propanol and 26.2 g. (0.1 mole) of bis-(dimethyallylamino)-methane in 36 ml. of dioxane and 15 ml. of water was heated on a steam-bath with stirring for two hours. The organic layer was separated, dried and distilled; b.p. 102° (3 mm.), $n^{22}{}_D$ 1.4710, $d^{22}{}_4$ 0.9056. A comparison of the properties of this product with those of the pure Mannich base and bis-(dimethallylamino)-methane shows that the Mannich base is the chief product. The infrared spectrum was identical to that obtained above for the Mannich base.

Because of the proximity of the boiling points of the Mannich base in this case and the bis-(dimethallylamino)-methane, a sample of the above product, 29 g., was treated with 4 g. of 98% formic acid and 6 g. of 37% formaldehyde to convert any unreacted bis-(dimethallylamino)-methane to methyldimethallylamine or a mixture of this amine and dimethallylamine, which easily could be separated from the Mannich base by distillation. This is a special modification of the Leuckart reaction described by Clarke, Gillespie and Weisshaus.[10] The product isolated by distillation differed only in insignificant amounts in physical properties from the pure Mannich base, and the infrared spectra were identical, indicating that the reaction of the methylenediamine with 2-methyl-2-nitro-1-propanol goes to completion.

Acknowledgment.—One of the compounds studied, N,N′-bis-(2-methyl-2-nitropropyl)-piperazine, was first prepared by the author by procedure (a) while employed by Rohm and Haas Co., Inc., Philadelphia, Pa., under the terms of OSRD Contract No. OEMsr-643. The analysis is by the R & H analytical laboratory. Permission to use this information has been granted by both Rohm and Haas Co. and the appropriate clearing agency for OSRD. Other analyses reported are by Peninsular ChemResearch, Inc., Gainesville, Fla., and the infrared spectra are by Mr. Robert S. Silas of this Laboratory.

GAINESVILLE, FLORIDA

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[10] H. T. Clarke, H. B. Gillespie and S. Z. Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Condensations of Nitroparaffins with Aldehydes. Preparation of γ-Dinitroparaffins[1]

BY G. BRYANT BACHMAN AND MARK T. ATWOOD[2]

RECEIVED JANUARY 29, 1955

The condensation of primary nitroparaffins with formaldehyde in the presence of small amounts of secondary amines to give γ-dinitroparaffins is reported. Only basic catalysts capable of forming Mannich base intermediates give good yields, although low yields are obtained even with a tertiary amine and with sodium carbonate. Diastereomers have been separated and shown to be interconvertible in the presence of base.

Relatively few γ-dinitroparaffins are known. Hass[3] and others have condensed ketones with nitromethane to give compounds of the general structure $R_2C(CH_2NO_2)_2$. The condensation of nitroparaffins with nitroölefins has been utilized to prepare a few γ-dinitroparaffins.[4] Snyder and Hamlin[5] reacted Mannich type bases from primary nitroparaffins with nitroparaffins to obtain 3,5-dinitroheptane and 2-methyl-2,4-dinitrohexane. Heim[6] condensed benzaldehyde with phenylnitromethane to obtain 1,3-dinitro-1,2,3-triphenylpropane.

It seemed to us that simple basic catalysis should be adequate to bring about a quite general condensation between the active methylene group of primary nitroparaffins and the carbonyl group of aldehydes, especially formaldehyde, to form γ-dinitro compounds. Accordingly, we have treated mixtures of two moles of various nitroparaffins and one mole of formaldehyde with catalytic amounts of primary, secondary and tertiary amines as well as with sodium carbonate and obtained the expected γ-dinitro compounds. The yields were best (up to 30%) when secondary amine catalysis was used, and we have therefore devised a reaction sequence involving secondary amines to explain the formation of γ-dinitroparaffin products.

$$R_2NH + CH_2O + RCH_2NO_2 \longrightarrow RCH(NO_2)CH_2NR_2 \quad (A)$$

$$RCHNO_2CH_2NR_2 \longrightarrow RCNO_2{=}CH_2 + R_2NH \quad (B)$$

$$RC(NO_2){=}CH_2 + RCH_2NO_2 \longrightarrow RCH(NO_2)CH_2CH(NO_2)R \quad (C)$$

However, the fact that a carefully purified tertiary amine and sodium carbonate were also found to catalyze the formation of γ-dinitroparaffins makes it necessary to propose a somewhat different mechanism for the formation of the intermediate nitroölefins in such cases.

$$RCH_2NO_2 + CH_2O \longrightarrow RCHNO_2CH_2OH \quad (D)$$

$$RCHNO_2CH_2OH \longrightarrow RCNO_2{=}CH_2 + H_2O \quad (E)$$

The relative ease of reaction (B) as compared to (E) probably accounts for the better results obtained with secondary amine catalysis. It should be noted that others[7] have stated that Mannich-like bases are unlikely intermediates in the condensation of nitromethane with acetone. However our results clearly imply the presence of such intermediates in the condensation of higher nitroparaffins with formaldehyde.

In accord with the above proposals, secondary and tertiary nitroparaffins do not undergo this reaction, because they are incapable of forming the necessary nitroölefin intermediates. Instead, the reaction appears to stop with the formation of a nitroalcohol in the case of secondary nitroparaffins. Thus, 2-nitropropane, formaldehyde and small

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[1] Presented before the Organic Division of the American Chemical Society at the Cincinnati meeting, March, 1955.

[2] From the Ph.D. thesis of M. T. Atwood, Purdue University, August, 1954. Commercial Solvents Corporation fellow, 1952–1954.

[3] H. B. Hass and J. Bourland, U. S. Patent 2,343,256 (March 7, 1946); M. S. Larrison and H. B. Hass, U. S. Patent 2,383,603 (August 28, 1945); H. B. Fraser and G. A. R. Kon, *J. Chem. Soc.*, 604 (1934).

[4] A. Lambert and H. A. Piggott, *ibid.*, 1489 (1947); also British Patent 584,789 (January 23, 1947); A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947); also British Patent 589,515 (June 23, 1947).

[5] H. R. Snyder and W. E. Hamlin, THIS JOURNAL, **72**, 5082 (1950).

[6] F. Heim, *Ber.*, **44**, 2016 (1911).

[7] A. Lambert and A. Lowe, *J. Chem. Soc.*, 1518 (1947).

TABLE I

γ-DINITROPARAFFINS

Compound	M.p., °C.	Yield, %[d]	Analyses, %					
			Carbon		Hydrogen		Nitrogen	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
$(CH_3CHNO_2)_2CH_2$[a]	43–44	4.0	37.03	36.82	6.22	6.10	17.28	17.37
$(CH_3CH_2CHNO_2)_2CH_2$[a,c]	32	20	44.20	44.35	7.42	7.64	14.73	14.86
$(CH_3CH_2CH_2CHNO_2)_2CH_2$[b]	55–56	20.7	49.52	49.42	8.31	8.12	12.87	12.92
$[(CH_3)_2CHCH_2CHNO_2]_2CH_2$	121–122	15.7	53.63	53.87	9.00	9.23	11.37	11.29
$[(CH_3)_2CHCH_2CHNO_2]_2CH_2$	55–57	13.3	53.63	53.82	9.00	9.04	11.37	11.29
$(n\text{-}C_6H_{13}CHNO_2)_2CH_2$	70	13.0	59.57	59.37	10.00	9.95	9.26	9.28
$(n\text{-}C_6H_{13}CHNO_2)_2CH_2$	44	12.0	59.57	59.49	10.00	10.10	9.26	9.49

[a] Only isomer found. [b] A liquid diastereomeric form was apparently isolated in 13.3% yield; $n^{20}{}_D$ 1.4432, $d^{20}{}_{20}$ 1.075, M_D calcd. 54.22, found 54.0. Unfortunately it decomposed before elemental analyses could be performed. [c] Snyder and Hamlin[5] report m.p. 30°. [d] Based on nitroparaffin consumed.

amounts of diethylamine yielded 2-methyl-2-nitropropanol as the only product.

Replacement of formaldehyde by acetaldehyde and chloral in the reaction with 1-nitropropane and diethylamine gave none of the expected γ-dinitroparaffin. With chloral the only product isolated was 1,1,2-trichloro-3-nitro-2-pentanol. Replacement of the nitroparaffin and formaldehyde by a β-nitroalcohol led successfully to dinitroparaffins. However, preformation of the nitroalcohol did not guarantee that the nitroparaffin radical it contained would be found in the principal dinitroparaffin produced. Thus we found that the reaction of 2-nitro-1-butanol with 1-nitrobutane gave largely 4,6-dinitrononane instead of 3,5-dinitroöctane.

$$CH_3(CH_2)_3NO_2 + CH_3CH_2CHNO_2CH_2OH \xrightarrow{(C_2H_5)_2NH} (CH_3(CH_2)_2CHNO_2)_2CH_2 + CH_3(CH_2)_2NO_2 \quad (F)$$

This indicates that the base-catalyzed equilibria involved between nitroalcohols and their corresponding nitroparaffins and aldehydes are so rapidly established that the final product of this synthesis is independent of which nitroalcohol of a given pair is used initially.

Inspection of the structural formulas of the γ-dinitroparaffins reveals that two centers of asymmetry exists in each and that these products should be separable into diasteromeric pairs. Previous investigators have not mentioned this fact nor have they described more than one product from each of their reactions. The diasteromers of 7,9-dinitropentadecane were separated by fractional crystallization from 95% ethanol and formed two solids; one, white plates, m.p. 70–71°, the other, small cubes, m.p. 44°. Treatment of either isomer with a base, such as n-butylamine, converted it into a mixture of the two forms. The diastereomers of 2,8-dimethyl-4,6-dinitrononane, exist in a liquid and a solid form. Isomeric forms of the other γ-dinitroparaffins prepared were not observed although they were probably present in small amounts.

The dinitro compounds prepared are listed in Table I together with their properties, analyses and yields.

Experimental

Preparation of γ-Dinitroparaffins.—The general procedure involved heating a mixture of 2 to 3 moles of nitroparaffin, 1 mole of paraformaldehyde and about 0.05 mole of catalyst to reflux for several hours, cooling, neutralizing with acid and distilling off low boiling materials under vacuum. The high boiling residue was steam distilled in the preparations of 2,4-dinitropentane and 3,5-dinitroheptane, and the expected products were isolated from the steam distillate by vacuum distillation and recrystallization from ether at Dry Ice temperature. The higher γ-dinitroparaffins were isolated from the high boiling residue by cooling to crystallization and filtering. In each preparation a considerable amount of tar was produced. This tar was believed to be composed mainly of polymerized nitroölefins.

Removal of water during the course of the reaction by azeotropic distillation with added benzene did not materially alter the yields of desired products, but did serve to indicate when the reaction was approaching completion by the amount of water collected.

Mono- and dibutylamines as well as piperidine were all used successfully although diethylamine was generally preferred because it gave higher yields.

The low yield obtained from nitroethane and the failure of the reaction with nitromethane can be attributed in part to the great ease of polymerization under basic conditions of the nitroölefin intermediates formed from these reagents. Nitroethane (from nitromethane and formaldehyde) is especially rapidly polymerized.

The Reaction between 1-Nitropropane, Formaldehyde and Triethylamine.—The object of this experiment was to see if a catalyst incapable of forming a Mannich base intermediate could catalyze the reaction in question. Commercial triethylamine was rigorously purified by treating its hydrochloric acid salt with sodium nitrite in aqueous solution and extracting the resultant solution with ether. This procedure should destroy any primary amine and cause the removal of any secondary amine by converting it into the nitrosamine, removable by extraction with ether. The remaining aqueous solution was then made basic with aqueous sodium hydroxide solution and extracted with ether. The combined ether extracts were dried over sodium sulfate. The ether was distilled off, and the remaining triethylamine was fractionated in a Todd Precise Fractionation Assembly packed with glass helices, at a reflux ratio of 50:1. About 20 ml. of liquid boiling at 89.5° was collected, $n^{20}{}_D$ 1.40023. This material did not give any of the qualitative tests for primary or secondary amines and showed no evidence for N–H bonding on infrared analysis.

The procedure was the same as that used in the preceding experiments. A white, crystalline solid, 3,5-dinitroheptane, was obtained in a conversion of 1.3% and yield of 1.5%. This solid, m.p. 28–30°, was recrystallized twice from ethanol and dried *in vacuo* over phosphorus pentoxide; m.p. 32°.

Anal. Calcd. for $C_7H_{14}N_2O_4$: C, 44.20; H, 7.42; N, 14.73. Found: C, 44.35; H, 7.64; N, 14.86.

A similar experiment using sodium carbonate as the only catalyst gave a 1% yield of 3,5-dinitroheptane, m.p. 28–30°.

The Reaction between 2-Nitro-1-butanol, 1-Nitrobutane and Diethylamine.—A mixture of 0.5 mole of 2-nitro-1-butanol, 1.0 mole of 1-nitrobutane, 0.13 mole of diethylamine and 100 ml. of $CHCl_3$ was refluxed so as to remove the water liberated in the reaction and azeotropically distilled with the $CHCl_3$. After 14 hr. 0.4 mole of water had been collected. The product mixture on refrigeration yielded 6.0 g. of 4,6-dinitrononane, m.p. 53–54°. Small amounts of other solids present were not identified.

Anal. Calcd. for $C_9H_{18}N_2O_4$: C, 49.52; H, 8.31; N, 12.87. Found: C, 49.50; H, 8.41; N, 12.87.

Preparation of Dibromodinitroparaffins.—Several γ-dinitroparaffins were derivatized by reaction with bromine under basic conditions to give the dibromo compound. This was accomplished by first dissolving the dinitroparaffin in saturated alcoholic sodium hydroxide, pouring this solution into 10% aqueous sodium hydroxide and adding an equivalent amount of bromine. The dibromo compound which precipitated rapidly was recrystallized from a mixture of methanol and water. The derivatives prepared are listed in Table II.

Table II

Dibromo Derivatives of γ-Dinitroalkanes

Derivative	M.p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
$(C_2H_5CBrNO_2)_2CH_2$	75	24.16	24.27	3.48	3.50
$(n\text{-}C_3H_7CBrNO_2)_2CH_2$	105–106	28.74	28.93	4.29	4.24
$[(CH_3)_2CHCH_2CBrNO_2]_2CH_2$	127	32.69	32.74	4.99	5.16
$(n\text{-}C_6H_{13}CBrNO_2)_2CH_2$	84	39.14	39.38	6.13	6.29

West Lafayette, Indiana

[Contribution from Defence Research Chemical Laboratories]

A New Molecular Rearrangement Involving Carbonium Ions[1]

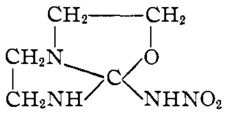
By A. F. McKay[2] and J. R. Gilpin

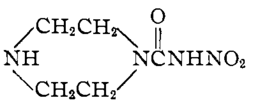
Received May 31, 1955

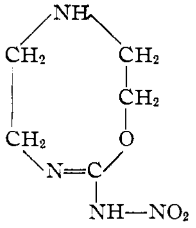
1-(β-Hydroxyethyl)-2-nitriminoimidazolidine in the presence of thionyl chloride rearranges to 1-nitro-2-keto-1,3,6-triazacyclooctane. Another structural isomer of (1-(β-hydroxyethyl)-2-nitriminoimidazolidine, 1-(β-nitraminoethyl)-2-imidazolidone, also is obtained. This new molecular rearrangement is explained as proceeding through carbonium ion intermediates. A new method has been developed for the preparation of 1-substituted-2,3,5,6-tetrahydro-1-imidaz[1,2-a]imidazoles.

Three compounds have been isolated from the chlorination of 1-(β-hydroxyethyl)-2-nitriminoimidazolidine[3,4] with thionyl chloride. One of these compounds was the expected 1-(β-chloroethyl)-2-nitriminoimidazolidine (VII) which melted at 143.5°. The other two white crystalline compounds melted at 182 and 206.5°, respectively. The compound melting at 182° gave analytical values in agreement with the empirical formula $C_5H_{10}N_4O_3$, which identified it as a structural isomer of the starting material 1-(β-hydroxyethyl)-2-nitriminoimidazolidine (V) (m.p. 132.5°).

The structural isomers of compound V are I, II, III, IV, IX, X and XI. The ultraviolet absorption spectrum of compound A[5] has a single maximum at a wave length of 235 mμ with a molar extinction coefficient of 5970. This eliminates structures II and III for compound A because nitroureas[6-8] possess a maximum at a wave length of about 260 mμ with a molar extinction coefficient between 9,000 and 12,000. Since compound A gives a negative color reaction with dimethylaniline in the Franchimont test,[9,10] structures IV, IX and XI are excluded. Finally structures I, IV, IX and XI are eliminated by the infrared spectrum of compound A. The infrared spectrum of compound A displays two N–H stretching bands at 3220 cm.$^{-1}$ and 3105 cm.$^{-1}$ as well as N–H deformation bands at 1573 and 1520 cm.$^{-1}$. It has a band at 1540 cm.$^{-1}$ attributed[11,12] to the NNO_2 group and a band at 1330 cm.$^{-1}$ characteristic of symmetrical nitro group vibrations. A very strong band appears at 1672 cm.$^{-1}$ indicative of a ureido carbonyl group. The ureido carbonyl band is displaced to higher wave numbers (1745–1760 cm.$^{-1}$)[12] when the adjacent nitrogen is substituted with a nitro group as in structure IV and XI. All of the bands exhibited by the spectrum of compound A would be expected for 1-(β-nitraminoethyl)-2-imidazolidone, which is the only structure left for compound A.[13]


I


II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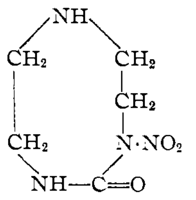
IV

Compound B (m.p. 206.5°) gives a deep green color with dimethylaniline in the Franchimont test. It gives a positive test for ionic chlorine and forms a picrate (m.p. 197–198°). Its analysis showed it to be a hydrochloride of a compound having the empirical formula $C_5H_{10}N_4O_3$. Thus this third

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[1] Issued as D. R. C. L. Report No. 171.

[2] Monsanto Canada Limited, Ville LaSalle, Quebec.

[3] A. F. McKay, J. R. G. Bryce and D. E. Rivington, *Can. J. Chem.*, **29**, 382 (1952).

[4] This compound was formerly referred to as 1-(β-hydroxyethyl)-2-nitramino-2-imidazoline. It actually exists as a resonance hybrid with the nitrimino form being one of the extreme contributing structures; *cf.* A. F. McKay, M. A. Weinberger, J. P. Picard, W. G. Hatton, M. Bedard and H. E. Rooney, This Journal, **76**, 6371 (1954).

[5] The compound melting at 182° will be referred to as compound A, while the one melting at 206.5° will be referred to as compound B, for convenience.

[6] A. F. McKay, J. P. Picard and P. E. Brunet, *Can. J. Chem.*, **29**, 746 (1951).

[7] A. F. McKay and C. Sandorfy, *ibid.*, **31**, 42 (1953).

[8] M. A. Weinberger and A F. McKay, This Journal, **77**, 1321 (1955).

[9] A. P. N. Franchimont, *Rec. trav. chim.*, **16**, 213 (1897).

[10] A. F. McKay, *Chem. Revs.*, **51**, 301 (1952).

[11] E. Lieber, D. R. Levering and L. J. Patterson, *Anal. Chem.*, **23**, 1594 (1951).

[12] A. F. McKay, C. E. Hubley and C. Sandorfy, in preparation.

[13] 1-(β-Nitraminoethyl)-2-imidazolidone has been synthesized and it has been shown to be identical with compound A by a comparison of their physical properties and by a mixed melting point determination. This synthesis will be reported at a later date.