molecular decomposition of the intermediate phenylmetallic compounds would account for the formation of biphenyl.

$$2[C_6H_5M] \longrightarrow C_6H_5\text{-}C_6H_5 + 2M \qquad (D)$$

Indeed, such a mechanism has been proposed for the decomposition of the arylsilver compounds.[10] Likewise, the decomposition of methylcopper to yield ethane can be explained by an interaction of two or more molecules of methylcopper.

$$2[CH_3Cu] \longrightarrow CH_3\text{-}CH_3 + 2Cu$$

The reactions of ethylmagnesium bromide with copper(I), copper(II) or thallium(I) halides (group 3, Table II) give rise to equal quantities of ethane and ethylene. In these cases a bimolecular decomposition might also be involved, but instead of coupling to form butane the ethyl radicals undergo disproportionation. The silver halides, and to a lesser extent gold(III) chloride, react with ethylmagnesium bromide to form butane which, again, could be the result of a bimolecular decomposition of the intermediately formed, unstable organosilver and gold compounds.

The comparative reactions of ethylmagnesium bromide with the chloride, bromide and iodide of silver (Table II) indicate that the halogen atom has little influence upon the course of the reaction. Reactions of methylmagnesium halides and dimethylmagnesium with salts of zirconium(IV), tantalum(V), chromium(III), copper(I), copper(II) and silver gave the same products in almost the same yields as obtained when methyllithium was used.

Experimental

Materials.—The metallic halides used in these experiments were completely anhydrous and of the highest purity. Most of them were analyzed for both metal and halogen content.

Stock solutions of methyllithium and ethylmagnesium bromide (about one molar) were prepared by the ordinary methods and stored under nitrogen. The solutions were standardized by acid titration.[11]

Apparatus and Procedure.—The apparatus consisted of a 250-ml. three-necked flask provided with a dropping funnel connected to a source of pure, dry nitrogen, a gas-tight, mechanical stirrer and an efficient reflux condenser. A rubber tube led from the top of the reflux condenser through a calcium chloride tube to a water-filled gas collector. The apparatus was dried in an oven at 150° for several hours then assembled while still hot and allowed to cool while nitrogen was slowly passed through it.

In the flask was placed a weighed quantity of the metal halide with 25 ml. of ether which had been dried over sodium. The calculated quantity of Grignard solution (or methyllithium) was measured into the dropping funnel by means of a pipet. While the mixture in the flask was stirred, the solution in the dropping funnel was added during 10 or 15 minutes, then the reaction was allowed to stand. When the evolution of gas appeared to have stopped, the mixture was stirred and refluxed on a water-bath for ten minutes and the gas remaining in the apparatus was swept out into the gas collector with nitrogen.

The total volume of collected gas was measured. The temperature and barometric pressure were noted and then aliquots of the gas were analyzed by standard combustion procedures. The apparatus was tested by heating in it a solution of ethylmagnesium bromide under reflux for two hours. No gas was evolved.

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[10] L. Joseph and J. H. Gardner, *J. Org. Chem.*, **5**, 61 (1940); E. A. Bickley and J. H. Gardner, *ibid.*, **5**, 126 (1940).

[11] H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, THIS JOURNAL, **45**, 150 (1923).

AMES, IOWA

[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

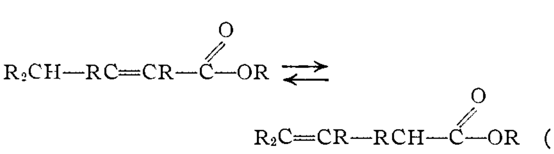
Base-catalyzed Isomerization and Tautomeric Equilibria of the System 2-Methyl-3-nitropropene and 2-Methyl-1-nitropropene

BY HAROLD SHECHTER AND JAMES W. SHEPHERD[1]

RECEIVED DECEMBER 4, 1953

Reaction of either 2-methyl-3-nitropropene (IX) or 2-methyl-1-nitropropene (X) with stoichiometric amounts of aqueous sodium hydroxide yields sodium 2-methyl-2-propenenitronate (XI); acidification of XI with dilute aqueous acetic acid at 0° results initially in formation (at least in part) of 2-methyl-2-propenenitronic acid (XII), tautomeric rearrangement of which occurs slowly to give mixtures of IX and X. Prolonged reaction of either IX or of X with trace amounts of dilute aqueous methanolic potassium hydroxide at room temperature yields an equilibrium mixture of IX (18–19%) and X (81–82%). The greater stability of X than of IX may be related to its prime resonance and hyperconjugative aspects. Mixtures of IX and X are obtained by reaction of 2-methyl-1-nitro-2-propyl acetate and sodium acetate (15.8% IX and 84.2% X) and by nitration of *t*-butyl alcohol (20% IX and 80% X). Reaction of methallyl bromide with silver nitrite yields IX. The identity and compositions of mixtures of IX and X were determined by infrared and refractive index methods.

The subject of tautomerism in alpha and beta unsaturated esters (equation 1), acids, other carbonyl derivatives and nitriles, etc., has been widely studied.[2] In general, it has been found that the formation of position isomers and establishment of equilibrium in such systems are catalyzed by acids or bases, and that the equilibrium relations between the alpha and beta isomers may be correlated with the resonance, hyperconjugative and steric aspects of their particular structures.[2b,c] There has been, however, a paucity of information concerning the rearrangement phenomena and tautomeric equilibria of alpha- and beta-unsaturated nitro com-



$$R_2CH{-}RC{=}CR{-}C({=}O){-}OR \rightleftarrows R_2C{=}CR{-}RCH{-}C({=}O){-}OR \qquad (1)$$

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[1] Abstracted from a thesis presented by J. W. Shepherd to the Graduate School of The Ohio State University, 1951, in partial fulfillment of the requirements for the M.S. degree.

[2] For compilations and discussions of these researches, the following sources are cited: (a) H. Adkins, Gilman's "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 1041–1043; (b) E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 281–287; and (c) J. W. Baker, "Hyperconjugation," Oxford University Press, London E. C. 4, 1952, pp. 58–67.

pounds. It was therefore the purpose of this investigation to study the possibility of base-catalyzed rearrangements of an isomeric pair of conjugated and unconjugated nitroalkenes and of obtaining information concerning the equilibrium relationships of such a system.

The participation of an aliphatic nitro group in the tautomeric equilibration[3] of α,β- and β,γ-unsaturated esters has been previously demonstrated in ethyl 3-methyl-2-nitro-2-butenoate (I) and ethyl 3-methyl-2-nitro-3-butenoate (II).[4] Reaction of I with potassium ethoxide (equations 2) occurs by proton transfer from a terminal methyl group and results in the slow formation of the potassium salt of III. Acidification of III gives initially the nitronic acid (IV), which then tautomerizes to II along with small amounts of the conjugated nitro ester I. The relative amounts of I (always the minor product) and II produced upon acidification of III are related to the particular experimental conditions. As expected, neutralization of II occurs much more rapidly than that of I to yield III, and the mixtures of I and II obtained upon acidification are identical with those obtained from I.

$$\begin{tikzcd}
\underset{\text{I}}{(H_3C)_2C{=}C(NO_2)CO_2C_2H_5} \arrow[d, shift right, "^-OEt"'] & \underset{\text{IV}}{CH_2{=}C(CH_3)C({=}NO_2H)CO_2C_2H_5} \arrow[d, shift right, "^-OEt"'] & \underset{\text{II}}{CH_2{=}C(CH_3)CH(NO_2)CO_2C_2H_5} \arrow[d, shift right, "^-OEt"'] \\
H_2\bar{C}C(CH_3){=}C(NO_2)CO_2C_2H_5 \arrow[u, shift right, "H^+"'] \arrow[r, leftrightarrow] & \underset{\text{III}}{CH_2{=}C(CH_3){-}C({=}NO_2^-)CO_2C_2H_5} \arrow[u, shift right, "H^+"'] \arrow[r, leftrightarrow] & CH_2{=}C(CH_3)\bar{C}(NO_2)CO_2C_2H_5 \arrow[u, shift right, "H^+"']
\end{tikzcd} \qquad (2)$$

It was concluded from this and similar investigations[5] that α-nitro-α,β- and α-nitro-β,γ-alkenoic esters undergo tautomeric isomerization upon reaction with bases and acids; however, much of these phenomena were attributed to the influences of the carbethoxy group.[2,4b]

Fraser and Kon[4b] have reported that 1-nitromethylcyclohexene (V) reacts rapidly with bases to give the expected salts VI. Acidification of these salts, VI, results initially in formation of 1-cyclohexene-1-methanenitronic acid (VII), isomerization of which occurs completely to give only V; there was no evidence for formation of nitromethylenecyclohexane[6] (VIII). Since similar results were obtained with 1-nitromethylcyclopentene, 1-(1-nitroethyl)-cyclohexene and 1-(1-nitropropyl)-cyclohexene,[4b] it was concluded that there is little tendency of β,γ-nitroalkenes to tautomerize to their α,β-isomers.[4b]

Levy, Scaife and Wilder-Smith have found that dehydration of 2-methyl-1-nitro-2-propanol with phosphoric anhydride gave 2-methyl-3-nitropropene (IX, 41% yield) and 2-methyl-1-nitropropene (X, 21.7% yield) in approximately a 2:1 ratio.[7] Reaction of 2-methyl-1-nitro-2-propyl acetate with potassium carbonate resulted in formation of a mixture of IX and X which contained approximately 8% of IX[7]; similarly, decomposition of 1,2-dinitro-2-methylpropane gave a mixture of IX and X which generally contained less than 10% of IX.[8] Since it has not been demonstrated that simple α,β- and β,γ-nitroalkenes are isomerable, it was therefore decided to determine the possibilities for base-catalyzed rearrangements and tautomeric equilibration of 2-methyl-3-nitropropene (IX) and 2-methyl-1-nitropropene (X).

A mixture of IX and X (15.8% IX, 84.2% X, see Experimental) was prepared in 76% yield by reaction of 2-methyl-1-nitro-2-propyl acetate and sodium acetate. Nitration of *t*-butyl alcohol resulted also in formation of a mixture of IX (20%) and X (80%). The mixtures of IX and X were separated into their pure components by fractional rectification at reduced pressure. Synthesis of IX also was effected in 40% yield, without being perceptibly contaminated with X, by reaction of methallyl bromide and silver nitrite (equation 3)

$$CH_2{=}C(CH_3)CH_2Br + AgNO_2 \longrightarrow CH_2{=}C(CH_3){-}CH_2NO_2 + AgBr \qquad (3)$$

It was necessary to establish the identity and determine the composition of mixtures of IX and X by methods which do not involve physical or chemical separations. The refractive indices of IX and X differ considerably (see Experimental); upon determining that the refractive indices of mixtures of pure IX and X can be related linearly with their per cent. compositions, it was then possible to determine the percentage composition of any mixture of IX and X from its refractive index. The infrared spectra of IX and X also have characteristic differences. The principal absorption maximum for a nitro group in IX (unconjugated) occurs (Fig. 1-A) at 6.43 (asymmetric stretching)[9a] and 7.32 (symmetrical stretching)[9a] μ,[9b] whereas that for the nitro group in X (conjugated) occurs (Fig. 1-B) at 6.60 and 7.41 μ. In mixtures of IX and X in dilute solution (Fig. 1-C), these principal peaks are sharply defined and well separated.[10] The infrared spec-

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(3) For presentation of facts and for discussion of the mechanisms of tautomerism of nitroalkanes and nitronic acids, the following references are cited: (a) A. F. Holleman, *Rec. trav. chim.*, **14**, 121 (1895); (b) A. Hantzsch and O. W. Schultz, *Ber.*, **29**, 699, 2253 (1896); (c) S. H. Maron and V. K. LaMer, THIS JOURNAL, **61**, 692 (1939); and (d) R. G. Pearson and R. L. Dillon, *ibid.*, **72**, 3574 (1950).

(4) (a) L. Bouveault and A. Wahl, *Compt. rend.*, **131**, 687, 748 (1900); *Bull. soc. chim.*, **25**, 808 (1901); (b) H. B. Fraser and G. A. R. Kon, *J. Chem. Soc.*, 604 (1934).

(5) Ethyl 3-ethyl-2-nitro-2-pentenoate, ethyl 3-methyl-2-nitro-2-hexenoate, and ethyl cyclohexylidenenitroacetate exhibit rearrangement characteristics analogous to those of I and II[4b]; the conjugated nitro unsaturated esters (equivalent to I) are produced only in trace or in minor amounts upon acidification of their alkaline solutions.

(6) The formation of V to the exclusion of VIII (the expected product on the basis of the resonance interaction derived by conjugation with the nitro group) may be related to the greater steric requirements of VIII than for V about the unsaturated centers and to the greater stability of endocyclic cyclohexene systems over that of their exocyclic isomers; H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).

(7) N. Levy, C. W. Scaife and A. E. Wilder-Smith, *J. Chem. Soc.*, 57 (1948).

(8) A. E. Wilder-Smith and C. W. Scaife, British Patent 580,256 (Sept. 2, 1946).

(9) (a) D. C. Smith, C. Y. Fan and J. R. Nielsen, *J. Chem. Phys.*, **18**, 707 (1950); R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953); (b) intense characteristic absorption also occurs in IX at 10.95 μ.

(10) A much more complete listing of the infrared spectra of IX and X and their mixtures is contained in reference 1.

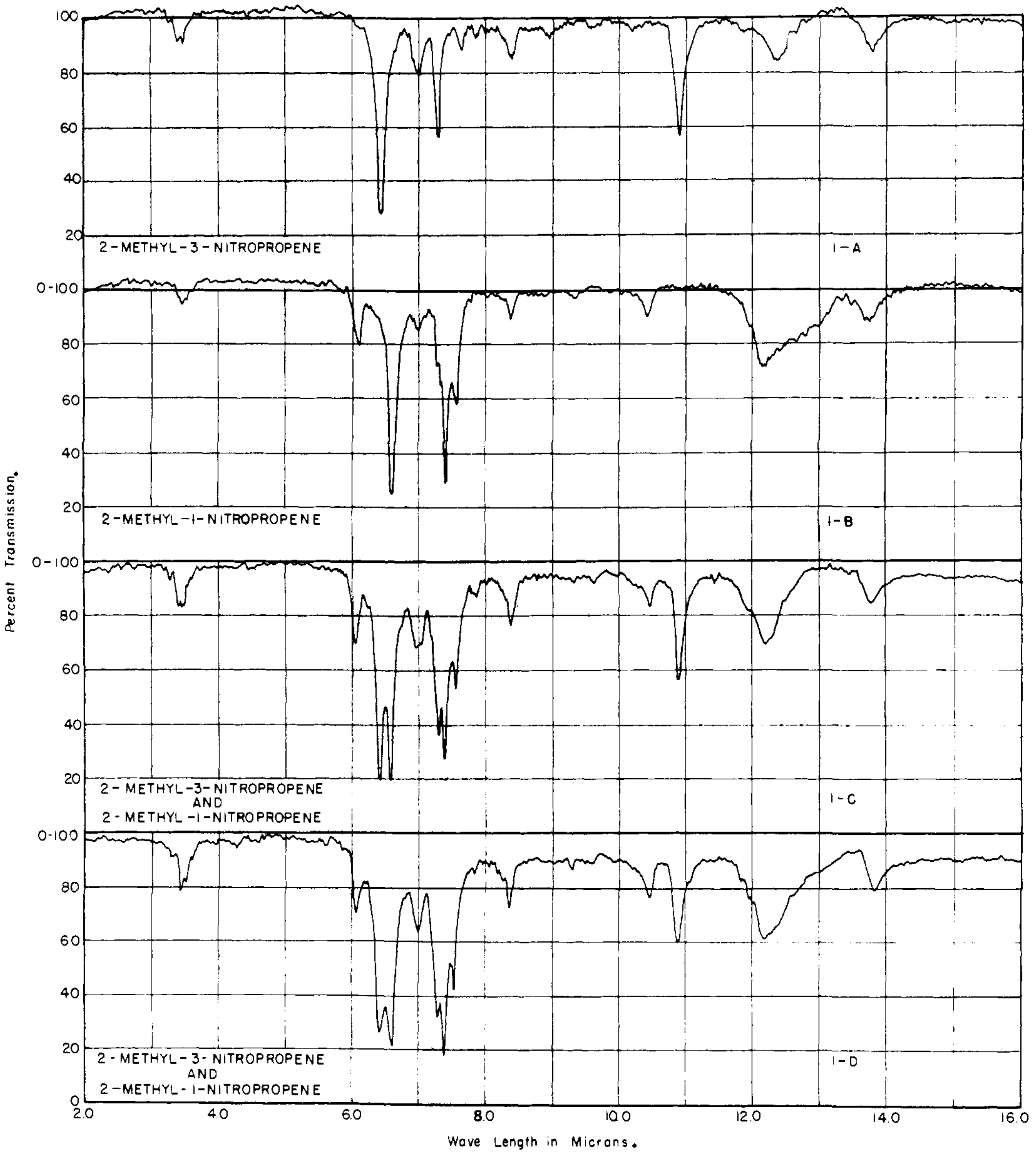

Fig. 1.—Infrared absorption spectra of: 2-methyl-3-nitropropene (IX, curve 1-A, 0.216 M in CCl_4), 2-methyl-1-nitropropene (X, curve 1-B, 0.208 M in CCl_4), a synthetic mixture of IX and X (curve 1-C, 0.391 M in CCl_4, 50.6 mole % IX, 49.4 mole % X), and a rearrangement mixture of IX and X (curve 1-D, 0.430 M in CCl_4, 42 mole % IX, 58 mole % X) obtained by reaction of IX with excess aqueous sodium hydroxide and subsequent acidification (see Experimental).[10] Baird infrared spectrophotometer, model B; 0.10-mm. cell.

tra of a series of reference mixtures of IX and X of known composition were then determined.[10] By referring to these standards, it was possible to determine whether a single nitroisobutylene had been isomerized and to determine the relative concentration of each of the isomeric pair.

In order to determine whether IX and X are isomerized to a mixture of each other, pure IX and pure X were treated with excess aqueous sodium hydroxide and then acidified slowly with dilute acetic acid and then dilute hydrochloric acid at 0°. Reaction of IX by this sequence led to the recovery (72.5%) of a mixture containing 42% IX and 58% X (infrared spectra, Fig. 1-D); a similar series with X resulted in isolation of a mixture (37.5%) of the composition 50% IX and 50% X.[11] From the behavior of IX and X upon reaction with alkali and then acidification, it appears quite likely (equations 4) that reactions of IX and of X with sodium hydroxide resulted in formation of the same species, sodium 2-methyl-2-propenenitronate (XI); subsequent acidification of XI gave initially 2-methyl-2-propenenitronic acid (XII), tautomerism of which yielded mixtures of IX and X.

The formation of XI from IX or from X and its role in the rearrangement sequences was also inferred from the ultraviolet spectra of IX, of X, and of the

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[11] The poor recovery from these experiments may be related to the ease of hydration and subsequent decomposition of X in the presence of aqueous bases.

$$\begin{tikzcd}
\underset{\text{IX}}{H_2C{=}C(-CH_3)-CH_2NO_2} \arrow[d, shift right, "OH^-"'] & \underset{\text{XII}}{H_2C{=}C(-CH_3)-CH{=}NO_2H} \arrow[d, shift right, "^-OH"'] & \underset{\text{X}}{(H_3C)_2C{=}CHNO_2} \arrow[d, shift right, "^-OH"'] \\
H_2C{=}C(-CH_3)-\bar{C}HNO_2 \arrow[u, shift right, "H^+"'] \arrow[r, leftrightarrow] & \underset{\text{XI}}{H_2C{=}C(-CH_3)CH({=}NO_2^-)} \arrow[u, shift right, "H^+"'] \arrow[r, leftrightarrow] & H_2\bar{C}-(CH_3-)C{=}CHNO_2 \arrow[u, shift right, "H^+"']
\end{tikzcd} \qquad (1)$$

rearrangement mixtures of IX and X, respectively, in the presence of excess sodium hydroxide (Figs. 2-A, B and C). It was found that all three mixtures exhibited maximum absorption at 280 mμ which may be attributed to the conjugated nitronate ion, XI.[12] The ultraviolet spectra (Fig. 2-D) of an alkaline solution of 2-methyl-1-nitro-2-propanol,[13] a possible product from base-catalyzed reaction of X and water, illustrated entirely different characteristics with principal absorption at 233 mμ.[12]

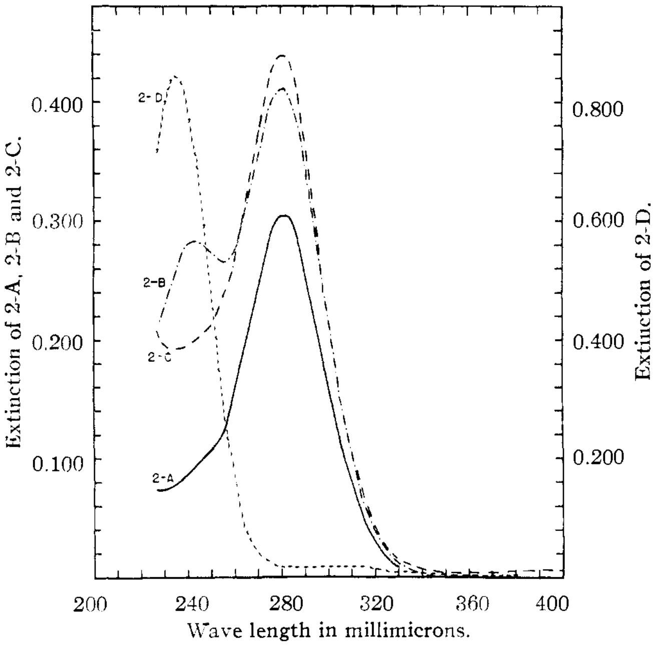

Fig. 2.—Ultraviolet absorption spectra of alkaline solutions of: 2-methyl-3-nitropropene (IX, curve 2-A, 2.70 × 10^{-5} *M*), 2-methyl-1-nitropropene (X, curve 2-B, 5.82 × 10^{-5} *M*), a mixture of 42% IX and 58% X (curve 2-C, 2.83 × 10^{-5} *M*), prepared by rearrangement of X, and 2-methyl-1-nitro-2-propanol (curve 2-D, 1.15 × 10^{-4} *M*); solvent, sodium hydroxide, 0.1 *N* in ethanol (50% by volume).

Evidence for the initial formation of XII and its subsequent tautomerization to IX and X was obtained by following the acidification (see Experimental) of aqueous solutions of XI potentiometrically. Upon addition of small quantities of acetic acid at 0°, the *p*H of the well-stirred mixture dropped instantly to a minimum value; however, the *p*H of the mixture then increased slowly and finally reached a much higher equilibrium value. These phenomena continued (for at least 3 hours) until the acidifications were almost complete. The slow change in acidity of freshly acidified salts of nitroalkanes is well known.[3] In general, acidification of alkanenitronates results mainly in rapid proton transfer to yield the alkanenitronic acid,[14] a relatively strong acid; subsequent reaction of alkanenitronate ions with the alkanenitronic acid[3d] or eventual recombination of the hydrogen and nitronate ions[3c,d] yields the isomeric nitroalkane, a relatively weak acid.[3] Since the properties of freshly acidified solutions of XI parallel those obtained from alkanenitronates, it is highly probable that XII is formed as a major but unstable intermediate. Whether the mechanisms of interconversion of IX, X, XI and XII are entirely analogous to those for tautomerism[3,14] of nitro and *aci*-nitroalkanes cannot be answered at present.

The rearrangements of IX and X were then investigated under conditions to give information concerning their possible equilibrium relationship. Upon storage in the presence of Pyrex glass and traces of dilute aqueous-methanolic potassium hydroxide, IX was isomerized at room temperature to a mixture of 18% IX and 82% X. Under approximately the same conditions X was isomerized to a mixture of 19% IX and 81% X. It is also of interest that the compositions of the mixtures of nitroisobutylenes obtained from reaction of 2-methyl-1-nitro-2-propyl acetate with sodium acetate and acetic acid (15.8% IX, 84.2% X) and from nitration of *t*-butyl alcohol (20% IX, 80% X) approximate those obtained by equilibrant-isomerization of IX and X.

The rearrangement of pure IX and of pure X into mixtures of IX and X of approximately identical compositions is interpreted to be evidence for the existence of an equilibrium between IX and X; the equilibrium is in favor of the conjugated nitro isomer X. The greater stability of X than of IX, in contrast to that of the system 1-nitromethylcyclohexene (V) and nitromethylenecyclohexane (VIII)[6] may be attributed primarily to conjugate and hyperconjugative resonance aspects rather than to steric considerations.

Acknowledgment.—The authors wish to express their thanks to Dr. Ralph B. Kaplan for providing the stimulus for inception of this research and for his many valuable comments throughout the investigation.

Experimental

2-Methyl-1-nitro-2-propyl Acetate.—Acetic anhydride (31.6 g., 0.31 mole, 20% excess) was added dropwise (20 min.) to a stirred mixture of 2-methyl-1-nitro-2-propanol[13] (31.0 g., 0.26 mole, b.p. 72–73° (7 mm.), $n^{20}\text{D}$ 1.4435, d^{20}_{20} 1.1357; lit.[7] $n^{20}\text{D}$ 1.443, d^{20}_{4} 1.132) and sulfuric acid (4 drops, 95% H_2SO_4) at a rate such as to maintain the temperature

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[12] Salts of simple mononitroalkanes usually exhibit principal absorption in the region of 233 mμ; absorption for salts of phenylnitromethane occurs principally at 291 mμ; G. Kortüm, *Z. physik. Chem.*, **B43**, 271 (1939).

[13] Prepared by the method of A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).

[14] Proton transfer to a mesomeric anion usually results first in formation of the tautomeric isomer which is the least stable thermodynamically; C. F. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 565.

of reaction at or slightly below 60°. After the addition had been completed, the mixture was kept at 60° for 30 min. Distillation of the mixture gave 2-methyl-1-nitro-2-propyl acetate (39.0 g., 0.24 mole) in 95% yield; b.p. (20 mm.), n^{20}_{D} 1.4305, d^{20}_{20} 1.249; lit.[7] n^{20}_{D} 1.432, d^{20}_{4} 1.123.

Reaction of 2-Methyl-1-nitro-2-propyl Acetate and Sodium Acetate.—A mixture of 2-methyl-1-nitro-2-propyl acetate (76.8 g., 0.477 mole) and finely-divided sodium acetate (4 g., 0.049 mole, anhydrous) in a Claisen distillation apparatus was heated gradually to 100° at a pressure of 50 mm.; the reaction mixture began to distil at a head temperature of 60°. After 39 g. of product had been removed, the pressure was lowered, and the remainder of the mixture (37 g.) was distilled at 72–80° (35 mm.). The distillate was added to an equal volume of water and an oily layer (39.7 g., 83% yield of nitroölefins) separated. The product was dissolved in ethyl ether and alternately washed with dilute sodium bicarbonate (2–4%) and saturated sodium chloride solutions until carbon dioxide was no longer evolved. The ether was stripped from the reaction product, and the residue was distilled at reduced pressures to give a mixture of 2-methyl-3-nitropropene (IX) and 2-methyl-1-nitropropene (X) (36.3 g., 76% yield), b.p. 60–61° (10 mm.), n^{20}_{D} 1.465.

The mixture of isomeric nitroisobutylenes obtained from a series of preparations was repeatedly rectified at a pressure of 25 mm. through a packed column (1 cm. × 45 cm., single turn glass helices) until the high and the low boiling components were of constant refractive index. The isomeric products obtained had the following properties: (1) 2-methyl-3-nitropropene (IX), b.p. 56° (25 mm.), n^{20}_{D} 1.4330, d^{20}_{20} 1.0191, *MR* (calcd.) 25.79, *MR* (found) 25.78; lit. b.p. 40–43° (13 mm.)[7]; and (2) 2-methyl-1-nitropropene (X), b.p. 72° (25 mm.), n^{20}_{D} 1.4710, d^{20}_{20} 1.0456, *MR* (calcd.) 25.79, *MR* (found) 27.01; lit. b.p. 45° (11 mm.)[7]; n^{17}_{D} 1.4723[15] and d^{0}_{0} 1.052.[4]

Reaction of 2-Methyl-2-propanol and Nitric Acid; 2-Methyl-3-nitropropene (IX) and 2-Methyl-1-nitropropene (X).—Fuming nitric acid (30 g.) was added to 2-methyl-2-propanol (30 g., 0.405 mole) at a rate such that the exothermic reaction maintained the mixture at rapid reflux. Extensive decomposition and polymerization of the mixture occurred during addition and reaction. Upon completion of the addition, the mixture was poured into water. The green oily product was separated and washed with water until the aqueous layer was not acidic; the oily product (2 g.) was yellow in color. The products resulting from six preparations were combined and distilled at reduced pressure to give a mixture (10.5 g.) of 2-methyl-3-nitropropene (IX, 20%) and 2-methyl-1-nitropropene (X, 80%), b.p. ~72° (25 mm.), n^{20}_{D} 1.4634. The composition of the mixture of isomeric nitroölefins was determined from its refractive index and infrared spectrum.

Reaction of Methallyl Bromide and Silver Nitrite; 2-Methyl-3-nitropropene (IX).—Methallyl bromide (69.0 g., 0.51 mole, b.p. 92–94°, n^{20}_{D} 1.4688, d^{20}_{20} 1.3222; lit.[16] n^{20}_{D} 1.46866, d^{20}_{4} 1.31335) was added dropwise in one hour at 0° to a stirred mixture of silver nitrite (116 g., 0.75 mole, recrystallized from hot water and dried in the dark over phosphorus pentoxide under vacuum), ethyl ether (anhyd., 250 ml.), and sea sand (150 g., washed and ignited). The stirred mixture was kept at 0° for 4 hours and at room temperature for 24 hours and then refluxed for 18 hours. The ether layer was decanted; the solid residue was extracted thoroughly with ethyl ether (100 ml.). The extracts were combined and washed with water, dilute sodium bicarbonate solution (2–4%), and saturated sodium chloride solution. After the ether had been removed, the residual oil was distilled at reduced pressure to give crude IX (26.0 g., b.p. 52–56° (25 mm.)); redistillation of the product gave 2-methyl-3-nitropropene (IX) (20.6 g., 0.204 mole) in 40% yield; b.p. 56° (25 mm.), n^{20}_{D} 1.4330.

Rearrangement of 2-Methyl-3-nitropropene (IX) with Excess Sodium Hydroxide and Subsequent Acidification.—2-Methyl-3-nitropropene (4.0 g., 0.04 mole) was added slowly to a stirred mixture of sodium hydroxide (1.8 g., 0.045 mole) and water (50 ml.) at 0°. After the mixture had been stirred for one hour at 0°, it was acidified by dropwise addition of acetic acid (50% by weight). The neutralization was followed continuously with a Macbeth *p*H meter. Upon addition of each drop of acetic acid, the *p*H dropped markedly (presumably) as a result of the instantaneous formation of 2-methyl-2-propenenitronic acid (XII), then increased slowly as the nitronic acid rearranged into its nitro isomers. The rate of addition was adjusted so that virtually complete rearrangement of the nitronic acid had occurred prior to the further addition of acid. When the *p*H of the mixture was not affected greatly upon addition of acid, acetic acid was added to decrease the *p*H of the mixture to 7 and then hydrochloric acid (10%) until the *p*H reached 6.5. The acidification procedure required 3.5 hours.

The acidified mixture was diluted with distilled water and then extracted with ethyl ether. The combined ether extracts were washed with distilled water and with sodium bicarbonate solution (2%) and then dried for 24 hours over sodium sulfate. Distillation of the extract, after removal of the ether at atmospheric pressure, yielded a mixture of 2-methyl-3-nitropropene (IX) and 2-methyl-1-nitropropene (X) (2.9 g., 72.5% recovery), b.p. 58–71° (25 mm.), n^{20}_{D} 1.4550. The infrared spectrum of the mixture contained bands characteristic of IX and X; no absorption for carbonyl groups was observed. On the basis of its refractive index, the mixture contained 42% IX and 58% X.

Isomerization of 2-Methyl-3-nitropropene (IX) Catalyzed by Traces of Potassium Hydroxide.—One drop of potassium hydroxide (5%) in methanol (80%) was added to 2-methyl-3-nitropropene (IX) (5.0 g., b.p. 56° (25 mm.), n^{20}_{D} 1.4330) in a Pyrex container. The refractive index of the mixture was checked immediately and found to be n^{20}_{D} 1.4329. The tube was sealed and stored at room temperature; the refractive index of the mixture was checked periodically. After 45 days, the liquid was yellow-colored and had a strong lachrymatory odor characteristic of 2-methyl-1-nitropropene (X). The mixture was distilled rapidly under nitrogen to give a volatile product (~5 g.) having the following physical constants: n^{20}_{D} 1.4580, b.p. 60–72° (25 mm.). The infrared spectrum of the mixture contained bands characteristic of IX and X. On the basis of its refractive index, the mixture contained 36% IX and 64% X.

The mixture was treated in a similar manner with methanolic potassium hydroxide for 30 days. After 5 days, the mixture had a deep red color. Distillation gave a mixture of IX and X, b.p. 63–71° (25 mm.), n^{20}_{D} 1.4638. On the basis of its refractive index, the mixture contained 19% 2-methyl-3-nitropropene (IX) and 81% 2-methyl-1-nitropropene (X).

Rearrangement of 2-Methyl-1-nitropropene (X) with Excess Sodium Hydroxide and Subsequent Acidification.—2-Methyl-1-nitropropene (X) (4.0 g. 0.04 mole, b.p. 72° (25 mm.), n^{20}_{D} 1.4697) containing 3% 2-methyl-3-nitropropene (IX) was added to a stirred solution of sodium hydroxide (1.8 g., 0.045 mole) and water (50 ml.) at 3°. After being stirred for 1.5 hours at 3°, the mixture was acidified by dropwise addition of acetic acid (50% by weight) in a manner similar to that described for IX. When the *p*H of the mixture was not affected greatly upon addition of acid, acetic acid was added to decrease the *p*H to 6.5 and then 10% hydrochloric acid until the *p*H reached 6.0. Six hours were necessary for completion of the acidification.

The mixture was diluted with water and then extracted with ethyl ether. The combined ether extracts were washed with dilute sodium bicarbonate solution (4%) and then with saturated sodium chloride solution. The ether was stripped, and the residual oil distilled to yield a mixture of IX and X (1.5 g., 37.5% recovery), b.p. 62–72° (25 mm.), n^{20}_{D} 1.4522. The infrared spectrum of the mixture contained bands characteristic of IX and X; no bands characteristic of carbonyl groups were present. The mixture contained 50% 2-methyl-3-nitropropene (IX) and 50% 2-methyl-1-nitropropene (X) on the basis of its refractive index.

Isomerization of 2-Methyl-1-nitropropene (X) Catalyzed by Traces of Potassium Hydroxide.—Potassium hydroxide (2 drops of 5% KOH in 80% methanol) was added to 2-methyl 1-nitropropene (X, 5.0 g., 0.05 mole, n^{20}_{D} 1.4694) containing 4% 2-methyl-3-nitropropene (IX) in a Pyrex container. The container was sealed and kept at 30° for 7 days. The mixture turned deep-red rapidly. The mixture was distilled rapidly under nitrogen to give a product (4.4 g.) having the following physical constants: n^{20}_{D} 1.4640, b.p. 65–72° (25 mm.). Infrared analysis of the mixture indicated the presence of IX and X; on the basis of its refractive index the material contained 18% 2-methyl-3-nitropropene (IX) and 82% 2-methyl-1-nitropropene (X).

COLUMBUS, OHIO

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