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

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

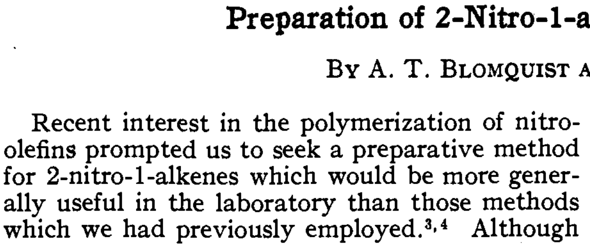
[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

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.



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

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

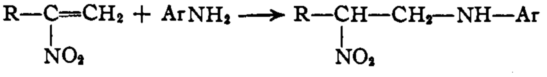
$$\underset{NO_2}{R'{-}CH}{-}CH_2{-}NR_2{\cdot}HCl \xrightarrow{\text{heat}} \underset{NO_2}{R'{-}C}{=}CH_2 + R_2NH{\cdot}HCl$$

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



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

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).

rectly from 1-nitropropane by condensation with one mole each of *p*-toluidine and formaldehyde according to the method of Johnson.[9] Treatment of 1-nitropropane with two moles of *p*-toluidine and of formaldehyde gave a di-substituted *p*-toluidine derivative, 2-nitro-2-ethyl-1,3-bis-(*p*-toluino)-propane.

Acknowledgment.—The authors wish to express their gratitude to Miss Lois Ann Capella who assisted in much of the preparative and analytical work.

Experimental[13]

Nitroparaffins.—Nitromethane, nitroethane and 1-nitropropane, obtained from the Commercial Solvents Corporation, were freshly distilled before use.

1-Nitrobutane, 1-nitropentane and 1-nitrohexane were prepared by the method of Victor Meyer.[14]

Nitro Amines.—These were prepared by the condensation of the appropriate nitroparaffin with a suitable N-hydroxymethylamine. The preparation of N-(2-nitrobutyl)-diethylamine illustrates the general procedure.

To a solution of 73 g. (1 mole) of redistilled diethylamine in an equal volume of water contained in a 1-liter flask fitted with stirrer, thermometer, dropping funnel and condenser there was added dropwise with rapid stirring 84 cc. (1.0 mole) of formalin (36% solution) over a period of half an hour. The temperature was maintained at 18° during the addition. The reaction mixture was then stirred at room temperature for an additional half hour after the addition of formalin was completed. To this aqueous solution of the N-hydroxymethylamine there was added all at once with rapid stirring 89 g. (1 mole) of 1-nitropropane. This addition was accompanied by an 8–10° rise in temperature. Rapid stirring of the mixture was continued for three to four hours. The two-layer mixture was then extracted with 100 cc. of ether, and the aqueous layer again extracted with 20 cc. of ether following the addition of 10 g. of sodium chloride. The ether solutions were combined, dried with anhydrous magnesium sulfate and distilled under reduced pressure. After removal of the ether the nitro amine was obtained by distillation at 2 mm. pressure under nitrogen. **N-(2-Nitrobutyl)-diethylamine**, 138 g. (79%), was obtained as a pale yellow liquid; b. p. 79° (2 mm.), n^{20}D 1.4405.

Anal. Calcd. for $C_8H_{18}N_2O_2$: mol. wt., 174. Found (by titration): mol. wt., 178, 180.

Some decomposition occurred when the product was distilled at 14 mm. as described by Cerf.[6]

Using the procedure outlined above, the following nitroamines were prepared in 70–75% yield.

N-(2-Nitroamyl)-diethylamine; b. p. 84° (1 mm.), n^{20}D 1.4421. *Anal.* Calcd. for $C_9H_{20}N_2O_2$: mol. wt., 188. Found (by titration): mol. wt., 191, 186.

N-(2-Nitrohexyl)-diethylamine; b. p. 91–93° (1 mm.), n^{20}D 1.4447. *Anal.* Calcd. for $C_{10}H_{22}N_2O_2$: mol. wt., 202. Found (by titration): mol. wt., 204, 202.

N-(2-Nitroheptyl)-diethylamine; b. p. 102–103° (1 mm.), n^{20}D 1.4465. *Anal.* Calcd. for $C_{11}H_{24}N_2O_2$: mol. wt., 216. Found (by titration): mol. wt., 222, 220.

N-(2-Nitropropyl)-diethylamine.—This base derived from nitroethane, when prepared by the general procedure, decomposed violently when attempts were made to distil it at low pressures (1 mm.). However, a product of reasonable purity was obtained by working up the usual reaction mixture from nitroethane and N-hydroxymethyl-diethylamine in the following manner. The organic layer was washed three times with cold water, dried over Drierite in the refrigerator for fourteen hours, and finally stripped of low-boiling material by heating to 45° for forty-five minutes under nitrogen at 2 mm. This gave an 83% yield of a golden-yellow liquid; n^{25}D 1.4420, d^{20}_4 0.9751; *MR*D calcd., 44.1; found, 43.1.

N-(2-Nitropropyl)-piperidine.—This base derived from nitroethane and N-hydroxymethylpiperidine was obtained in 41% yield and could be distilled; b. p. 87° (1 mm.), n^{20}D 1.4469.

Anal. Calcd. for $C_8H_{16}N_2O_2$: mol. wt., 171. Found (by titration): mol. wt., 178, 176.

2-Nitro-2-methyl-1,3-bis-(N-piperidyl)-propane.—This substance was formed as an accessory product in the preparation of N-(2-nitropropyl)-piperidine and was isolated as a residue in the distillation of the nitropropylpiperidine. From a 0.5 mole run there was obtained 6 g. of solid material which after crystallization from ethyl alcohol melted at 101.5–102°.[15]

Anal. Calcd for $C_{14}H_{27}N_3O_2$: N, 15.60. Found: N, 15.75.

2-Nitro-1,3-bis-(N-piperidyl)-propane.—All attempts to effect the condensation of nitromethane with N-hydroxymethylamines in a 1:1 mole ratio were unsuccessful. Regardless of the proportion of reactants and the mode of addition nitromethane always condensed with 2 moles of the N-hydroxymethylamine. Thus with N-hydroxymethylpiperidine only 2-nitro-1,3-bis-(N-piperidyl)-propane was formed. Henry[16] claims to have prepared this compound but did not describe its preparation and properties, nor did he report its analysis.

Addition of 0.5 mole of nitromethane to an aqueous solution containing 0.5 mole of N-hydroxymethylpiperidine gave 54 g. (85% based on the amine) of crude product which was obtained as light tan crystals from ethyl alcohol, m. p. 93.5–94°.

Anal. Calcd. for $C_{13}H_{25}N_3O_2$: C, 61.14; H, 9.85; N, 16.46; mol. wt., 255. Found: C, 61.26; H, 9.90; N, 16.57; mol. wt. (cryoscopic in benzene), 253.

This substance was also prepared by adding 2 g. of piperidine to a solution of 1 g. of 2-nitro-1,3-propanediol in 10 cc. of methyl alcohol. After refluxing the mixture for two hours, 1 g. of crystalline material separated on cooling which, after recrystallization from ethyl alcohol, melted at 93.5–94°. A m. p. of a mixture of this preparation and the material obtained from nitromethane showed no depression.

2-Nitro-1-alkenes.—The nitroölefins were obtained by pyrolysis of the respective nitro amine hydrochlorides under reduced pressure. By operating under reduced pressure the nitroölefin was removed rapidly from the zone of heating and losses resulting from thermal polymerization were minimized. As the various nitroölefins were prepared by essentially the same procedure only one of these is described in detail.

2-Nitro-1-pentene.—The hydrochloride of N-(2-nitroamyl)-diethylamine was prepared by passing dry hydrogen chloride for four hours into a cooled stirred solution of 58.2 g. (0.31 mole) of the amine in four times its volume of dry toluene. The initially formed white precipitate later redissolved upon the continued passage of the hydrogen chloride to yield a blue-green solution.[17] This solution was transferred to a 500-cc. Claisen flask and after removal of the toluene and excess hydrogen chloride by heating with a water-bath (final bath temperature 70°) at 50 mm. pressure a white solid remained. Heating was then continued with an oil-bath and at a regulated pressure of 100 mm. The solid began to melt at 90° while at 115–120° it started to decompose smoothly to yield a blue-green liquid distilling at 110–115° (vapor temperature). The pyrolysis was complete within forty-five

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[13] All melting points and boiling points are uncorrected.

[14] Meyer, *et al.*, *Ann.*, 171, (1874): 175, 88 (1875); 180, 111 (1876).

[15] Henry reported a m. p. of 98–99°; *cf.* ref. 4.

[16] Henry, *Ber.*, 38, 2027 (1905).

[17] This curious solubility behavior was also observed for the nitro amine hydrochlorides derived from 1-nitropentane and 1-nitrohexane. In preparing the hydrochloride of N-(2-nitrobutyl)-diethylamine in toluene two liquid layers were formed. The hydrochloride of N-(2-nitropropyl)-piperidine separated quantitatively from toluene as a crystalline solid.

minutes with the final temperature within the flask being 165°. The crude distillate, 35.2 g. (99%), was dissolved in ether, the ether solution washed with water and dried over anhydrous magnesium sulfate in the refrigerator. After removal of the ether the crude product was distilled under reduced pressure using a 14 × 0.75 in. column packed with 0.75 in. glass helices. There was obtained 25 g. (75%) of pure product; b. p. 68° (50 mm.), $n^{20}\text{D}$ 1.4403.

Anal. Calcd. for $C_5H_9NO_2$: N, 12.17. Found: N, 12.28.

The residue in the pyrolysis was shown to be diethylamine hydrochloride by its m. p. after crystallization from ethyl alcohol (220–224°, lit. 215–223°) and conversion to its benzenesulfonyl derivative, m. p. 59–60°.

2-Nitropropene was obtained similarly by pyrolysis at 105–160° of the hydrochloride of N-(2-nitropropyl)-piperidine under 70 mm. pressure in 50% yield. It was identical with the 2-nitropropene prepared by other methods.[3]

2-Nitro-1-butene was obtained in 73% yield by pyrolysis of the hydrochloride of N-(2-nitrobutyl)-diethylamine at 100–175° under 100 mm. pressure; b. p. 60.5° (50 mm.), $n^{20}\text{D}$ 1.4356. It was identical with an authentic sample of 2-nitro-1-butene synthesized by pyrolysis of the benzoate of 2-nitro-1-butanol.[18]

2-Nitro-1-hexene was obtained in 70% yield by pyrolysis of N-(2-nitrohexyl)-diethylamine at 105–165° under 50 mm. pressure; b. p. 81–82° (50 mm.), $n^{20}\text{D}$ 1.4462.

Anal. Calcd. for $C_6H_{11}NO_2$: N, 10.86. Found: N, 10.89.

2-Nitro-1-heptene was obtained in 70% yield by pyrolysis of N-(2-nitroheptyl)-diethylamine at 110–150° under 50 mm. pressure; b. p. 93–94° (30 mm.), $n^{20}\text{D}$ 1.4482.

Anal. Calcd. for $C_7H_{11}NO_2$: N, 9.76. Found: N, 9.85.

p-Toluidine Derivatives of the 2-Nitro-1-alkenes.—Solid derivatives of the nitroölefins were readily obtained through reaction with *p*-toluidine. The general procedure used in their preparation is described. To 5 g. of the pure 2-nitro-1-alkene, cooled to 0–5°, there was added an equivalent amount of *p*-toluidine. The solution became warm and deep red in color. After maintaining the reaction mixture at 60° for five minutes it was cooled to room temperature and the crude product crystallized. Pure derivatives, as bright yellow solids, were obtained in 80–95% yield after one recrystallization from ethyl alcohol. These compounds are listed in Table I.

TABLE I

N-(2-NITROALKYL)-*p*-TOLUIDINES

Compound, *p*-toluidine	M. p., °C.	N analyses, % Calcd.	N analyses, % Found
N-(2-Nitropropyl)-	81.5–82.5	14.42	14.38
N-(2-Nitrobutyl)-	67.5–68.5	13.45	13.37
N-(2-Nitroamyl)-	72 –72.5	12.60	12.86
N-(2-Nitrohexyl)-	68.5–69	11.86	12.18
N-(2-Nitroheptyl)-	72.5–73.5	11.19	11.51

The *p*-toluidine derivatives of samples of 2-nitropropene and 2-nitro-1-butene prepared by other methods[3] were identical with those described in Table I.

N-(2-Nitrobutyl)-*p*-toluidine (Table I) was also prepared by an independent method. Using the procedure of Johnson,[9] 1-nitropropane, formaldehyde and *p*-toluidine reacted to give a 26% yield of the crude *p*-toluidine derivative, m. p. 60–66°. After recrystallization from methanol its m. p., 67.5–68.5°, was not depressed when mixed with the toluidine derivative prepared from 2-nitro-1-butene.

2-Nitro-2-ethyl-1,3-bis-(*p*-toluino)-propane, a di-substituted *p*-toluidine derivative, was prepared as a check on the mono-substituted derivative described above. To a refluxing mixture of 107 g. (1 mole) of *p*-toluidine, 44.5 g. (0.5 mole) of 1-nitropropane, 1 g. of potassium hydroxide and 300 cc. of ethyl alcohol, 82 g. (1 mole) of 37% formalin solution was added over a period of six hours. After refluxing an additional two hours and standing at room temperature for two days the mixture was cooled in ice and filtered. There was obtained 35 g. (25%) of light tan crystals melting at 101–102° which were recrystallized from ethyl alcohol, m. p. 103–104°.

Anal. Calcd. for $C_{19}H_{25}N_3O_2$: N, 12.84. Found: N, 12.73.

Summary

A series of 2-nitro-1-alkenes has been readily obtained by thermal decomposition of appropriate nitro amine hydrochlorides derived from 1-nitroalkanes.

The 2-nitro-1-alkenes may be characterized by crystalline solid derivatives formed by their reaction with *p*-toluidine.

ITHACA, N. Y. RECEIVED JULY 28, 1947

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[18] Tapp, Thesis, Cornell University, 1943.

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

Reactions with Tetraphenylcyclopentadienone. II. Condensation with 1-Phenyl-1,3-butadiene[1]

BY OLIVER GRUMMITT AND ERNEST I. BECKER[2]

2,3,4,5-Tetraphenylcyclopentadienone (tetracyclone) is of interest in diene chemistry through its addition reactions with α,β-unsaturated carbonyl compounds[3] and with conjugated dienes.[4,5] In the case of butadiene the adduct contains two tetracyclone groups as the result of 1,2 and 3,4 addition at the 2,5 positions of the tetracyclone ring.[4] With cyclopentadiene only one tetracyclone reacts, the addition occurring at the 2,3 double bond and at the 2,5 positions of tetracyclone.[5]

These addition reactions are usually considered

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[1] Presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, April 15, 1947.

[2] Sherwin-Williams Research Fellow in Organic Chemistry, 1946. Present address: Polytechnic Institute of Brooklyn, Brooklyn, New York.

[3] For example, with maleic anhydride: *cf.* Dilthey, Schommer, and Trosken, *Ber.*, **66B**, 1627 (1933), and Allen and Sheps, *Can. J. Research*, **11**, 171 (1934).

[4] Dilthey, Schommer, Hoschen and Dierichs, *Ber.*, **68B**, 1159 (1935).

[5] Grummitt, Klopper and Blenkhorn, THIS JOURNAL, **64**, 604 (1942).