

Anal. Calcd. for $C_{17}H_{18}O_4N_3S$: N, 11.76. Found: N, 11.8.

2-(*o*-Sulfanilamidophenyl)-oxazole.—The preceding acetyl derivative was hydrolyzed by refluxing the substance with twenty-five times its weight of 12% hydrochloric acid for forty minutes. By neutralization with ammonium hydroxide the product was precipitated in 80% yield. On recrystallization from 65% alcohol, using decolorizing charcoal, white prisms were obtained; m. p. 172.5–173.5°.

Anal. Calcd. for $C_{15}H_{13}O_3N_3S$: C, 57.13; H, 4.16; N, 13.33. Found: C, 57.2; H, 4.32; N, 13.4.

2-Phenyloxazole.—To a solution of 1.3 g. (0.0081 mole) of II in 20 cc. of 18% hydrochloric acid, cooled to 0–10°, was added with stirring 0.585 g. (0.0085 mole) of sodium nitrite in 5 cc. of water. After standing fifteen minutes at 0–10°, there was added 15 cc. of 50% hypophosphorous acid. The reaction mixture was placed in an icebox for eight hours and then let stand overnight at room temperature. The solution was cooled in ice and made basic with 20% sodium hydroxide solution. An inorganic precipitate was filtered and washed with ether. The filtrate was ex-

tracted with ether and the ether extracts dried over anhydrous potassium carbonate. After removal of the ether, the residue was distilled from an oil-bath. There was obtained 0.25 g. (21%) of a colorless oil; b. p. 225–228° (760 mm.), (oil-bath at 270°). The substance had a pronounced odor, somewhat resembling methyl salicylate.

Anal. Calcd. for C_9H_9ON : C, 74.47; H, 4.86; N, 9.65. Found: C, 74.2; H, 4.78; N, 9.40.

Picrate.—Recrystallized from dilute alcohol as yellow needles; m. p. 115–116°.

Anal. Calcd. for $C_{18}H_{10}O_3N_4$: C, 48.13; H, 2.69; N, 14.97. Found: C, 48.1; H, 2.56; N, 14.8.

Summary

1. 2-Phenyloxazole and certain ortho-substituted derivatives have been prepared.

2. Preliminary pharmacological tests on 2-(*o*-sulfanilamidophenyl)-oxazole indicated antistrep-tococcal activity.

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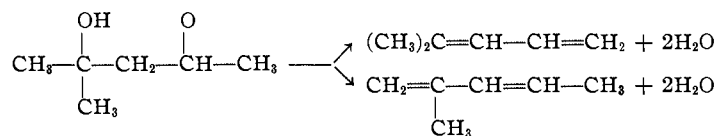
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Preparation and Isolation of 4-Methyl-1,3-pentadiene^{1,2}

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The preparation of pure 4-methyl-1,3-pentadiene has occasioned considerable difficulty.³ Its formation by dehydration of the readily available 2-methyl-2,4-pentanediol is easily accomplished,

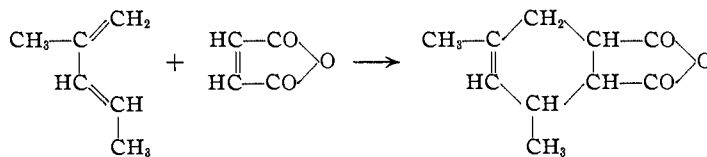


but the principal product is the isomeric 2-methyl-1,3-pentadiene from which it cannot be separated satisfactorily by physical means.^{3c}

Turning to the chemical methods, we have found that reaction with maleic anhydride under controlled conditions effects a clean separation of the two isomers and permits the isolation of the desired diene. The 2-methyl derivative reacts under all conditions to form an addition compound, 3,5-dimethyl- Δ^4 -

tetrahydrophthalic anhydride, and to some extent to form a polymer, but the 4-methyl compound forms only a polymer and no adduct.^{3c} In the presence of antipolymerization catalysts, at low temperatures, and with a suitable choice of solvents, the polymerization reactions may be suppressed almost completely and pure 4-methyl-1,3-pentadiene isolated from the reaction mixture.

Table I summarizes the results of these changes in conditions on the yields of polymer and adduct and on the molecular weight of the polymer. It



will be noted that the temperature exerts a far greater influence on the yield than does the nature of the solvent, except in the case of water, in which hydrolysis of the anhydride changes one of the reactants. The maximum yield of polymer (52.6%) and the maximum yield of adduct (77%) total more than 100%, hence it is clear that under

(1) Presented before the Organic Division at the Atlantic City meeting of the American Chemical Society, September 8–12, 1941.

(2) From the M.S. dissertation of Charles G. Goebel.

(3) Cf. (a) Van Keersbilck, *Bull. soc. chim. Belg.*, **38**, 205 (1929); (b) Krestinski, *Ber.*, **55**, 2760 (1922); (c) Kyriakides, *THIS JOURNAL*, **36**, 994 (1914); (d) Diels and Alder, *Ann.*, **470**, 98 (1929); (e) Farmer, *et al.*, *J. Chem. Soc.*, 511 (1930); 3221 (1931); 1065 (1937); (f) Whitby and Gallay, *Can. J. Research*, **6**, 281 (1932); (g) Dupont and Darmon, *Bull. soc. chim. Memoires*, **6**, 1208 (1939).

A few heteropolymerization experiments were carried out with the original diene mixture using benzoyl peroxide as a catalyst. Polymers having molecular weights of about 9000 were obtained with maleic anhydride and styrene and maleic anhydride and vinyl acetate. Appreciable but undetermined amounts of adduct were present in these polymers. On the other hand, no polymers were obtained with the diene, and diethyl fumarate or diethyl maleate. Furthermore, in the absence of maleic anhydride the diene mixture did not polymerize readily with either styrene or vinyl acetate. Heated alone with benzoyl peroxide a mixture of polymers as described by Whitby and Gallay^{3f} was obtained.

The authors wish to express their appreciation for the generous amounts of the diene mixture supplied for this work by the Commercial Solvents Corporation.

Experimental

The Diene Mixture.—The mixture of dienes employed in this work was prepared in the research laboratories of the Commercial Solvents Company by distilling 2-methyl-2,4-pentanediol with a little hydrobromic acid. The product as we received it was first distilled through a 20-plate Lecky column⁵ to remove any unchanged diol and other impurities present. The fraction of b. p. 75–77° was collected and stored in a brown glass bottle in the dark. It was a water-white liquid of pleasant odor and added bromine instantly.

The Isolation of 4-Methyl-1,3-pentadiene.—The following procedure is representative, except in the use of larger amounts, of the standardized procedure used to study the effects of variations in temperature, solvents, and catalysts (see Table I). To an ice-cold mixture of 0.5 g. of hydroquinone, 392 g. of maleic anhydride, and 1 liter of dioxane was added 328 g. of diene mixture, with frequent shaking and over a two-hour period. After standing in an ice box for three days, the dioxane and unreacted diene were removed by steam distillation. The upper layer of distillate was washed, dried, and fractionated through a 20-plate Lecky column. The fraction boiling at 75.5–77.0° was collected; yield, 76 g. (23% of the rectified diene mixture). On redistillation 90% boiled constantly at 76.3° (760 mm.). From the residue of the steam distillation was recovered 570 g. (72% yield) of 3,5-dimethyl- Δ^4 -tetrahydrophthalic acid, m. p. 154°. The anhydride, m. p. 57°, was obtained by heating above the melting point until dehydrated and recrystallizing from petroleum ether.

The homogeneity of the isolated 4-methyl-1,3-pentadiene was shown as follows: a mixture of 4.9 g. of maleic anhydride, 4.1 g. of diene and 20 g. of toluene was refluxed for one hour, cooled, and poured into petroleum ether. The insoluble, gummy polymer after thorough washing with fresh petroleum ether weighed 8.62 g. (96%). The solvent on evaporation yielded only a small amount of maleic an-

hydride, identified by its melting point (55°) and its mixed melting point with an authentic sample.

Oxidation of 4-Methyl-1,3-pentadiene.—A mixture of 5 g. of diene, 50 g. of potassium permanganate, 600 ml. of water and 1 kg. of ice, shaken frequently until the ice had melted, stood overnight. The solution, decolorized with manganous sulfate and neutralized with sodium carbonate, was distilled and the first 50 ml. of distillate tested with 2,4-dinitrophenylhydrazine. The recrystallized orange precipitate melted at 126° both alone and when mixed with an authentic sample of acetone 2,4-dinitrophenylhydrazone. After filtration and continued distillation nearly to dryness, the residual salts were acidified with dilute sulfuric acid and the distillation resumed. The distillate rapidly reduced aqueous silver nitrate to metallic silver, indicating formic acid. The filtrate from this reaction was evaporated to 10 ml. and cooled. No crystals of silver acetate appeared.

Oxidation of the 4-Methyl-1,3-pentadiene-Maleic Anhydride Heteropolymer.—Four grams of the polymer in 300 ml. of dioxane was oxidized as above with 40 g. of potassium permanganate. Large quantities of manganese dioxide separated, showing that oxidation had occurred. A solution of 1 g. of the recovered polymer in 25 g. of dioxane showed a specific viscosity of 0.850, while that for a similar solution of the original polymer was 0.875. These figures indicate that no appreciable degradation of the polymer chains occurred on oxidation.

Heteropolymerizations.—The polymerization of the diene mixture (1 mole) with maleic anhydride (2 moles) and either styrene (1 mole) or vinyl acetate (1 mole) in the presence of benzoyl peroxide (0.05%) took place readily at ice-bath temperatures with the evolution of much heat. The product in the case of styrene was an amber colored, brittle material, which was soluble in acetone and dioxane, soluble in warm benzene and toluene, and insoluble in carbon tetrachloride, chloroform, alcohol and petroleum ether. During the steam distillation to remove the adduct, which was present in appreciable amounts, the product showed no tendency to soften. The product in the case of vinyl acetate was a white, brittle solid. Steam distillation again showed the presence of an appreciable amount of the adduct. The product just softened in boiling water, and showed similar solubilities to those of the styrene heteropolymer.

Unsuccessful polymerizations which were attempted include the following: (a) diene mixture (1 mole), styrene (1 mole), benzoyl peroxide (0.05%), refluxed two hours; (b) same as (a) with vinyl acetate instead of styrene; (c) purified 4-methyl-1,3-pentadiene (1 mole), diethyl maleate (1 mole), benzoyl peroxide (0.05%), refluxed two hours; (d) same as (c) with diethyl fumarate instead of diethyl maleate.

Polymerization of the diene mixture alone using benzoyl peroxide (0.05%) as catalyst and refluxing for six hours gave a viscous solution with a reddish brown color. After removal of unchanged monomer and cooling, the product was a gray, sticky, rubber-like solid with red streaks in it. According to Whitby and Gallay^{3f} the gray substance is formed by the polymerization of the 2-methyl diene and the red substance by the dimerization of the 4-methyl diene. The red substance was more readily soluble in acetone than the gray.

(5) Lecky and Ewell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 544 (1940).

