[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

N-Bromosuccinimide as a Dehydrogenating Agent[1]

BY RODERICK A. BARNES

The structure proof for most hydroaromatic compounds rests upon the fact that treatment with a dehydrogenating agent such as selenium, sulfur, platinum or palladium at temperatures of 250–450°, converts them to known aromatic substances. A large number of cases has accumulated in the literature in which the usual dehydrogenation process has been accompanied by rearrangements, migrations and ring closures. These render the use of such reagents of questionable value in an absolute structure proof.[2]

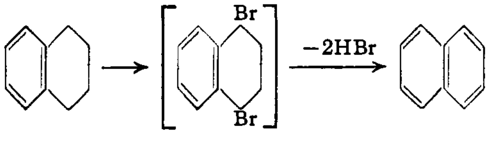
This investigation was undertaken in order to demonstrate the use of a low temperature bromination–dehydrobromination process for achieving dehydrogenation, with N-bromosuccinimide as a selective brominating agent.[3] A procedure has been developed which is satisfactory especially for compounds of the tetralin type which have one hydroaromatic ring attached to a benzenoid ring.

TABLE I

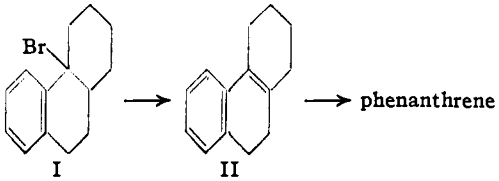
Compound	Product	Yield, %
Tetralin	Naphthalene	74
sym-Octahydroanthracene	Anthracene	69
Tetrahydrophenanthrene	Phenanthrene	79
sym-Octahydrophenanthrene	Phenanthrene	63
as-Octahydrophenanthrene	Phenanthrene	21
	1-Bromophenanthrene[a]	12
Dibenzyl	Stilbene	56
	Stilbene dibromide	10
Acenaphthene	Acenaphthylene	20
	Dihydroxyacenaphthene[b]	8
Decalin	1,5-Dibromonaphthalene	9
	x-Tetrabromo-9,10-octalin	14
Cyclohexene	*m*-Dibromobenzene	58
	p-Dibromobenzene	

[a] This product was isolated in only one experiment, phenanthrene being the only pure product in four subsequent experiments. [b] This substance must have resulted by reaction of the dibromide with water and alkali when the mixture was processed as for tetralin.

The preliminary bromination of tetralin can be completed before any appreciable dehydrobromination takes place, which indicates that a fairly stable dibromotetralin must be the intermediate.



In the case of *as*-octahydrophenanthrene, an immediate and exothermic reaction took place with evolution of large amounts of hydrogen bromide. This fact is in agreement with the properties to be expected of the tertiary bromide (I).

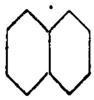


I II

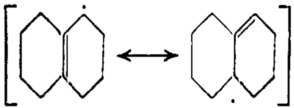
The relatively lower yield of phenanthrene in this case is probably due to the many possibilities for further reaction of the hexahydrophenanthrene (II). The fact that 1-bromophenanthrene was isolated in one experiment is in harmony with the results obtained with decalin. The structure of the brominated phenanthrene was proved by comparison with an authentic sample[4]; both samples were oxidized with chromic anhydride to yield 1-bromo-9,10-phenanthrenequinone[5] (m. p. 238–240°).

Equimolar amounts of decalin and N-bromosuccinimide reacted in the presence of benzoyl peroxide to form a tetrabromoöctalin as the major product. With 3.5–4.0 moles of N-bromosuccinimide a mixture of substances resulted from which there was isolated in addition to the tetrabromide, 1,5-dibromonaphthalene and a small amount of an isomer which melted at 76–78°.[6] The only evidence as to the structure of the tetrabromide was furnished by the observation that 9,10-octalin reacted readily with 4 moles of N-bromosuccinimide to yield the same tetrabromide; no hydrogen bromide was evolved in this reaction.

The formation of the tetrabromide from decalin is consistent with the idea that the N-bromosuccinimide bromination proceeds by way of a free radical intermediate.[7] Thus the intermediate (III) in the initial attack is stable only by virtue of its tertiary character, while the further reaction of 9,10-octalin in which the intermediate (IV) is a resonance-stabilized free radical, proceeds at a very much greater rate with resultant formation



III



IV

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[1] Presented in part at the Atlantic City meeting of the A. C. S., April, 1947.

[2] Linstead, *Ann. Repts. Chem. Soc.*, **33**, 294 (1936).

[3] Further work is in progress to test this method in cases where the usual dehydrogenations cause rearrangements.

[4] This sample was kindly furnished by Professor W. E. Bachmann: see Bachmann and Boatner, THIS JOURNAL, **58**, 2194 (1936).

[5] This is probably the same substance previously reported by Sandqvist, *Ber.*, **48**, 1149 (1915), m. p. 233–234°, and proved by him to be either 4- or 1-bromophenanthrenequinone. The bromophenanthrenequinone which melts at 126° must therefore be the 4-isomer.

[6] Although analytically pure this substance was never obtained in sufficiently large amounts to permit recrystallization to a pure isomer. 1,4-Dibromonaphthalene melts at 82°.

[7] Hey, *Ann. Repts. Chem. Soc.*, **41**, 191 (1944).

of a tetrabromide even with equimolar quantities of reactants.

Early attempts to aromatize cyclohexene by reaction with 2–3 moles of N-bromosuccinimide failed; however, 6 moles of the reagent produced a mixture of dibromobenzenes in 58% yield. The liquid mixture was found to be largely the meta isomer containing about one third of the solid para isomer. Since benzene does not react with N-bromosuccinimide at an appreciable rate, the dibromobenzenes must have resulted by aromatization of a dibromocyclohexene or dibromocyclohexadiene intermediate.[8]

Experimental[9]

sym-Octahydroanthracene and *sym*-octahydrophenanthrene were prepared by reaction of aluminum chloride with tetralin; they were separated and purified by the method of Schroeter.[10] *as*-Octahydrophenanthrene was prepared by cyclization of 1-β-phenylethyl-1-cyclohexanol with sulfuric acid[11] and 9,10-octalin was prepared according to the direction of Bartlett, Condon and Schneider.[12] The other hydrocarbons used in this work were purified commercial products.

The procedures used in carrying out the dehydrogenations are illustrated by the following examples.

Dehydrogenation of Tetralin.—A mixture of tetralin (250 mg.), N-bromosuccinimide (680 mg.), benzoyl peroxide (10 mg.) and carbon tetrachloride (15 ml.) was refluxed for thirty minutes. No hydrogen bromide was liberated during this time.[13] Potassium acetate (3 g.) and acetic acid (1 ml.) were added and the mixture refluxed for an additional half hour. The reaction mixture was poured onto ice and sodium hydroxide (2 g.). The product was isolated by ether extraction and evaporation of the solvents. The crude crystalline product was sublimed at atmospheric pressure to yield 180 mg. (74%) of pure naphthalene, m. p. and mixed m. p. 79–80°.

Dehydrogenation of *as*-Octahydrophenanthrene.—A solution of the hydrocarbon (0.93 g., n^{25}_{D} 1.5519) in carbon tetrachloride was refluxed with N-bromosuccinimide (3.56 g.), benzoyl peroxide (200 mg.), potassium acetate (4 g.) and acetic acid (5 ml.) for four hours. The reaction mixture was poured into water and extracted with benzene. The residue after evaporation of the solvents was sublimed at 20 mm. to give 445 mg. of a sticky solid which after two recrystallizations from methanol melted at 96.5–98°; yield 187 mg. (21%). A mixture of this sample and phenanthrene melted at 97–99°; both samples formed picrates which melted at 143–144° separately or when mixed.

The mother liquors from the crystallization contained an oil which gave a positive qualitative test for bromine, however, in all but one experiment no brominated compounds were isolated in pure form. This experiment differed from the others only in that the N-bromosuccinimide used (5.5 moles) was a finely powdered mixture containing 0.1 mole per cent of benzoyl peroxide which had been allowed to stand for several days before use. After sublimation and recrystallization from methanol there was isolated 320 mg. (12% based on 1.48 g. of hydrocarbon) of a substance which melted at 109–110°. A mixed melting point of this sample with an authentic sample of 1-bromophenanthrene[4] showed no depression. Both of the samples were oxidized with chromic anhydride in acetic acid to yield the same 1-bromophenanthrenequinone which melted at 238–240°.

Anal. Calcd. for $C_{14}H_7O_2Br$: C, 58.56; H, 2.46. Found: C, 58.98; H, 2.71. The melting point of a mixture of this substance with 2-bromophenanthrenequinone (m. p. 233–234°) prepared by bromination of phenanthrene[14] was 190–208°.

Reaction of Decalin with N-Bromosuccinimide.—A mixture of decalin (2.76 g.), N-bromosuccinimide (3.56 g.), benzoyl peroxide (200 mg.) and carbon tetrachloride (40 ml.) was refluxed until the solution became colorless (twenty minutes). The reaction mixture was washed with water and the carbon tetrachloride removed. The unchanged decalin was distilled on the water-pump, leaving a residue which crystallized on cooling. Two recrystallizations from ethyl acetate yielded *x*-tetrabromoöctalin which melted at 188–189°.

Anal: Calcd. for $C_{10}H_{12}Br_4$: C, 26.58; H, 2.68; Br, 70.74. Found: C, 25.97; H, 2.81; Br, 71.00.

x-Tetrabromoöctalin (1.35 g.) was the only product isolated from the reaction of 9,10-octalin (1.36 g.) with N-bromosuccinimide (7.12 g.). No hydrogen bromide was evolved in this reaction.

By reaction of decalin (5.0 g.) with 4 moles of N-bromosuccinimide there resulted a semi-solid product which was fractionally crystallized from ethyl acetate and ethanol to yield 2.3 g. (14%) of *x*-tetrabromoöctalin, 1.0 g. (9%) of 1,5-dibromonaphthalene (m. p. 127–129°) and 20 mg. of a substance which melted at 76–78°.

Anal. Calcd. for $C_{10}H_6Br_2$: C, 41.99; H, 2.11. Found: C, 41.54; H, 1.96.

The structure of 1,5-dibromonaphthalene was proved by comparison with an authentic sample prepared from 5-bromo-1-naphthylamine[15] by the method of Hodgson and Whitehurst.[16]

Reaction of Cyclohexene with N-Bromosuccinimide.—Cyclohexene (6.15 g.) was dissolved in carbon tetrachloride (75 ml.) and refluxed for twelve hours with N-bromosuccinimide (80 g.); benzoyl peroxide (3 g.) was added in several portions during this time. The carbon tetrachloride was removed and the residue washed with water, dried and distilled to yield 10 g. (58%) of crude dibromobenzenes which boiled at 215–225°. This material was redistilled at 22 mm. through a 45-cm. Podbielniak column, b. p. 102–103°.

Anal. Calcd. for $C_6H_4Br_2$: C, 30.55; H, 1.70. Found: C, 30.74; H, 1.68.

The redistilled product solidified at −15° and the last trace of solid had melted at 10°. A solution of the mixture (1.0 g.) in petroleum ether (20 ml.) was cooled to −30° and filtered quickly; this procedure was repeated to yield 185 mg. of *p*-dibromobenzene, m. p. and mixed m. p. 86–87°. The petroleum ether was removed from the filtrate and the residue treated with fuming nitric acid (8 ml.) at 0°. The reaction mixture was poured into water and the solid product was filtered and pressed dry on a porous plate, m. p. 55–57°. Crystallization from dilute methanol yielded 640 mg. of 2,4-dibromonitrobenzene which melted at 61.5–62°. This substance and 3,4-dibromonitrobenzene[17] (m. p. 58.5–59°) liquified when mixed at room temperature.

Summary

A procedure has been described for the conversion of hydroaromatic to aromatic compounds at a lower temperature than by the usual methods.

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(8) Ziegler, *et al.*, *Ann.*, **551**, 80 (1942), have reported that cyclohexadiene reacted only very slowly with N-bromosuccinimide; no monobromodiene was isolated.

(9) All melting points are corrected.

(10) Schroeter, *Ber.*, **57**, 1997 (1924).

(11) Perlman, Davidson and Bogert, *J. Org. Chem.*, 1, 288 (1936).

(12) Bartlett, Condon and Schneider, THIS JOURNAL, **66**, 1531 (1944).

(13) The liberation of hydrogen bromide during the reaction is characterized by the simultaneous appearance of an orange-red color due to the liberation of free bromine: N-bromosuccinimide + HBr ⇄ Br_2 + succinimide.

(14) Schmidt and Junghans, *Ber.*, **37**, 3558 (1904).

(15) Guareschi, *Ann.*, **222**, 297 (1883).

(16) Hodgson and Whitehurst, *J. Chem. Soc.*, 80 (1947).

(17) Holleman, *Rec. trav. chim.*, **25**, 198 (1906).

The first example of the reaction of N-bromosuccinimide with a saturated hydrocarbon has been reported.

NEW YORK, N. Y. RECEIVED AUGUST 5, 1947

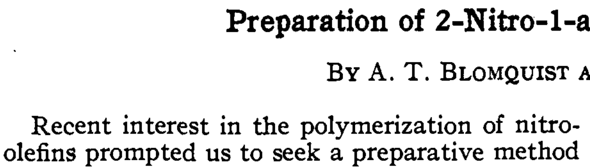
[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Preparation of 2-Nitro-1-alkenes from Nitro Amines[1]

BY A. T. BLOMQUIST AND T. H. SHELLEY, JR.[2]

Recent interest in the polymerization of nitroolefins prompted us to seek a preparative method for 2-nitro-1-alkenes which would be more generally useful in the laboratory than those methods which we had previously employed.[3,4] Although nitro amines derived from nitroparaffins have been studied extensively by a number of investigators[5–9] there is no recorded study of the use of those substances as intermediates for the synthesis of olefinic derivatives. The excellent account of the application of a wide variety of Mannich bases to the synthesis of olefinic compounds[10] suggested that suitable nitro amines prepared from 1-nitroalkanes should afford 2-nitro-1-alkenes on pyrolysis.

Accordingly, the synthetic method outlined in the succeeding formulation was studied for the series of straight-chain 1-nitroalkanes from nitromethane through 1-nitrohexane.



$$R_2NH + CH_2O \longrightarrow R_2N{-}CH_2OH$$

$$R'CH_2NO_2 + R_2N{-}CH_2OH \longrightarrow R'\underset{NO_2}{CH}{-}CH_2{-}NR_2 + H_2O$$

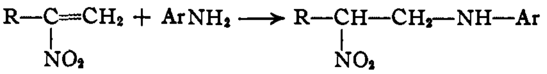
$$R'{-}\underset{NO_2}{CH}{-}CH_2{-}NR_2{\cdot}HCl \xrightarrow{\text{heat}} R'{-}\underset{NO_2}{C}{=}CH_2 + R_2NH{\cdot}HCl$$

Following the procedure of Cerf,[6] Senkus[8] and of Johnson,[9] nitro amines derived from diethylamine, formaldehyde and the 1-nitroalkanes 1-nitropropane through 1-nitrohexane were obtained readily in excellent yield (70–80%) as colorless to pale-yellow liquids which could be distilled without decomposition under reduced pressure. The base derived from nitroethane and diethylamine, however, decomposed violently when its distillation was attempted. By substituting piperidine for diethylamine nitroethane formed a nitroamine which could be purified by distillation without difficulty. Nitromethane, under all conditions studied, afforded only a di-substituted base when treated with N-hydroxymethylpiperidine.

Pyrolysis of the free nitro amines derived from the nitroparaffins was not regarded as a suitable method for obtaining the desired nitroölefins for several reasons. Nitroölefins are known to be reactive toward amines[11,12] and their polymerization is catalyzed by bases.[3] On the other hand, pyrolysis of the nitro amine hydrochlorides would obviate these difficulties. It was observed that thermal decomposition of the several nitro amine hydrochlorides proceeded smoothly and rapidly at moderate temperatures. Initial decomposition started at temperatures in the neighborhood of 100–115° and was complete by gradually raising the pyrolysis temperature to 165–175°. By carrying out the decompositions under reduced pressure (50–100 mm.) the nitroölefins were all removed rapidly from the zone of heating. The several nitroölefins were obtained as blue-green, lachrymatory liquids in excellent yield after purification by redistillation (70–80%).

Since it was not possible to convert nitromethane into a suitable nitro amine, nitroethylene could not be prepared by the procedure described above.

In searching for solid derivatives which might be used to characterize the 2-nitro-1-alkenes attention was given the reaction of aromatic amines with nitroölefins first reported by Wieland and Sakellarios[11] and extended by Worrall.[12] According to these investigators primary aromatic amines should add to the 2-nitro-1-alkenes as follows



$$R{-}\underset{NO_2}{C}{=}CH_2 + ArNH_2 \longrightarrow R{-}\underset{NO_2}{CH}{-}CH_2{-}NH{-}Ar$$

p-Toluidine added rapidly and smoothly to the nitroölefins affording solid crystalline derivatives which were easily purified. Unfortunately, the melting points of all of the *p*-toluidine derivatives prepared were found to lie in a rather narrow temperature range (*ca.* 68–82°).

Some evidence bearing on the structure of these derivatives was obtained through an independent synthesis of one of them, namely, N-(2-nitrobutyl)-*p*-toluidine. It was prepared di-

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(1) This paper is an abstract of part of the doctoral dissertation presented by T. H. Shelley, Jr., to the Graduate Faculty of Cornell University in June, 1947.

(2) Allied Chemical and Dye Fellow in Chemistry, 1946–1947.

(3) Blomquist, Tapp and Johnson, THIS JOURNAL, 67, 1519 (1945).

(4) An excellent summary of other methods of preparing nitroolefins is given in the recent article by Gold, *ibid.*, 68, 2544 (1946).

(5) Henry, *Bull. classe sci., Acad. roy Belg.*, [3] 32, 36 (1896); [3] 33, 412 (1897).

(6) Cerf, *Bull. soc. chim. France*, [5] 4, 1451, 1460 (1937).

(7) Duden, Bock and Reid, *Ber.*, 38, 2036 (1905).

(8) Senkus, THIS JOURNAL, 68, 10 (1946).

(9) Johnson, *ibid.*, 68, 12 (1946); 68, 14 (1946).

(10) Blicke, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 303.

(11) Wieland and Sakellarios, *Ber.*, 52, 903 (1919).

(12) Worrall, THIS JOURNAL, 43, 919 (1921); *ibid.*, 49, 1598 (1927).