

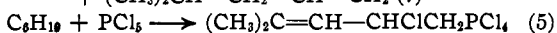
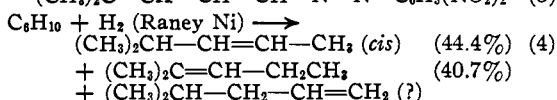
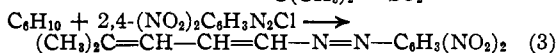
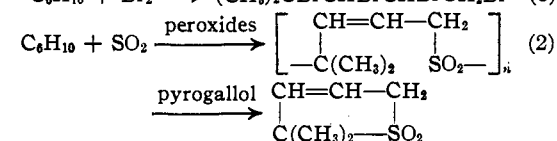
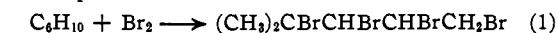
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Reactions of 4-Methyl-1,3-pentadiene^{1,2}

BY G. BRYANT BACHMAN AND ROGER E. HATTON

Numerous attempts have been made to find suitable conditions under which 4-methyl-1,3-pentadiene³ might undergo a typical Diels-Alder addition with activated monoenes such as crotonaldehyde, crotonic acid, benzoquinone and maleic anhydride. Even in the presence of anti-oxidants and at elevated temperatures the desired reactions were not found to occur.

This diene undergoes the following reactions in the expected fashion



It is evident that 4-methyl-1,3-pentadiene is capable of addition at both of its double bonds, and that under certain circumstances it will even undergo 1,4 addition. That it fails to give Diels-Alder adducts and polymerizes like a monoene³ is probably attributable to steric hindrance between the two end methyl groups and the other reactant molecules tried, all of which are larger than the sulfur dioxide molecule.

Experimental

Preparation of 4-Methyl-1,3-pentadiene.—4-Methyl-1,3-pentadiene was isolated by the method of Bachman and Goebel³ and purified by rectification to b. p. 75.5–76.5°.

Determination of the Bromine Number.—Following the procedure of Lewis and Bradstreet,⁴ bromine numbers of 379, 382 (at room temperature) and 381 (at 0°) were found. The calculated value for two double bonds is 390.

Attempted Diene Syntheses.—The following procedures are representative of a number of experiments. To a refluxing solution of 16.3 g. of maleic anhydride, 0.05 g. of hydroquinone, and 45 ml. of dioxane was added 13.7 g. of 4-methyl-1,3-pentadiene over a twenty minute period. After eighteen hours, the volatile materials were removed by steam distillation and the water residue cooled and examined in vain for an adduct.

A mixture of 4.72 g. of benzoquinone, 3.6 g. of 4-methyl-1,3-pentadiene, and 30 ml. of benzene was sealed in a Carius tube and heated to 100–105° for seventy-two hours, and the resulting mass examined for adduct by extraction

with water. None was obtained. Runs were also made at 150–155° and at 195–200°. Crotonic acid and butadiene were also tried in place of the benzoquinone.

Reactions with Sulfur Dioxide.—A sealed tube containing 10.8 g. of 4-methyl-1,3-pentadiene, 20 g. of sulfur dioxide, 20 ml. of ether, and 0.1 g. of pyrogallol was heated for twelve hours at 101–102°. After ether and excess sulfur dioxide had been removed under vacuum, two layers were observed, a yellow upper layer containing no sulfur, and a dark lower layer. The lower layer was cooled and crystallized by seeding, the seed crystals having been prepared by dissolving a small amount of the oil in ether and cooling. After recrystallization from carbon tetrachloride and then ether, a white crystalline cyclic sulfone, m. p. 30.5–31°, was obtained; yield 9.3 g., 49%.

Anal. Calcd. for C₆H₁₀SO₂: S, 21.9; mol. wt., 146. Found: S, 21.8, 21.6; mol. wt., 153.

The cyclic sulfone (0.5 g.) was dissolved in carbon tetrachloride (5 ml.) and bromine (0.05 g.) added. The precipitated product was recrystallized twice from carbon tetrachloride and recovered as light yellow crystals, m. p. 116.5–117.5°, yield 0.85 g., 81%.

Anal. Calcd. for C₆H₁₀SO₂Br₂: C, 23.5; H, 3.3; S, 10.5; Br, 52.3; mol. wt., 306. Found: C, 23.1, 23.7; H, 3.5, 3.6; S, 10.4, 10.6; Br, 52.4, 52.3; mol. wt., 308.

To a solution continuously saturated with sulfur dioxide and containing 0.1 g. of benzoyl peroxide was added 3.6 g. of 4-methyl-1,3-pentadiene. After several days, a white amorphous polymeric sulfone separated, m. p. 95–100° (dec.), yield 1.2 g., 33%.

Anal. Calcd. for C₆H₁₀SO₂: C, 49.3; H, 6.8; S, 21.9. Found: C, 50.8; H, 7.7; S, 18.2.

Diazo Coupling.—Three grams of 2,4-dinitroaniline was heated with 60 cc. of 2:1 hydrochloric acid until dissolved, 60 cc. of 2:1 acetic acid was added, and the mixture was cooled and diazotized. Next, 2.16 g. of 4-methyl-1,3-pentadiene was added with shaking. After recrystallization of the colored ppt. from acetone-water, deep orange crystals of a hydrate were obtained which melted at 139.5–140.5°, yield 2.2 g., 48.5%.

Anal. Calcd. for C₁₂H₁₂N₄O₄·H₂O: C, 49.0; H, 4.8. Found: C, 48.9, 48.7; H, 4.8, 5.0.

After recrystallization from ethyl acetate-petroleum ether, a light orange anhydrous material which decomposed at 86–87° with the evolution of nitrogen was obtained.

Anal. Calcd. for C₁₂H₁₂N₄O₄: C, 52.1; H, 4.3. Found: C, 52.0, 51.9; H, 4.4, 4.5.

Addition of Phosphorus Pentachloride.—To 25 g. of phosphorus pentachloride in 100 ml. of carbon disulfide was added slowly 3.6 g. of 4-methyl-1,3-pentadiene in 50 ml. of carbon disulfide. The white, very hygroscopic crystals which formed immediately with the evolution of heat were removed by filtration using a protecting piece of rubber dam. After recrystallization from carbon disulfide, the product (yield 10.8 g., 88%) melted at 109–109.5° (dec.). It reacted violently with water to liberate hydrogen chloride and to form a slightly soluble yellow oil which resisted recrystallization.

Anal. Calcd. for C₆H₁₀PCl₅: Cl, 60.9. Found: Cl, 60.9, 60.5.

Hydrogenation.—The hydrogenation was carried out in a Parr hydrogenator at 60 lb. and room temperature. 4-Methyl-1,3-pentadiene (18 g., 0.22 mole) was dissolved in 100 ml. of dry dioxane and 1 g. of Raney nickel added. Hydrogen (0.225 mole) was absorbed rapidly. The reaction product was filtered from the catalyst, dried, and fractionated through a Podbielniak-type column (height 140 cm., internal diameter, 8 mm.).

The principal fractions obtained were dissolved in

(1) Read before the Organic Section at the Buffalo meeting of the American Chemical Society, September, 1942.

(2) Based on the M.S. dissertation of Roger E. Hatton, Purdue University, Lafayette, Indiana.

(3) Isolation in pure form: Bachman and Goebel, *THIS JOURNAL*, **64**, 787 (1942).

(4) Lewis and Bradstreet, *Ind. Eng. Chem., Anal. Ed.*, **13**, 387 (1941).

chloroform and the calculated amount of bromine in chloroform added separately to each. The resulting dibromides were then distilled under vacuum. From comparisons with the published constants of Boord and Schmidt⁵ for the olefins and their dibromides it is probable that the hydrogenation products obtained were as follows: Fraction I, b. p. 53.0°, 4-methyl-1-pentene; Fraction II, b. p. 58.0°, *cis*-4-methyl-2-pentene; Fraction III, b. p. 65.0°, 2-methyl-2-pentene.

The per cent. yields on these fractions were 5.9, 44.4, and 40.7, respectively. It is possible that Fraction I was *trans*-4-methyl-2-pentene, b. p. 54.2–55.2,⁵ instead of 4-methyl-1-pentene, b. p. 53.6–53.9.⁵ An insufficient quantity was available for conversion to the dibromide and complete identification.

(5) Boord and Schmidt, *THIS JOURNAL*, **54**, 754, 760 (1932).

Summary

The reactions of 4-methyl-1,3-pentadiene with bromine, sulfur dioxide, a diazonium salt, phosphorus pentachloride, and hydrogen have been investigated and the products characterized. Additions to the 1,2-, 3,4- and 1,4-positions were observed.

Reactions of 4-methyl-1,3-pentadiene with several activated mono-enes under various conditions could not be made to yield cyclic products of the Diels-Alder type. This inertness is attributed to steric hindrance.

LAFAYETTE, IND.

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Utilization of Aliphatic Nitro Compounds. X. The Condensation of Aromatic Diazonium Salts and Hydroxides with Amino-Substituted Secondary Nitroalkanes

BY GERHARD VAN BIEMA¹ WITH ED. F. DEGERING

It has been shown by Feasley and Degering² and Gochenour and Degering³ that arylazo derivatives can be prepared from secondary nitroparaffins, $RCH(NO_2)R'$, as well as from secondary nitroalcohols of the type $RCH(NO_2)(CH_2)_x-OH$. The products obtained by coupling such compounds with various diazonium compounds were brightly colored, crystalline substances, some of which were capable of dyeing fabrics.

the preparation of 1-N-morpholino-2-nitro-2-(4-chlorophenylazo)-propane, as follows:

p-Chloroaniline, 3.18 g. (0.025 mole), was dissolved in 15 ml. of concentrated hydrochloric acid (sp. gr. 1.19) and 20 ml. of water. Sodium nitrite, 1.88 g., in about 30 ml. of water, was then added from a dropping funnel with constant stirring. Stirring was continued for ten more minutes after the addition. A solution of 4.35 g. (0.025 mole) of 1-N-morpholino-2-nitropropane in 10 ml. of concentrated hydrochloric acid (sp. gr. 1.19) and 30 ml. of water

TABLE I

Amine diazotized	Nitro-amine coupled ^a	Appearance of azo-compound	Corrected m. p. of product, °C.	Nitrogen, %			Approximate yield, %
				Calcd.	Found		
Aniline	M	Yellow crystals	127.6	20.15	20.1	20.1	22
β -Naphthylamine	M	Red plates	152.1	17.07	16.4	16.5	25
β -Naphthylamine	B	Red powder	130.8	14.58	14.0	14.6	17
Anthranilic acid	M	Gold plates	172.5	17.40	11.8	12.1 ^d	13
<i>p</i> -Aminobenzoic acid	M ^b	Yellow crystals	198.4	17.40	17.0	17.3	26
<i>p</i> -Chloroaniline ^c	B	Orange needles	109.9	15.18	15.0	15.3	7
<i>p</i> -Chloroaniline ^c	M	Orange crystals	126.8	17.90	17.6	17.6	26
<i>o</i> -Nitroaniline	M	Orange needles	117.8	21.65	21.6	20.9	32
<i>m</i> -Nitroaniline	M	Yellow crystals	129.6	21.65	21.2	21.4	41
<i>p</i> -Nitroaniline	M	Yellow needles	147.9	21.65	26.0	25.9 ^d	46
2,4-Dichloroaniline	M	Orange needles	92.6	16.13	15.5	15.7	48
<i>p</i> -Aminoazobenzene	M	Lt. brown powder	166.8	22.0	22.2	22.4	80

^a M = 1-N-morpholino-2-nitropropane; B = 1-di-*n*-butylamino-2-nitrobutane. ^b = basic coupling. ^c Decomposes on prolonged standing. ^d Constitution not satisfactorily established.

The present investigation was undertaken with the object of preparing from 1-di-*n*-butylamino-2-nitrobutane and 1-N-morpholino-2-nitropropane, derivatives which might be useful as dyes. The diazotization of the two nitroamines, prepared by the method of Cerf de Mauny,⁴ is illustrated by

was similarly added. The solution turned yellow, then orange, and a bright orange solid was formed which was recovered from the solution by filtration. The product was dried over anhydrous potassium carbonate in a vacuum desiccator and recrystallized from 200 ml. of 30% ethanol, yielding 2 g. of bright orange needles melting at 124.5° (cor. 126.8°).

In order to determine whether the yields could be improved by varying the pH of the coupling solution a series of couplings was carried out quantitatively, the pH of the solutions after coupling being measured by means of a pH-meter equipped with a glass electrode. Best results

(1) An abstract of a thesis submitted to the Faculty of Purdue University by Gerhard Van Biema in partial fulfillment of the requirements for the degree of Master of Science, December, 1943.

(2) C. F. Feasley and Ed. F. Degering, *J. Org. Chem.*, **8**, 12ff. (1943).

(3) C. Gochenour, M.S. Thesis, Purdue University, 1943.

(4) H. Cerf de Mauny, *Bull. soc. chim.*, [5] **4**, 1451–1460 (1937).