

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Reaction of Aliphatic Diazo Compounds with Acids¹BY DAVID Y. CURTIN² AND SAMUEL M. GERBER

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The reaction of 1-diazo-2-butene or 3-diazo-1-butene with 3,5-dinitrobenzoic acid in ether has been shown to lead to unrearranged ester in each case. On the other hand, either diazo compound reacts with aqueous perchloric acid to yield a mixture of crotyl alcohol and methylvinylcarbinol. Diazoneopentane reacts with 3,5-dinitrobenzoic acid in ether to give trimethylethylene as the principal product together with small amounts of rearranged and unrearranged benzoates. Diazoneopentane, when treated with aqueous sulfuric acid, gave principally *t*-amyl alcohol together with trimethylethylene. The same products were obtained from neopentylamine and nitrous acid.

It has been generally accepted that a diazonium ion is an intermediate in both the reaction of primary amines with nitrous acid^{3,4} and in the reaction of aliphatic diazo compounds with acids.⁵⁻⁷

ime.⁸⁻¹⁰ However, the reaction with benzoic acid in ether of the aliphatic diazo compounds corresponding to the above amines leads only to the rearranged esters.^{11,12} This is inconsistent with the concept of a common intermediate in both reactions and has led us to a study of the reaction of aliphatic diazo compounds with acids in hydroxylic and non-hydroxylic media.

We have prepared the diazo compounds, 1-diazo-2-butene (I) and 3-diazo-1-butene (II) from the corresponding *N*-nitrosourethans. The reaction of II in absolute ether with 3,5-dinitrobenzoic acid led to the corresponding ester without rearrangement. Adamson and Kenner¹¹ had previously reported that the reaction of 1-diazo-2-butene with 3,5-dinitrobenzoic acid in ether gave a crotyl 3,5-dinitrobenzoate, m.p. 50-51°. Repetition of this work, however, gave a 3,5-dinitrobenzoate, m.p. 70.5-71.5°. Hatch and Nesbitt¹³ have reported that *trans*-crotyl 3,5-dinitrobenzoate melts at 70.5° and the *cis*-isomer at 51°. Although Adamson and Kenner¹¹ do not report the preparation of their starting crotylamine, one possible explanation for their results may be that they were working with the *cis*-isomers.

The reaction of I with either 1 or 0.05 *M* aqueous perchloric acid led to a mixture of crotyl alcohol and methylvinylcarbinol. Similar results were obtained from the reaction of II with the same reagents. The products obtained were identified by boiling point, refractive index and comparison of their infrared spectra with the infrared spectra of crotyl alcohol (Fig. 1) and methylvinylcarbinol (Fig. 2).

Fractions from the reaction of both I and II gave infrared curves which are in good agreement with the curve for pure methylvinylcarbinol (Fig. 2). Crotyl alcohol may be seen to be present in fractions from both I and II by comparison of the curves with that of crotyl alcohol (Fig. 1). However, the presence of at least one substance other than crotyl alcohol is indicated by the infrared spectra of the crotyl alcohol fractions. The presence of a carbonyl-containing substance was suggested by absorption in the infrared at 1700 cm.⁻¹. Attempts to find chemical evidence for a carbonyl-containing material in the fraction of which the spectrum is given in Fig. 1 were unsuccessful. In separate

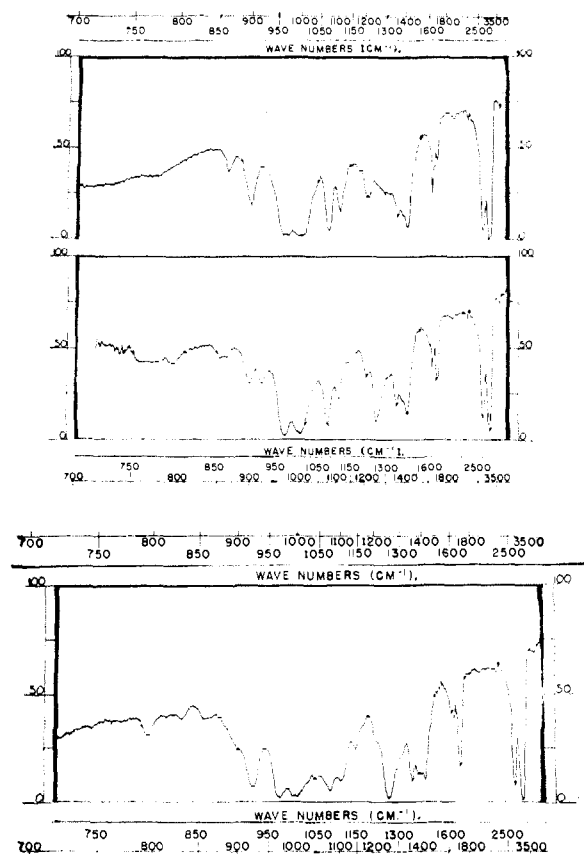


Fig. 1.—Upper curve, *trans*-crotyl alcohol; middle curve, crotyl alcohol fraction from 1-diazo-2-butene; lower curve, crotyl alcohol fraction from 3-diazo-1-butene.

A mixture of rearranged and unrearranged products results from the action of nitrous acid on the primary aliphatic amines from *n*-propyl- to *n*-octylam-

(1) Abstracted from the Ph.D. thesis submitted to Columbia University by Samuel M. Gerber.

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(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 295.

(4) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford Univ. Press, New York, N. Y., 1949, p. 181.

(5) Reference 4, p. 288.

(6) B. Eistert, in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 518.

(7) E. D. Hughes, C. K. Ingold and J. H. Ridd, *Nature*, **166**, 642 (1950).

(8) F. C. Whitmore and R. S. Thorpe, *THIS JOURNAL*, **63**, 1118 (1941).

(9) F. C. Whitmore and D. P. Langlois, *ibid.*, **54**, 3441 (1932).

(10) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 838 (1934).

(11) D. W. Adamson and J. Kenner, *ibid.*, 286 (1935).

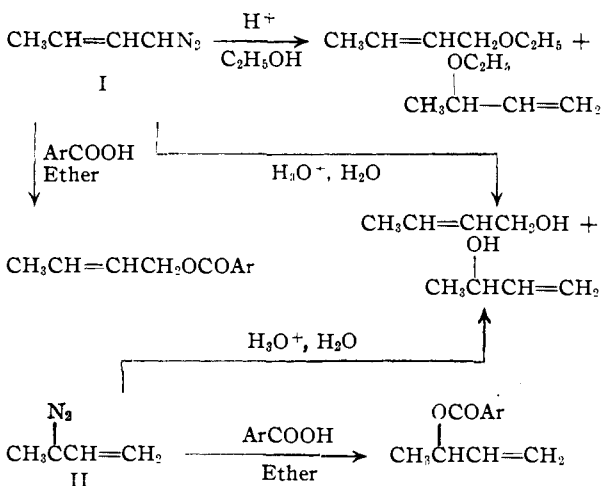
(12) A. F. McKay, W. L. Ott, G. W. Taylor, M. N. Buchanan and J. F. Crooker, *Can. J. Research*, **B28**, 683 (1950).

(13) L. F. Hatch and S. S. Nesbitt, *THIS JOURNAL*, **72**, 727 (1950).

experiments, crotyl alcohol and methylvinylcarbinol were shown not to be interconverted under conditions of the reaction and isolation.

No conclusions as to the precise quantity of crotyl alcohol present in the fractions have been drawn. However, in view of the evidence for the relative purity of the methylvinylcarbinol fractions, the similarity in the proportions of methylvinylcarbinol from either I or II is of interest.

The reaction of I with 0.05 *M* ethanolic sulfuric acid was also investigated. Again a mixture of allylic isomers was obtained. The mixture was shown to consist of about 25% methylvinylcarbinyl ethyl ether and 75% crotyl ethyl ether. The stability of crotyl ether to the reaction conditions and isolation procedure was demonstrated.



The reaction of I and II with acids was complicated by what seems to be an uncatalyzed ring closure to form a pyrazole. Adamson and Kenner¹¹ and Hurd and Lui¹⁴ have reported the isolation of pyrazole from an ethereal solution of 1-diazo-2-propene. 3-(5)-Methylpyrazole was isolated from an ethereal solution of I which was allowed to stand for 16 hours. A similar product or derivative thereof could not be isolated from II, although the red color of an ethereal solution of II disappeared on standing.

The reaction of I and II with 3,5-dinitrobenzoic acid in absolute ether to give unrearranged products may be explained by either the one-step or the ion-pair mechanism suggested by Roberts, Watanabe and McMahon.¹⁵ As the work of these authors suggested, such processes would not be favored in the reaction of I or II with either aqueous perchloric acid or ethanolic sulfuric acid. This idea is confirmed by the formation of mixtures of products from either I or II under these conditions.

Since the beginning of this investigation, Roberts and Mazur¹⁶ have found that the reaction of crotylamine or methylvinylcarbinylamine with nitrous acid gives similar mixtures of crotyl alcohol and methylvinylcarbinol. The results obtained in the reaction of I and II with aqueous perchloric acid suggest that the same type of intermediate RR'

CHN₂⁺, is involved in these reactions. A similar intermediate may be postulated for the reaction of I with ethanolic sulfuric acid.

Hellerman and Garner¹⁷ reported that the reaction of 2-diazo-1,1,1-triphenylethane with benzoic acid in ether gave 1,1,2-triphenylethyl benzoate and

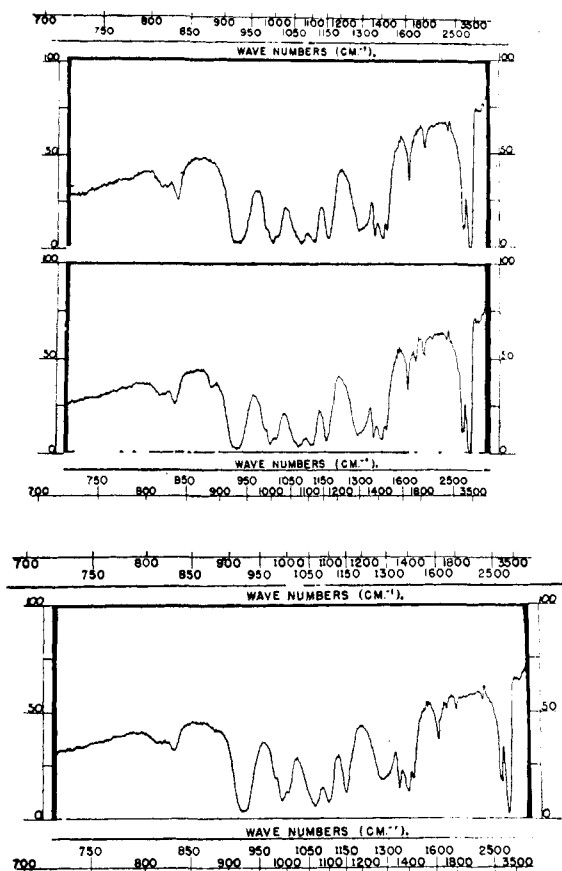


Fig. 2.—Upper curve, methylvinylcarbinol; middle curve, methylvinylcarbinol fraction from 1-diazo-2-butene; bottom curve, methylvinylcarbinol fraction from 3-diazo-1-butene.

triphenylethylene. The reaction of the corresponding amine with nitrous acid gave only triphenylethylene.¹⁸ It was hoped that, by using a diazo compound with less tendency toward rearrangement, it might be possible to find a difference in the amount of rearrangement in non-hydroxylic solvents as compared with hydroxylic solvents.

For this reason diazoneopentane (III) was prepared. The principal product obtained in the reaction of III with 3,5-dinitrobenzoic acid in absolute ether was trimethylethylene (41%). Amyl 3,5-dinitrobenzoate (1.2%) and neopentyl 3,5-dinitrobenzoate (0.28%) were separated from the ester mixture also formed in 2.2% yield. (Yields are based on nitroso compound used in the syntheses of III.) Neopentyl 3,5-dinitrobenzoate was shown to be stable to the reaction conditions and to the fractional crystallization process. The olefin was identified by conversion to 2,3-dibromo-3-methylbu-

(14) C. D. Hurd and S. C. Liu, *THIS JOURNAL*, **57**, 2656 (1935).

(15) J. D. Roberts, W. Watanabe and R. E. McMahon, *ibid.*, **73**, 2521 (1951).

(16) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

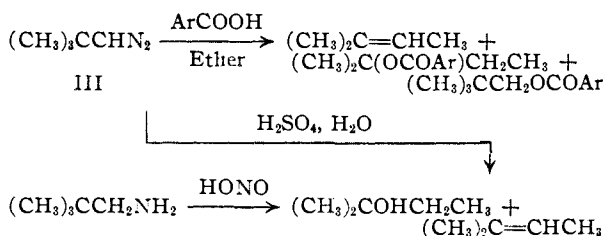
(17) L. E. Hellerman and R. L. Garner, *ibid.*, **57**, 139 (1935).

(18) L. E. Hellerman, M. L. Cohn and R. F. Hoen, *ibid.*, **50**, 1716 (1928).

tane. When ligroin was used as the solvent, 2.5% mixed esters and 34% olefin were obtained.

The reaction of III with 0.05 *M* sulfuric acid in water was found to give *t*-amyl alcohol and trimethylethylene, in 32 and 14% yields, respectively, based on nitroso compound. Neopentyl alcohol was not found. The *t*-amyl alcohol was characterized by conversion to the 3,5-dinitrobenzoate. The stability of neopentyl alcohol to the reaction conditions has been demonstrated by Whitmore and Rothrock.¹⁹

t-Amyl alcohol, in 30% yield, has been the sole product reported in the reaction of neopentylamine with nitrous acid.^{20,21} The reaction of neopentylamine with nitrous acid was repeated and the only products isolable were *t*-amyl alcohol (79.2%) and trimethylethylene (0.94%). The hydration of trimethylethylene to *t*-amyl alcohol which may occur to an appreciable extent under the reaction conditions was not investigated. The identity of the products obtained here, with those obtained in the reaction of III with aqueous acid, is consistent with the existence of a common intermediate, $(\text{CH}_3)_3\text{CCH}_2\text{N}_2^+$ in the two reactions.



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Experimental²²

Reduction of Crotonaldoxime to Crotylamine.—The procedure for the reduction was essentially that of Nystrom and Brown.²³

From 140 g. (1.9 moles) of crotonaldoxime²⁴ was obtained a 50% yield of crotylamine, b.p. 82–85°, n_{D}^{20} 1.4087. Redistillation gave b.p. 83.5–84.5° (761 mm.), n_{D}^{20} 1.4113°. The derivatives reported below were prepared from this material.

The chloroplatinate was prepared as yellow cubes, recrystallized from water, m.p. 198–200° (dec.) (lit. m.p. 203–204°).²⁵

The picrate was formed in ethanol, recrystallized from 95% ethanol, m.p. 156.5–157.5°.

Anal. Calcd. for $\text{C}_4\text{H}_9\text{N}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$: C, 40.07; H, 4.02; N, 18.66. Found: C, 40.19; H, 4.04; N, 18.91.

The phenylthiourea was prepared and recrystallized from ethanol, m.p. 106–107°. Galand²⁶ reported m.p. 106° with softening at 103°, but no analysis.

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{S}$: C, 64.03; H, 6.84. Found: C, 64.62; H, 6.94.

(19) F. C. Whitmore and H. S. Rothrock, *THIS JOURNAL*, **64**, 3431 (1932).

(20) L. Tissier, *Ann. chim. phys.*, [6] **29**, 335 (1893).

(21) M. Freund and F. Lenze, *Ber.*, **23**, 2865 (1890); **24**, 2150 (1891).

(22) Elementary analyses by Clark Microanalytical Laboratory, Urbana, Illinois, Schwarzkopf Microanalytical Laboratory, Elmhurst, N. Y., and Elek Microanalytical Laboratory, Los Angeles, Calif. All melting points are corrected.

(23) R. F. Nystrom and W. G. Brown, *THIS JOURNAL*, **69**, 1197 (1947).

(24) T. Schindler, *Monatsh.*, **12**, 410 (1891).

(25) F. Galand, *Bull. soc. chim. Belg.*, **39**, 529 (1930).

Butylamine chloroplatinate was prepared for purpose of comparison. Attempts at recrystallization caused decomposition. It was purified instead by washing successively with water, 95% ethanol and ether, m.p. 226° (dec.).

Anal. Calcd. for $(\text{C}_4\text{H}_9\text{NH}_2\cdot\text{HCl})_2\text{PtCl}_4$: C, 17.27; H, 4.35. Found: C, 17.46; H, 4.35.

A mixed melting point with crotylamine chloroplatinate gave m.p. 195–196° (dec.).

Crotylamine from *N*-Crotylphthalimide.—Crotylamine, b.p. 84–85° (mostly 84.2°), n_{D}^{20} 1.4290, was best prepared (in 76.2% yield) according to Roberts and Mazur.¹⁶

Methylvinylcarbinyl Chloride from Crotyl Alcohol.—It was found that when the mixture of primary and secondary chloride obtained from the reaction of thionyl chloride with crotyl alcohol was distilled slowly (high reflux ratio) in the presence of a few crystals of anhydrous ferric chloride it was possible to isomerize essentially all of the crotyl chloride to the lower boiling methylvinylcarbinyl chloride. This procedure gave a 73% yield of methylvinylcarbinyl chloride, b.p. 63.8–64°, n_{D}^{20} 1.4125. When the thionyl chloride reaction was carried out as above but the product was distilled directly, a 53% yield of a mixture consisting of secondary chloride (75%) and primary chloride (25%) was obtained.

Methylvinylcarbinylamine from *N*-(Methylvinylcarbinyl) Phthalimide.—Methylvinylcarbinylamine, b.p. (762 mm.) 61.3–61.5°, n_{D}^{20} 1.4110 (lit. b.p.¹⁷ 63–64°, n_{D}^{20} 1.4098) was best prepared (in 72% yield) according to Roberts and Mazur.¹⁶

***N*-Crotylurethan.**—The method of preparation was identical with the procedure given in "Organic Syntheses"²⁶ for *N*-methylurethan except that 1.25 moles each of ethyl chloroformate and sodium hydroxide to one mole of amine was used. A 96% yield of product, b.p. (8 mm.) 94°, n_{D}^{20} 1.4471, was obtained.

Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{NO}_2$: C, 58.7; H, 9.2; N, 9.8. Found: C, 59.0; H, 9.2; N, 9.5.

***N*-Methylvinylcarbinylurethan**, b.p. (8 mm.) 80°, n_{D}^{20} 1.4403, was prepared by the procedure above in 93% yield.

Anal. Calcd. for $\text{C}_7\text{H}_{13}\text{NO}_2$: C, 58.7; H, 9.2; N, 9.8. Found: C, 59.0; H, 9.0; N, 9.8.

***N*-Nitroso-*N*-crotylurethan**, b.p. (0.6 mm.) 57°, b.p. (0.2 mm.) 44°, n_{D}^{20} 1.4543, was prepared by a slight modification of the procedure described in reference 27. It was found that if the reaction mixture was allowed to stand for 12 hours after the nitrosation, the yield was improved (75%). The use of potassium carbonate as a neutralizing agent and desiccant as suggested, caused decomposition of the nitroso compound. For this reason sodium bicarbonate was used to neutralize the reaction mixture. Portionwise distillation of the product is advised since, in one case, an explosion occurred during distillation.

Anal. Calcd. for $\text{C}_7\text{H}_{12}\text{N}_2\text{O}_3$: C, 48.9; H, 7.0; N, 16.3. Found: C, 49.1, 48.1, 49.5; H, 6.5, 6.5, 7.0; N, 16.0, 15.6.

***N*-Nitroso-*N*-methylvinylcarbinylurethan**, b.p. (0.3 mm.) 38–39°, n_{D}^{20} 1.4466, was prepared by the procedure above.

Anal. Calcd. for $\text{C}_7\text{H}_{12}\text{N}_2\text{O}_3$: C, 48.9; H, 7.0; N, 16.3. Found: C, 49.4; H, 7.4; N, 15.7.

Reaction of Diazobutenes (I and II) with 3,5-Dinitrobenzoic Acid.—Each of the *N*-nitrosourethans was converted to the corresponding diazo compound by a procedure previously described²⁸ for diazomethane. However, the reaction and subsequent distillation were carried out under vacuum at 40 mm. pressure. The diazo compound was collected in two traps, each containing 100 cc. of ether cooled by a Dry Ice-acetone mixture. During the reaction the system was swept with a slow stream of dry nitrogen. In a trial run a yield of 32% (0.9 g.) of *n*-butyl 3,5-dinitrobenzoate could be obtained from *N*-nitroso-*N*-butylurethan. (Titration with benzoic acid²⁹ showed 53 ± 6%.)

An ether solution of diazo compound (23% yield by benzoic acid titration) prepared from *N*-nitroso-*N*-crotylure-

(26) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc. New York, N. Y., 1943, p. 278.

(27) Ref. 26, p. 464.

(28) B. Eistert, in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 562.

(29) Reference 26, p. 165.

TABLE I
 REACTION OF I AND II WITH PERCHLORIC ACID

Diazo compound	Reaction mixture	Total material isolated (g.)	% Yield based on nitroso compound	Crotyl alcohol		Methylvinylcarbinol		Methylvinylcarbinol % of total
				B.p., °C.	n_D^{25}	B.p., °C.	n_D^{25}	
I	1 M HClO ₄	1.51	7.7	^a		96-98	1.398	50
I	0.05 M HClO ₄	1.93	9.0	119-123	1.424	97-100	1.409	50
II	1 M HClO ₄	1.64	10.6	^b	1.417	98-99	1.405	70
II	0.05 M HClO ₄	1.63	10.8	116-122	1.419	96-98	1.408	50

^a *trans*-Crotyl 3,5-dinitrobenzoate was obtained from this fraction. ^b In this experiment a considerable amount of a substance, b.p. 142-145°, n_D^{25} 1.4300, was obtained which was apparently dicrotyl ether (lit.³⁰ b.p. 143-145°, n_D^{25} 1.4275).

than (34 g., 0.20 mole) was treated with 41.4 g. (0.20 mole) of 3,5-dinitrobenzoic acid in 1.5 l. of ether. After removal of the ether 6.1 g. of amorphous oily solid was obtained which after recrystallization gave a 21% yield (based on titrated diazobutene) of *trans*-crotyl 3,5-dinitrobenzoate, m.p. 68.5-71°, which showed no m.p. depression when admixed with authentic ester prepared below.

N-Nitroso-N-methylvinylcarbinylurethan 15.2 g. (0.089 mole) was converted to II similarly. However, in this case the red color of the diazo compound disappeared if the ether solution was allowed to warm to room temperature. For this reason 3,5-dinitrobenzoic acid (18.8 g., 0.89 mole) was added at -80°. Evaporation of the ether and removal of excess acid gave 0.38 g. (0.0014 mole, 1.6% yield based on nitrosourethan) of methylvinylcarbinyl 3,5-dinitrobenzoate, m.p. 58.5-59.5°. A mixed m.p. with an authentic sample described below showed no depression. In spite of the low yield it seems certain that a negligible amount of the allylic isomer was present.

Reaction of the Two Diazobutenes (I) and (II) with Aqueous Perchloric Acid.—The diazobutenes were prepared as above but were passed directly into 1 M or 0.05 M perchloric acid at 0°. The aqueous solution of the products was then saturated with potassium carbonate, extracted with ether, dried in the ether solution and distilled through a concentric tube column.

Typical infrared spectra of the various fractions are shown in Figs. 1 and 2. Since the crotyl alcohol fractions from the diazo reactions have relatively strong carbonyl bands in the infrared, an attempt was made to isolate the carbonyl compound as the 2,4-dinitrophenylhydrazone but without success.

Authentic *trans*-crotyl alcohol, b.p. 120-122°, n_D^{25} 1.4279, was prepared by the procedure of Hatch and Nesbitt.¹³ When 8 g. of this material was subjected to the reaction conditions above 6 g. could be recovered unchanged. No low boiling fraction corresponding to methylvinylcarbinol was obtained although a viscous dark-colored residue (0.25 g.) remained after the distillation. Under similar conditions, methylvinylcarbinol (b.p. 94.2-96.2°, n_D^{25} 1.4121, obtained from the Shell Chemical Company) gave no recovered product boiling above 98°.

trans-Crotyl 3,5-dinitrobenzoate, m.p. 73-73.5°, was prepared and submitted for analysis since, although it has been reported previously to melt at 70.5³¹ and at 70°,¹³ no analysis was reported.

Anal. Calcd. for C₁₁H₁₀N₂O₆: C, 49.7; H, 3.8; N, 10.5. Found: C, 49.4; H, 3.6; N, 10.5.

Methylvinylcarbinyl 3,5-dinitrobenzoate, m.p. 59-59.5°, was prepared according to McElvain³² from authentic methylvinylcarbinol.

Anal. Calcd. for C₁₁H₁₀N₂O₆: C, 49.7; H, 3.8; N, 10.5. Found: C, 49.9; H, 4.0; N, 10.9.

Cyclization of I.—I, prepared from 5.9 g. of nitrosourethan (0.034 mole) (16% yield indicated by titration), was allowed to stand at room temperature. The red color had disappeared completely in 16 hours. Distillation gave an oily residue which was treated with picrylsulfonic acid in ethanol to give 3-methylpyrazole picrylsulfonate, m.p. 216.5-217.5° (dec.).

Anal. Calcd. for C₈H₇N₂·C₆H₃O₆S: C, 31.9; H, 2.71; N, 18.6. Found: C, 32.5; H, 2.5; N, 18.5.

(30) C. Prevost, *Ann. chim.*, [10] 10, 155 (1928).

(31) W. G. Young and L. J. Andrews, *THIS JOURNAL*, 66, 423 (1944).

(32) S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 193.

The picrate, m.p. 142-145°, of the above residue was prepared in dry benzene and recrystallized from ethanol-ether (lit. m.p.³³ 142°).

Reaction of (I) with Ethanol.—I was prepared from 17.3 g. (0.10 mole) of N-nitroso-N-crotylurethan by the procedure above and collected in a solution of 20 cc. of anhydrous ethanol containing 0.10 g. of sulfuric acid (Dry Ice-acetone-bath). The reaction was repeated four times and the reaction mixtures combined. The isolation procedure was that used by Catchpole and Hughes.³⁴ The mixed ethers were distilled from sodium until the refractive index remained constant. The yield was 2.5 g. (0.025 mole, 4.9%) of mixed ethers, n_D^{25} 1.3962.

To effect separation of the mixed ethers, the mixture was distilled through a concentric tube column to give 0.35 g. of methylvinylcarbinyl ethyl ether, b.p. 76°, n_D^{25} 1.3858, and 0.78 g. of crotyl ethyl ether, b.p. 98-100°, n_D^{25} 1.4016. A center cut (0.57 g., n_D^{25} 1.3990) from the refractive index-composition curve obtained below contained about 85% of crotyl ethyl ether and 15% of its allylic isomer.

Ethyl crotyl ether, b.p. 97.5-100°, n_D^{25} 1.4014 and methylvinylcarbinyl ethyl ether, b.p. 74.8-75.2°, n_D^{25} 1.3862, were prepared by the method of Catchpole and Hughes.³⁴ If the refractive index-composition curve is assumed to be linear the original mixture above contains 65% crotyl ethyl ether and 35% methylvinylcarbinyl ethyl ether.

A solution of ethyl crotyl ether (3.0 g.) was allowed to stand with 0.27 g. of sulfuric acid in 45 cc. of ethanol for 18 days after which the solution was neutralized and the product isolated and distilled as above. No low boiling fraction was obtained and 1.53 g. of crotyl ethyl ether was recovered (b.p. 100-101°, n_D^{25} 1.4010).

Pivalonitrile was prepared from pivalamide by the procedure for isobutyronitrile in "Organic Syntheses."³⁵

Neopentylamine.—Pivalonitrile was reduced with lithium aluminum hydride to neopentylamine, b.p. 80°, n_D^{25} 1.4000, in 86% yield by the method given by Nystrom and Brown,³⁶ employing, however, a 1:1:1 ratio of amine to lithium aluminum hydride. Neopentylamine picrate, m.p. 204-205°, was prepared and recrystallized from benzene. Ingold and Patel³⁷ report m.p. 205° for the picrate and b.p. 80-82° for the free base. An attempted reduction of pivalamide by the method described by Uffer and Schlittler³⁸ using lithium aluminum hydride was unsuccessful, and only recovered amide was obtained.

Neopentylurethan, b.p. (8 mm.) 86.5°, n_D^{25} 1.4308, was prepared from the amine by the method described for the other urethans above.

Anal. Calcd. for C₈H₁₇NO₂: C, 60.3; H, 10.8; N, 8.8. Found: C, 60.6; H, 10.9; N, 8.7.

N-Nitroso-N-neopentylurethan, b.p. (0.2 mm.) 43°, n_D^{25} 1.4374, was prepared in the same way as the nitroso compounds above.

Anal. Calcd. for C₈H₁₆N₂O₃: C, 51.0; H, 8.6; N, 14.9. Found: C, 51.3; H, 8.9; N, 15.3.

Reaction of Diazoneopentane (III) with 3,5-Dinitrobenzoic Acid. (a) In Ether.—III, prepared from N-nitroso-N-neopentylurethan (50 g., 0.27 mole) by the method described above, was collected in ether. The resultant solution was added to excess 3,5-dinitrobenzoic acid in ether.

(33) S. Cusmano, *Gazz. chim. ital.*, 70, 227 (1940).

(34) A. G. Catchpole and E. D. Hughes, *J. Chem. Soc.*, 4 (1948).

(35) *Org. Syntheses*, 25, 61 (1945).

(36) R. F. Nystrom and W. G. Brown, *THIS JOURNAL*, 70 (1948).

(37) C. K. Ingold and C. S. Patel, *J. Chem. Soc.*, 67 (1933).

(38) A. Uffer and E. Schlittler, *Helv. Chim. Acta*, 31, 1397 (1948).

The trimethylethylene was distilled with the ether and titrated with bromine by the method of Stanerson and Levin³⁹ which indicated that a 41% yield was formed (based on nitrosourethan). Addition of excess bromine to the solution, washing with bisulfite and two successive distillations gave a 25% yield of 2-methyl-2,3-dibromobutane, b.p. (16 mm.) 57–59°, n_D^{20} 1.5091 (lit.⁴⁰ b.p. (19 mm.) 63°, n_D^{20} 1.5090). The residue from the distillation of the trimethylethylene consisted of 1.7 g. of a mixture of dinitrobenzoate esters. From 1.35 g. of such a mixture obtained in a similar experiment, was isolated by fractional crystallization 0.52 g. of *t*-amyl 3,5-dinitrobenzoate, m.p. and mixed m.p. with an authentic sample described below, 115.5–116°, and 0.12 g. of neopentyl 3,5-dinitrobenzoate, m.p. and mixed m.p. 91.5–92.5°.

(b) **In Ligroin.**—When the ether in the above experiment was replaced by ligroin the yield of trimethylethylene by titration was 33% and the yield of esters, 0.69 g., m.p. 113–115°, and 1.2 g., m.p. 57–72°.

Reaction of III with Dilute Sulfuric Acid.—III was prepared as above from 50 g. of nitrosourethan and collected in 100 cc. of 0.045 *N* sulfuric acid cooled in an ice-salt-bath. A second trap cooled by acetone and Dry Ice was attached to the first. When the reaction was finished the aqueous solution was warmed to drive the trimethylethylene formed

into the Dry Ice-acetone traps. The trimethylethylene was distilled to give 2.75 g. (14% yield), b.p. 37–39.5°, n_D^{20} 1.3800. From the aqueous solution was obtained 7.6 g. (32% yield) of *t*-amyl alcohol, b.p. 101–106°, n_D^{20} 1.4028. These yields are based on the nitroso compound. Each fraction obtained in the distillation was treated with 3,5-dinitrobenzoyl chloride according to Reichstein⁴¹ and found to give *t*-amyl 3,5-dinitrobenzoate. No neopentyl derivative could be obtained.

Neopentyl 3,5-Dinitrobenzoate.—Neopentyl alcohol, b.p. 113°, m.p. 51–55°, was prepared by the reduction of pivalic acid in 83% yield with lithium aluminum hydride⁴² and converted to the 3,5-dinitrobenzoate 93–93.5° by the method of Reichstein.⁴² Since the previous workers have reported no analysis, that of our product is included.

Anal. Calcd. for $C_{12}H_{14}N_2O_6$: C, 51.1; H, 5.0; N, 9.9. Found: C, 51.4; H, 5.0; N, 10.0.

t-Amyl 3,5-dinitrobenzoate has been prepared previously a number of times but without elementary analysis. For this reason, the analysis of our product, m.p. 115.5–116.5°, is included.

Anal. Calcd. for $C_{12}H_{14}N_2O_6$: C, 51.1; H, 5.0; N, 9.9. Found: C, 51.4; H, 5.0; N, 10.0.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Condensations by Sodium. XXXII. Dissociation and the Cation Influence in Amylsodium and Similar Organosodium Reagents¹

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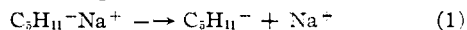
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Potassium and sodium *t*-pentoxides, in the order given, accelerate the pyrolysis of amylsodium at 50°. These alkoxides similarly accelerate the chemical reaction of amylsodium. From these results and earlier work the formation of radicals during the reactions of amylsodium appears likely. Interpretations based on such an assumption are shown and the energy contributed from the formation of sodium chloride in the reaction of the sodium reagent with an alkyl chloride is discussed. Associated salts may affect the reactions of amylsodium either by accelerating the dissociation to radicals or by providing appropriate positions for adsorption of a reacting molecule. Several reactions of organoalkali metal reagents are interpreted from the electrophilic viewpoint.

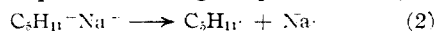
From time to time during the extensive study of organosodium compounds which is being made in this Laboratory some insight into the manner by which these reagents function has been possible. For example, in the Wurtz reaction of an alkyl chloride with sodium all products were observed to pass through an organosodium intermediate² and the facts which previously seemed to demand a free radical were found inconclusive and fully explained as the behavior of an organosodium compound. Later the reagents were thought to have cation as well as anion activity and a classification as electrophilic^{3–5} appeared useful for interpreting and predicting reactions. An attempt to modify the cation influence in the polymerization of butadiene by amylsodium led to the accidental discovery of the Alfin catalyst⁶ with its unique property of pro-

ducing, at extreme rapidity, a polybutadiene of around 7,000,000 weight average molecular weight⁷ with no cross-linking. The present work, which began with the supposition that the ion-pair in amylsodium acts solely as ions, has uncovered the idea that this reagent probably functions also as a radical or radical pair whose activities are restricted to the spot where the electron attracting influence of the cation acts.

The arguments which led to this idea are as follows: (a) a dissociation of solid amylsodium into separated ions, as in equation (1), might under some circumstances require considerable energy, (b) an



alternative dissociation to radicals, as in equation (2), would require no charge separation, (c) de-



composition of amylsodium to radicals was found in an earlier study⁸ to occur at room temperature and probably also at zero degrees and the common experience in this Laboratory is for all preparations of amylsodium to suffer some reversion to metallic sodium and hydrocarbon while standing overnight,

(1) The authors are indebted to the Office of Rubber Reserve, Reconstruction Finance Corporation, for financial assistance of this and other work.

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