that 95–98% of the theoretical chloride ion had formed. The white solid was recrystallized from C.P. acetone to yield 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide, 37.8 g., m.p. 77–78°.

Anal. Calcd. for $C_7H_{12}N_2O_4$: C, 44.67; H, 6.43; N, 14.89. Found: C, 44.71; H, 6.24; N, 14.28.

The alcoholic filtrate I was evaporated at reduced pressure to a volume of approximately 150 ml. Ethyl ether (100 ml.) was added and the mixture was kept in a refrigerator for 24 hours. The yellow solid which formed was filtered; the filtrate II was saved. The yellow solid was washed with water (100 ml.) and filtered to yield additional 3-methyl-4-(2-nitro-2-propyl)-isoxazoline oxide, 4.4 g. The total yield of isoxazoline oxide was 42.2 g., 36% of theoretical. (The reaction temperatures were varied from −20° to 30°; at the higher temperatures the yields of isoxazoline oxide ranged from 10–15% and the amounts of tarry residues were much greater). The aqueous filtrate, after acidification, gave a carbonyl group reaction with 2,4-dinitrophenylhydrazine; this reaction arises from conversion of sodium 2-propanenitronate by the Nef[27] reaction to acetone.

Filtrate II was evaporated at reduced pressure, the resulting thick sirup was cooled for 2 days in a refrigerator. A solid precipitated and was filtered (5.2 g.); the filtrate III was saved. The white solid, after recrystallization from ether, was identified as 2,3-dimethyl-2,3-dinitrobutane, m.p. 205–207°, lit.[24] 209°; no depression by an authentic[24] sample (m.p. 208–210°).

The filtrate III was distilled to give a yellow liquid, b.p. 50–75° at 2 mm. Ether (10 ml.) was added and the solution was cooled to −78°. A yellow solid precipitated which was filtered from the cold solution; the filtrate IV was saved. The yellow solid, 5-methyl-2-nitro-2,4-hexadiene (3.2 g., 3.5% yield) melted at 25–28° after several recrystallizations from cold ether. Its infrared spectrum contains well-defined bands at 6.15 (conjugated diene system), 6.65 (nitro group conjugated with diene system) and 7.65 μ (nitro group); absorption in the ultraviolet region (95% ethanol) occurs at 230 mμ (ϵ_{max} 7,700) and 335 mμ (ϵ_{max} 11,700), respectively.[1,28]

Anal. Calcd. for $C_7H_{11}NO_2$: C, 58.57; H, 7.80; N, 9.93. Found: C, 58.11; H, 7.06; N, 9.15.

The filtrate IV was distilled to yield a yellow liquid[9] (33 g.): b.p. 50–58.5° (0.8 mm.), $n^{20}D$ 1.4812–1.5042. Repeated distillations[1] failed to result in effective purification of this mixture. The combined residues[9] (20.3 g.) from all

---

(27) J. U. Nef, *Ann.*, **280**, 263 (1894).

(28) E. A. Braude, E. R. H. Jones and G. G. Rose, *J. Chem. Soc.*, 1104 (1947), report that the ultraviolet spectra of conjugated nitroolefins contain from one to three bands of similar intensities (6–10μ apart) in the region of 225–260 mμ; ϵ_{max} 3300–9700. 1-Nitro-1,3-pentadiene absorbs at 225 mμ (ϵ_{max} 5500) and 298 mμ (ϵ_{max} 12,000); β-nitrostyrene absorbs at 227 mμ (ϵ_{max} 9500) and 309 mμ (ϵ_{max} 16,500).

distillations were steam distilled to give additional 2,3-dimethyl-2,3-dinitrobutane (1.2 g.); the total yield of 2,3-dimethyl-2,3-dinitrobutane (6.4 g.) was 11%.

3-Methyl-4-(2-isopropenyl)-isoxazole.—3-Methyl-4-(2-nitro-2-propyl)-isoxazoline oxide (25 g., 0.14 mole) was stirred vigorously with 2% aqueous sodium hydroxide (200 ml.) at 55–60°. Within several minutes, the isoxazoline oxide had dissolved to give a clear yellow solution. After 5 minutes, cloudiness developed and an oil separated at the bottom of the reaction mixture. The mixture was heated for one hour at 55–60°, cooled, and then extracted with ethyl ether; the aqueous layer, upon acidification, evolved oxides of nitrogen. The ether extract was dried over sodium sulfate, concentrated and then distilled at 60° (1 mm.) to give a volatile product (condensed at −80°) and a high boiling residue (12.4 g., extensively decomposed). Redistillation of the volatile product gave 3-methyl-4-(2-isopropenyl)-isoxazole (1.4 g., 8.1% yield), a colorless liquid of powerful, fragrant odor, insoluble in water and soluble in usual organic solvents, b.p. 70–71° (17 mm.), $n^{20}D$ 1.4863, infrared spectra Fig. 1E. The isoxazole reacted with saturated mercuric chloride to give a white solid which softens and then dissociates at 124–126°.

Anal. Calcd. for C_7H_9NO: C, 68.29; H, 7.32; N, 11.38. Found: C, 68.27; H, 7.17; N, 11.31.

The high boiling residue was distilled in a Hickman-type still (0.08 mm., considerable decomposition) to give a viscous yellow oil (3.2 g.); redistillation of this product (0.02 mm., b.p. ~ 50°) gave a colorless oily liquid (2.8 g.), $n^{20}D$ 1.5335 which turned dark-red quickly on storage. Consistent analyses for this material could not be obtained because of its rapid decomposition; the analyses fell within the ranges expected for mixtures of 3-methyl-4-(2-nitro-2-propyl)-isoxazole (VII) and 3-methyl-4-(2-isopropenyl)-isoxazole (VIII) (similar agreement was obtained from the infrared and ultraviolet spectra of the product). The freshly-distilled liquid dissolves slowly in dilute aqueous alkali to give a product having the characteristic odor and many of the properties of 3-methyl-4-(2-isopropenyl)-isoxazole; it is thus believed to consist mainly of unstable 3-methyl-4-(2-nitro-2-propyl)-isoxazole (VII).

Ultraviolet Spectra of VIII and of Trimethylisoxazole.— The ultraviolet spectra of VIII and of trimethylisoxazole in 50% ethanol (1 × 10⁻⁴ M, resp.) are simple and almost identical; each spectrum exhibited only very little fine structure. The absorption spectrum for VIII is described as: extended absorption at 220 mμ (log ε 4.13), continuous decreased absorption over the range 220–270 mμ (log ε range of 4.13–2.71), and weak absorption at 270–400 mμ. The spectrum of trimethylisoxazole indicates maximum absorption at 223 mμ (log ε 3.92) with continuous decreased absorption over the range 223–250 mμ (log ε range of 3.92–2.78) and weak absorption over the range 250–400 mμ.

COLUMBUS, OHIO

An Improved Procedure for Preparing Primary Nitroalkanes by the Victor Meyer Reaction

BY C. W. PLUMMER AND N. L. DRAKE

An improved procedure is described for preparing six primary nitroalkanes of high purity in much better yields than those formerly obtained.

A search of the literature has revealed the need of a good laboratory procedure for preparing the higher homologs of primary nitroalkanes. These have been prepared almost exclusively by two methods: (1) the well-known reaction between an alkyl halide and silver nitrite,[1] and (2) the reaction of an α-halocarboxylic acid with sodium nitrite.[2]

Of these, the first gives considerably better yields, although they are low. More recently, a few primary nitroalkanes have been prepared by the 1,4-addition of an alkylmagnesium bromide to an α,β-unsaturated nitroölefin.[3] In general, the yields are comparable to those obtained from the Victor Meyer reaction.

The review and extension of the Victor Meyer re-

---

(1) V. Meyer and O. Stuber, *Ber.*, **5**, 203 (1872).

(2) H. Kolbe, *J. prakt. Chem.*, **5**, 427 (1872).

(3) G. D. Buckley and E. Ellery, *J. Chem. Soc.*, 1494 (1947).

TABLE I

COMPARATIVE YIELDS AND PHYSICAL CONSTANTS OF PRIMARY NITROALKANES

Product	Yield, %	B.p. °C.	Mm.	n^{25}D	$d^{25}{}_4$	MD[15] Obsd.	MD[16] Calcd.	Yield, %	n^TD	Previously recorded T		d
1-Nitrobutane	63.8	58.0–58.3	23	1.4080	0.9673	26.24	26.30	37[9]	1.4108	20[7]	$d^{20}{}_{20}$	0.975[11]
2-Methyl-1-nitropropane	44.0	60.3–60.7	44	1.4050	.9602	26.32	26.30	16[8]	1.4050	25[8]	$d^{25}{}_{25}$	0.9625[8]
1-Nitropentane	66.6	75 –76	23	1.4161	.9493	30.97	30.92	...	1.4218	20[13]	$d^{20}{}_4$	0.9475[13]
3-Methyl-1-nitrobutane	61.0	68.0–68.3	24	1.4143	.9458	30.97	30.92	28[10]	1.41806	20.6[12]	$d^{20.6}{}_4$	0.9599[12]
1-Nitrohexane	69.4	91 –92	24	1.4218	.9354	35.62	35.54	40[9] 43[8]	1.4245	20[7]	$d^{20}{}_4$	0.9488[13]
1-Nitroheptane	60.6	107–108	25	1.4263	.9269	40.16	40.16	...	....	...	$d^{17}{}_4$	0.9476[14]

action by Reynolds and Adkins[4] suggests that yields of between 55–70% of primary nitroalkanes may be obtained by treating the corresponding alkyl bromides with an excess of silver nitrite with no solvent, running the reactions cold for several hours, and then heating under gentle reflux until all the bromide has reacted (5–6 hours). On the basis of analytical data, the products isolated were claimed to be mixtures consisting only of alkyl nitrites and nitroalkanes.

Considerable doubt has been cast on the validity of these results by the later work of Kornblum[5] which clearly demonstrates that under the reaction conditions used by Reynolds and Adkins, considerable amounts of alkyl nitrate, as well as the decomposition products of alkyl nitrite (alcohol and aldehyde) are formed.

In spite of the low yields obtained, the Victor Meyer reaction is still the most convenient general method of preparing homologs of primary nitroalkanes higher than 1-nitropropane. Modifications of the original procedure have not, up until now, included the use of lower reaction temperatures which, in the light of Kornblum's work, should be an obvious improvement. A number of experiments carried out in this Laboratory have indicated that in some preparations, the solvent petroleum ether is preferable to a dialkyl ether, the solvent commonly employed. In addition, there was some evidence that at low temperatures (<20°), the reaction was too slow to be practicable.

In consideration of the above, an improved procedure was developed for the preparation of six primary nitroalkanes of high purity and in good yields. Table I compares present yields and physical constants with selected values from the literature. It also lists the calculated molecular refractivities and the observed values.

With the exception of 2-methyl-1-nitropropane, which was prepared from the corresponding iodide, alkyl bromides were the starting materials. That the products were obtained in a high state of purity was shown by the following

(1) They were colorless and completely soluble in 15% aqueous sodium hydroxide at room temperature.
(2) The data obtained from final distillation (see below).
(3) A good agreement with previously reported constants (Table I).
(4) The agreement between observed and calculated molecular refractions.

The method consists of adding, as rapidly as possible, a 5% excess of silver nitrite to a cold solution of the alkyl halide in about an equal volume of pe-

troleum ether (45–55°), allowing the temperature of the stirred reaction mixture to rise to 40°, and maintaining this temperature (±3°) by occasional cooling, until all the alkyl halide has reacted (6–8 hours). No effort was made to shield the reaction mixture from light. Isolation of the crude product is effected by conventional methods. Most of the principal impurity, alkyl nitrite, is removed at reduced pressure through a short column. The residue is treated with cold, concentrated sulfuric acid[6] containing a little urea (to remove any nitrous acid), and the resulting solution is poured over ice. Extraction with light petroleum ether gives a yellow liquid which is almost pure product, as demonstrated by the final distillation. Little, if any, forerun is obtained, and the entire contents of the pot (excepting a trace of brown residue and 1–3 ml. of column hold-up) distils within a temperature range of one degree or less. In all preparations, the several fractions taken within this temperature range had the same refractive indices (±0.0003).

Experimental

The silver nitrite used was prepared by the addition of a solution of sodium nitrite to a solution of silver nitrate. The silver nitrite was filtered off, washed thoroughly with ice-water, then with 95% ethanol, air dried in a dish protected from light for one day, and finally over calcium chloride at reduced pressure for one day. It was stored in a brown bottle protected from the light, and was used up to 10 weeks after it was prepared.

The alkyl halides were purchased from the Matheson Company. They were purified before use by sulfuric acid washing, water washing, and drying over sodium sulfate.

The reaction was carried out in a three-necked flask fitted with a thermometer, reflux condenser and mercury-sealed Hershberg stirrer.

The column used in the final distillations was a 1.5 cm. × 70 cm. Vigreux with inner and outer air jackets. The outer jacket was insulated with glass wool and aluminum foil. The distilling head was of a design to permit varying the reflux ratio during distillation.

Details of a typical experiment are given below.

(4) R. B. Reynolds and H. Adkins, THIS JOURNAL, **51**, 279 (1929).

(5) N. Kornblum, et al., ibid., **69**, 307 (1947); **70**, 746 (1948).

(6) The use of concentrated sulfuric acid to remove impurities was adapted from the work of N. Kornblum, et al.[5]

(7) N. Kornblum and G. E. Graham, THIS JOURNAL, **73**, 4041 (1951).

(8) H. B. Hass, E. B. Hodge and V. M. Vanderbilt, Ind. Eng. Chem., **28**, 339 (1936).

(9) A. I. Vogel, "A Text Book of Practical Organic Chemistry," 2nd Ed., Longmans, Green and Company, New York, 1951, pp. 305–306.

(10) P. C. Ray and P. Neogi, Proc. Chem. Soc., **23**, 246 (1907).

(11) C. L. Gabriell, Chem. Industries, **45**, [7] 664 (1939).

(12) T. Mousset, Bull. acad. roy. Belg., 662 (1901).

(13) L. Henry, Rec. trav. chim., **24**, 352 (1905).

(14) R. A. Worstall, Am. Chem. J., **20**, 210 (1898).

(15) Molecular refractivities found by the equation of Lorenz and Lorentz MD $= (n^2 - 1)/(n^2 + 2) \times (M/d)$.

(16) Values of atomic refractivities taken from R. L. Shriner and R. C. Fuson, "A Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 107.

The Preparation of 1-Nitropentane.—A solution of 135 g. (0.894 mole) of *n*-amyl bromide in 100 ml. of petroleum ether (45–55°), contained in a 500-ml. three-necked flask fitted with a reflux condenser, mercury-sealed Hershberg stirrer and thermometer, was chilled in an ice-bath to 3°. A 5% excess (145 g.) of silver nitrite was added as rapidly as possible, the ice-bath removed, and the temperature of the well-stirred mixture allowed to rise to 40° ($^{1}/_{2}$ hour). The temperature of the exothermic reaction was kept at 38–42° for 5.5 hours by external cooling. A bromide test on the reaction liquor was negative at the end of this time. (It was carried out by warming a sample with alcoholic potassium hydroxide, acidifying with dilute nitric acid, and adding a solution of silver nitrate).

The mixture was filtered, and the silver salts washed on the funnel with 7 × 50 ml. of petroleum ether (45–55°). Removal of the solvent and low-boiling by-products (mostly alkyl nitrite) was carried out up to a bath temperature of 83° (25 mm.). A 15-cm. Vigreux column was used. The pale yellow liquid residue weighed 80.3 g.

The crude product thus obtained was added dropwise to a stirred solution of 5 g. of urea in 250 ml. of concentrated sulfuric acid at 0°. The temperature was kept between 0–2° by the rate of addition and by chilling in an ice–salt-bath (twenty minutes for complete addition). The resulting yellow solution was stirred for 10 minutes longer at 0°, and then, with manual stirring, poured over 500 g. of cracked ice to which had been added 200 ml. of petroleum ether (45–55°). The container was chilled in a salt–ice-bath during this process. After separation of the layers, the aqueous layer was extracted with 2 × 150 ml. of petroleum ether (45–55°). The combined organic layers were washed with 3 × 800 ml. of saturated sodium chloride solution and dried over calcium chloride. Removal of the solvent under reduced pressure left 72.0 g. of pale yellow liquid which was rectified at 23 mm. through the column described above. Three fractions were taken. The combined fractions weighed 69.60 g., corresponding to 66.6% of that calculated.

Fraction	B.p., °C.	$n^{25}D$	Wt., g.	Color
1	75.0–75.5	1.4152	0.55	Colorless
2	75.5–76.0	1.4154	6.45	Colorless
3	76.0–76.1	1.4154	62.60	Colorless

COLLEGE PARK, MARYLAND

Azo-bis Nitriles.[1] Decomposition of Azo Compounds. A Special Case of Carbon–Carbon Hyperconjugation in a Free Radical Reaction

BY C. G. OVERBERGER AND ALEXANDER LEBOVITS

Azo nitriles prepared from methyl cyclobutyl ketone, methyl cyclopentyl ketone and methyl cyclohexyl ketone have been prepared and characterized. The rates of decomposition have been measured and compared with the rate of decomposition of the azo nitrile from methyl cyclopropyl ketone. The evidence strongly indicates that the enhanced rate of decomposition of the methyl cyclopropyl azo nitrile is due to delocalization of the carbon–carbon bond in the cyclopropane ring (hyperconjugation). This is the first reported case of carbon–carbon radical hyperconjugation which has strong experimental support.

There is considerable evidence largely based on calculations of ionization potentials that hyperconjugation is of much greater importance in carbonium ion transition states than in radical ones.[2] Although there is some experimental indication that hyperconjugation of hydrogen atoms in radical transition states may influence the rate of some reactions, there is no experimental evidence for carbon–carbon hyperconjugation in a radical reaction.

This paper describes the preparation and decomposition of the azo nitriles derived from methyl cyclobutyl, methyl cyclopentyl and methyl cyclohexyl ketones and compares these results with those previously obtained from the decomposition of methyl cyclopropyl ketone.[3]

The evidence strongly supports a case of carbon–carbon radical hyperconjugation previously suggested.[3] These results again emphasize the value of radical formers which decompose by kinetically clean processes independent of solvent effects, for studying the effect of structure on reactivity.

A. Preparation of Azo Compounds

1. Discussion.—The azo compounds from methyl cyclobutyl, methyl cyclopentyl and methyl cyclohexyl ketones were prepared according to previously described procedures.[4] Methyl cyclobutyl ketone was prepared by reaction of cyclobutanecarbonyl chloride with the magnesium salt of malonic ester. This preparation represents a useful procedure for its synthesis.[5] The cyclopentyl and cyclohexyl ketones were prepared from the corresponding cycloalkylmagnesium bromides and acetic anhydride at low temperatures according to the general procedure of Newman and Smith.[6] No attempt is made here to record the numerous reported syntheses of these three cycloalkyl ketones; it is sufficient to state that they have not been reported prepared by the methods described here.

Both stereoisomers, the *dl* and *meso* forms of the azo compounds of methyl cyclobutyl ketone and methyl cyclopentyl ketone were isolated and characterized. Two stereoisomeric 1,2-disubstituted hydrazines were isolated from the reaction with methyl cyclopentyl ketone. Separation was effected by fractional crystallization. The separa-

(1) This is the tenth in a series of articles concerned with the decomposition of azo compounds. For the ninth paper in this series, see C. G. Overberger, P. T. Huang and T. B. Gibb, Jr., THIS JOURNAL, **75**, 2082 (1953).

(2) E. C. Baugham, M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

(3) C. G. Overberger and M. B. Berenbaum, THIS JOURNAL, **73**, 2618 (1951).

(4) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

(5) H. G. Walker and C. R. Hauser, *ibid.*, **68**, 1386 (1946).

(6) M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948).