 mm.), $n^{20}_{\rm D}$ 1.4925, yield 58%.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 75.0; H, 9.6; sapn. equiv., 208. Found: C, 74.8; H, 9.5; sapn. equiv., 208.5.

Saponification of the ester yielded a pure specimen of the carboxylic acid, m.p. 95.5°.

Ultraviolet spectrum was obtained with a Beckman quartz spectrophotometer. The spectrum was measured in ethanol at concentration of 0.001 molar.

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[5] All b.ps. and m.ps. are uncorrected.

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(8) O. Grummitt, *et al.*, THIS JOURNAL, **67**, 156 (1946).

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High Temperature Heat Contents of Magnesium Orthotitanate and Magnesium Dititanate

BY R. L. ORR AND J. P. COUGHLIN

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An earlier paper[1] from this Laboratory reported high temperature heat content values for the metatitanates of calcium, iron and magnesium. The present paper contains similar data for magnesium orthotitanate and magnesium dititanate.

Materials.—The magnesium titanates were prepared from reagent-grade magnesium oxide and pure titania (99.8% TiO_2, after ignition). Stoichiometric quantities of the oxides were thoroughly mixed, compressed (15,000 lb./sq. in.) into pellets, and heated for prolonged periods at 1300 to 1500°. At intervals, the products were cooled, ground to −100 mesh, analyzed, adjusted in composition, re-formed into pellets, and reheated, until reaction was complete.

The magnesium orthotitanate analyzed 49.53% TiO_2 and 0.21% SiO_2, as compared with the theoretical 49.77% TiO_2. Tests for free magnesia showed only a negligible amount. The X-ray diffraction pattern gave no evidence of impurities.

The magnesium dititanate analyzed 79.63% TiO_2 and 0.16% SiO_3, as compared with the theoretical 79.85% TiO_2. Tests for free magnesia were negative. The X-ray diffraction pattern agreed with that of Jander and Bunde,[2] and gave no evidence of impurities.

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