

II it was possible to estimate the relative rates of the reactions of Equations 5 and 6. On the assumption that each reaction was first order with respect to each reagent and that any subsequent reactions of bromine would be considerably slower, Equation 7 was derived and was integrated to give Equation 8. The rate constants for Equations 5 and 6 are

$$\frac{dx}{dy} = \frac{Ak_5}{xk_6} - 1 \quad (7)$$

$$x + y = (k_5/k_6)A \ln\left(\frac{A}{A - (k_5/k_6)x}\right) \quad (8)$$

represented by k_5 and k_6 , respectively, while x , y , and A are the concentrations of hydrogen bromide, bromine, and ethyl alcohol (assumed to be constant), respectively. Over the entire range of alcohol concentrations, which were used, the reaction of Equation 6 was found to be $(1.3 \pm 0.3)10^4$ times as fast as that of Equation 5 at room temperature (26°).

EXPERIMENTAL

Pure anhydrous N-bromoacetamide. Crude NBA⁶ was dissolved in a minimum amount of warm water (60°), and the solution was cooled in an ice bath. The crystals were dried thoroughly in an anhydrous atmosphere and then dissolved in cold absolute ether. This solution was chilled and evaporated. The crystals which formed were thoroughly dried at room temperature and then at 45° . A yield of about 50% of NBA, m.p. 108° , was obtained from the purification. The melting point checks well with that of Hofmann² and is considerably higher than those observed (usually around 103°) for products obtained by crystallization from chloroform.^{6,10}

Anal. Calcd. for $\text{C}_2\text{H}_4\text{NOBr}$: C, 17.41; H, 2.92; N, 10.15; Br, 57.93. Found for product of m.p. 108° : C, 17.39; H, 2.89; N (Dumas), 10.21; Br, 57.80. Found for product of m.p. $102\text{--}103^\circ$: C, 16.80; H, 3.11; N, 10.93; Br, 57.30.

Iodometric determination of N-bromoacetamide. A carefully weighed sample of 0.2–0.8 g. of NBA was dissolved in about 25 ml. of water and enough 6N sulfuric acid was added to give a final solution of the desired normality. Potassium iodide (about 3 g.) was then added in enough water to make a total volume of 100 ml. The iodine formed was titrated with standard sodium thiosulfate. The results are tabulated in Table I.

Decomposition of N-bromoacetamide in chloroform and ethyl alcohol. Commercial chloroform was washed free of alcohol by several extractions with concentrated sulfuric acid. The chloroform was washed with water, dried over anhydrous sodium sulfate, and distilled as needed. Samples of 0.1–1.0 g. of NBA were dissolved in 100 ml. of the chloroform, chloroform–ethyl alcohol mixtures, or absolute ethyl alcohol. The solutions were sealed into Pyrex tubes with a minimum of air space and illuminated by a fused silica mercury arc. The tip of each tube was then broken beneath the surface of water. The water solution was first treated with an excess of potassium iodide and titrated with standard sodium thiosulfate solution to determine the amount of reducible bromine present. The solution was then boiled for two minutes, treated with an excess of potassium iodate, and again titrated with standard thiosulfate solution to determine the amount of acid present. The acid was also

(10) E. P. Oliveto and C. Gerold, *Org. Syntheses*, **31**, 17 (1951).

determined in many experiments by titration with standard sodium hydroxide solution following the iodometric titration of bromine. The two methods gave comparable results. Representative data are tabulated in Table II.

Qualitative experiments on the decomposition of N-bromoacetamide. A bromine color rapidly developed when a chloroform solution of NBA with or without ethyl alcohol present was illuminated with ultraviolet radiation. The color reached a maximum intensity, as it was followed by a spectrophotometer, and then the color slowly faded as crystals of bisacetamide hydrobromide precipitated. The melting point varied from 127° to 139° and the material may have been contaminated by monoacetamide hydrobromide or by acetamide. Dry hydrogen bromide reacted with acetamide in chloroform to yield bisacetamide hydrobromide of m.p. $140\text{--}141^\circ$ while the value 139.5° has been reported.¹¹ In other experiments a chloroform-insoluble liquid with the color of bromine was observed partway through the decomposition reaction. Eventually this liquid deposited crystals of bisacetamide hydrobromide and gradually disappeared. It is probable that this liquid was a mixture composed mostly of *N*-bromoacetamide and acetamide with bromine dissolved in it. In some experiments evaporation of the chloroform solution led to the isolation of small amounts of acetamide. Diacetylhydrazine, m.p., 140° , might be expected as a product, but methods of isolation, which were successful with an authentic sample,¹² did not yield this material from the decomposition solutions.

Detection of acetaldehyde. A solution of 1.4 g. (0.010 mole) of NBA in 20 g. of chloroform and 5 g. of absolute ethanol was stirred rapidly with 2.5 g. of calcium carbonate in diffuse light. Only a very light bromine color was observed. After thirty minutes the solution was filtered and then shaken with water in the presence of a little copper wire. Addition of excess 2,4-dinitrophenylhydrazine solution to the aqueous layer yielded 0.40 g. (18%) of acetaldehyde 2,4-dinitrophenylhydrazone, m.p. $155\text{--}159^\circ$, which after two crystallizations melted at $165\text{--}167^\circ$ and did not depress the melting point of an authentic sample.

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Diels-Alder Reactions on 1,2-Cyclohexenedicarboxylic Anhydride

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1,2-Cyclohexenedicarboxylic anhydride (Δ^1 -tetrahydrophthalic anhydride) has been reported to undergo the Diels-Alder reaction with butadiene^{1,2} to form the octalin derivative, 1,4,4a,5,6,7,8,8a-octahydro-4a,8a-naphthalenedicarboxylic acid. In the present investigation some new octalin derivatives have been prepared by using other dienes with this anhydride. Six dienes were allowed to react with the dienophile in a sealed reaction tube, and adducts were obtained with isoprene and di-

(1) K. Alder and K. H. Backendorf, *Ber.*, **71B**, 2199 (1938).

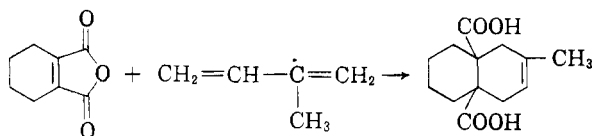
(2) P. Brigl and R. Herrmann, *Ber.*, **71B**, 2280 (1938).

TABLE I
DIENE ADDUCTS OF 1,2-CYCLOHEXENEDICARBOXYLIC ANHYDRIDE

Deriv. of Diene adduct	M.P., °C. ^a	Yield, ^b %	Formula	Analyses			
				Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
Isoprene							
Acid	200-203 ^c	60	C ₁₃ H ₁₈ O ₄	65.5	65.7	7.61	7.66
Anhydride ^d			C ₁₃ H ₁₆ O ₃	70.9	70.6	7.32	7.19
Imide ^e	137		C ₁₃ H ₁₇ O ₂ N	71.2	71.1	7.82	7.82
2,3-Dimethyl Butadiene							
Acid	194 ^c	57	C ₁₄ H ₂₀ O ₄	66.6	66.5	7.99	7.99
Anhydride ^f	54-55		C ₁₄ H ₁₈ O ₃	71.8	71.7	7.74	7.75
Imide ^g	145		C ₁₄ H ₁₉ O ₂ N	72.1	71.8	8.21	8.13

^a All melting points are corrected. They were taken in capillaries unless otherwise indicated. ^b Yields were determined after one recrystallization. ^c This value was determined on the hot stage of a low power microscope. ^d n_D^{25} , 1.5052; b.p. 143° (3 mm.). ^e N, anal.: 6.38 (calcd.), 6.08 (found). ^f n_D^{27} , 1.5060; b.p. 154° (4 mm.). ^g N, anal.: 6.00 (calcd.), 6.14 (found).

methylbutadiene as summarized in Table I. Butadiene gave results comparable with those reported.^{1,2} Only starting material and polymers were obtained with furan, chloroprene, and cyclopentadiene. The adducts were isolated as the octalindicarboxylic acids. The imide derivatives were prepared by way of the anhydrides by treatment of the acids with acetyl chloride followed by concentrated aqueous ammonia solution.



The 2,3-cyclohexenedicarboxylic anhydride also has the double bond conjugated with one of the carboxyl functions and it would be expected to undergo the Diels-Alder reaction. Only starting material and polymers were isolated from reactions of this compound with isoprene, however. This Δ^2 isomer has been reported³ to undergo thermal isomerization to the Δ^1 isomer, but none of the latter compound nor any of its octalin addition product could be isolated from the reaction mixture.

EXPERIMENTAL

1,2-Cyclohexenedicarboxylic anhydride. The isomer was prepared by heating 4,5-cyclohexenedicarboxylic anhydride (Δ^4) with 1% phosphorus pentoxide at 200° for 48 hr.⁴

2,3-Cyclohexenedicarboxylic anhydride. The Δ^4 isomer was partially isomerized with phosphorus pentoxide to yield a mixture of the Δ^3 , Δ^2 , and Δ^1 isomers.⁴ This mixture was

converted to the Δ^2 isomer by heating with sodium hydroxide solution.⁵⁻⁷

Other reagents. The dienes were commercially available. The Δ^4 -tetrahydrophthalic anhydride was kindly supplied by the National Aniline Division of the Allied Chemical and Dye Corp.

Diels-Alder reactions. The general procedure which was originally reported¹ was followed. In a typical run, a mixture of 6 ml. of benzene, 1 g. of hydroquinone, 7.0 ml. (4.8 g., 0.071 mole) of isoprene, and 2.0 g. (0.012 mole) of the anhydride was heated for 12 hr. at 175° in a 90-ml. Monel metal Carius tube supplied by High Pressure Equipment Co. The dimerized olefin was distilled at reduced pressure from the yellow solution, and the residue was heated for 30 min. with excess 10% potassium hydroxide. The solution was treated with charcoal, filtered, and extracted several times with ether. The basic solution was acidified and the product was collected by filtration. The 2-methyl-1,4,4a,5,6,7,8,8a-octahydro-4a,8a-naphthalenedicarboxylic acid was recrystallized from boiling acetonitrile. The product could also be recrystallized from an ethyl alcohol-water mixture. The adducts from butadiene and 2,3-dimethylbutadiene were prepared in a similar fashion. All of the acids were white crystalline solids.

Anhydrides. The acids were heated with excess acetyl chloride. The isoprene adduct and the 2,3-dimethylbutadiene adduct were distilled as colorless oils. The butadiene adduct was a white crystalline solid obtained from petroleum ether.

Imides. Excess 28% aqueous ammonia was added to the anhydride and the water was boiled off. The residue was heated in an oven at 100° for 15 min. The resulting product was recrystallized from an ethyl alcohol-water mixture to yield a white crystalline imide in each case.

Gas chromatography. The anhydrides from isoprene and 2,3-dimethylbutadiene were analyzed on a Perkin-Elmer Vapor Fractometer. At 215° with helium as a carrier gas at 25 lb./in.² gage and 0.68 ml./sec. and with a 2 m. column (4 mm. i.d.) filled with silicone oil on Celite the isoprene adduct gave a well defined peak at 15.0 min. and the 2,3-dimethylbutadiene adduct gave one at 19.0 min. In neither case was any contaminant detected. The Δ^1 -tetrahydrophthalic anhydride gave a peak at 21.0 min. under the same conditions at 148°.

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