

The above result is reasonable in view of a figure of 1.46% calculated by extrapolation from the data for bromination in the *liquid phase* at 85–215°. It is also consistent with the values of 5–10% of  $\beta$ -isomer reported in nitration,<sup>4</sup> because nitration is known to be a less selective reaction than bromination by molecular bromine.<sup>12</sup>

#### EXPERIMENTAL

**Materials.** The 50% aqueous acetic acid was prepared from purified acetic acid as described before.<sup>2</sup> The recrystallized naphthalene sample melted at 80.0–80.4°,<sup>13</sup> and  $\beta$ -bromonaphthalene was prepared by the method of Newman and Wise.<sup>14</sup> It was recrystallized repeatedly from slightly aqueous ethanol, and the final sample melted sharply at 55.7–55.9°.

**Bromination of naphthalene and isolation of  $\beta$ -isomer.** In one of the three runs, about 3 mc of  $\text{Br}^{82}$  as bromide ion, and as obtained from the Oak Ridge National Laboratory, was dissolved in about 400 ml. of a 0.01M potassium bromide solution. Ten ml. of this solution was evaporated to dryness, and the residue was dissolved in 50 ml. of a stock solution of 50% aqueous acetic acid, 0.1M in potassium bromide and about 0.1M in bromine. A 25-ml. sample of this solution was added to 475 ml. of a solution which contained the other reagents in such concentrations as to give a final reaction mixture, 0.01M in naphthalene and 0.1M in potassium bromide. The initial bromine concentration, determined by titration of two 10-ml. samples of the active bromine solution was exactly 0.005M. One 5-ml. sample was withdrawn from the reaction mixture for counting of the total activity and was diluted to 500 ml. with 95% aqueous ethanol (sample A). After 17 hours at  $25.00 \pm 0.02^\circ$ , ten ml. of the reaction mixture was titrated for completion of reaction (98.72%). A small amount of sodium bisulfite was added to destroy unreacted bromine in the reaction mixture. To this was added 4.3000 g. of pure inactive  $\beta$ -bromonaphthalene dissolved in acetone, and more acetone was added to keep the solution homogeneous. About 1 l. of cold water was then added and the reaction mixture was extracted with one 300-ml. and four 200-ml. portions of petroleum ether. The organic layer was washed with 5% sodium bicarbonate solution, using a total of 500 ml., and then with water. The solvent was dried and evaporated, and the remainder was crystallized five times from slightly aqueous ethanol. The final sample (sample B, 1.3519 g.) melted at 55.6–55.8°, with very slight softening at 55.1°.

**Counting and calculations.** The  $\text{Br}^{82}$  activity was measured with an Atomic Instrument Co. Model 810A well-type scintillation counter and a Model 1090 scaler with a pulse-height discriminator. Only  $\gamma$ -activity was counted and the discriminator was set to accept only the higher energy  $\gamma$ -particles. Samples of  $\beta$ -bromonaphthalene in a solution of exactly 5-ml. volume were counted in a calibrated Pyrex test tube. The total sample was immersed in the well. Because only high energy  $\gamma$  particles were counted, the counting rate was independent of the solvent and other possible solute species. In all cases, times for 10,000 counts were recorded in order to keep the uncertainty constant.

The above sample of recovered  $\beta$ -bromonaphthalene (sample B), dissolved in acetone to exactly 5 ml., had an activity of 5.85 counts per second, corrected for the background count. Five ml. of the diluted reaction mixture (sample A) had a count of 4.29 counts per second, cor-

rected for background and for radioactive decay during the time interval between counting samples A and B. On account of the dilution, the activity of the total reaction mixture is therefore  $4.29 \times 10^4$  counts per second. Because of the immediate establishment of the tribromide equilibrium, the  $\text{Br}^{82}$  is randomly distributed between bromide and bromine, and the fraction of activity in the bromine molecule is  $\frac{0.005 \times 2}{0.11} = 0.09091$ , and hence the activity

in the total amount of bromine that has reacted is  $4.29 \times 10^4 \times 0.9872 \times 0.09091$  or  $3.850 \times 10^3$  counts per second. One half of that amount, or  $1.925 \times 10^3$  counts per second, has entered the naphthalene molecules. Corrected for 15 ml. of solution withdrawn for counting and titration, the total counts for  $\alpha$ - plus  $\beta$ -bromonaphthalene are 1867 counts per second. The amount of  $\beta$ -bromonaphthalene recovered was 31.44%, and hence the activity for the total  $\beta$ -isomer is  $5.85/0.3144$ , or 18.61 counts per second, neglecting the weight of the very small amount of  $\beta$ -isomer formed during substitution. The fraction of  $\beta$ -isomer is therefore  $18.61/1867$  or 0.997%. After counting, the  $\beta$ -isomer was once more recrystallized, when 0.8426 g. of material melting sharply at 55.8–56.0° was obtained. Counting of this sample afforded a value of 0.987% of  $\beta$ -isomer, or an average of 0.992%.

In order to obtain some information about the depression of the melting point of pure  $\beta$ -bromonaphthalene on admixture with possible contaminants, artificial mixtures were prepared and their melting points determined by the usual capillary method. Mixtures of pure  $\beta$ -bromonaphthalene with 5% and 2% by weight of naphthalene, which under the experimental conditions is the most likely contaminant, melted at 53.2–54.0° and at 54.4–55.4°, respectively, with some softening below these temperatures. A mixture of 95% of  $\beta$ - and 5% of  $\alpha$ -bromonaphthalene melted at 44.2–52.2°. All of the purified samples of the  $\beta$ -isomer used for counting purposes contained therefore considerably less than these amounts of impurities, because no sample started to melt below 55°.

In the calculation of the weighted average, a statistical error of 1% was applied to each counting, and reasonable errors were estimated for titration and dilution.

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### Reaction of Methylenedinitramine and Formaldehyde with Various Diaminoalkanes<sup>1</sup>

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The condensation of methylenedinitramine (I), formaldehyde, and several primary aliphatic amines

(12) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953).

(13) All melting points are corrected.

(14) M. S. Newman and P. H. Wise, *J. Am. Chem. Soc.*, **63**, 2847 (1941).

(1) Presented in part before the Pacific Southwest Regional Meeting of the American Chemical Society, Long Beach, Calif., May 5, 1956.

has been reported by Chapman<sup>2</sup> and Wright;<sup>3</sup> the products were the 1-alkyl-3,5-dinitro-1,3,5-triazacyclohexanes,<sup>2</sup> 1,3-dialkyl-5-nitro-1,3,5-triazacyclohexanes,<sup>2</sup> and 1,3-dialkyl-5,7-dinitro-1,3,5,7-tetraazacyclooctanes.<sup>3</sup> Similarly, ethylenedinitramine, methylamine, and formaldehyde yielded 1-methyl-3,6-dinitro-1,3,6-triazacycloheptane.<sup>4</sup> However, the condensation of I with formaldehyde and aliphatic diamines has not been reported.

The diamines H<sub>2</sub>N(CH<sub>2</sub>)<sub>n</sub>NH<sub>2</sub> (where n = 2,3,4,5,6,7, and 8) were found to interact with methylenedinitramine (I) in formalin solutions at 0° to yield crystalline derivatives as shown in Table I. In most of the reactions addition of the amine to the formalin solution of I caused the precipitation of the cyclic derivatives; but in a few runs where no deposition occurred the product was removed by extraction with methylene chloride. With the 1,3-diaminopropane and 1,4-diaminobutane higher yields were obtained by the slow addition of potassium carbonate to a solution of I and the amine hydrochloride in formalin.

In the case of the ethylenediamine there was produced the 3-nitro-1,3,5-triazabicyclo[3.2.1]octane (IIa) which apparently resulted from the degradation of the nitramine I to the dimethylolnitramide. HOCH<sub>2</sub>N(NO<sub>2</sub>)CH<sub>2</sub>OH; the latter subsequently underwent a Mannich reaction with the formaldehyde and the amine to yield IIa which was slowly precipitated. Wright and co-workers<sup>5</sup> reported that a mixture of nitramide,<sup>6</sup> formalin, and ethylenediamine also produced IIa. Lambertson<sup>7</sup> has shown that methylenedinitramine is unstable in solutions of pH 3-8. The pH of the reaction mixtures were found to be within this range and a slow evolution of gas was noted when the temperature of the formalin solutions exceeded 10°. Lambertson<sup>7</sup> suggested that the production of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane from an aqueous solution of the monoammonium salt of I and formaldehyde involved the formation of nitramide, or its methylol derivative. Chapman<sup>2</sup> also postulated the formation of dimethylolnitramide from I to explain the isolation of the 1,3-dialkyl-5-nitro-1,3,5-triazacyclohexanes from formalin solutions of I and alkylamines. With 1,3-diaminopropane, the 3-nitro-1,3,5-triazabicyclo[3.3.1]nonane (IIb) was easily obtained; 1,3-diamino-butane gave a corresponding derivative, *i.e.*, the 3-nitro-8-methyl-1,3,5-triazabicyclo[3.3.1]nonane (IIc). However, 1,4-diamino-

(2) F. Chapman, P. G. Owston, and D. Woodcock, *J. Chem. Soc.*, 1638 (1949).

(3) E. Aristoff, J. A. Graham, R. H. Meen, G. S. Myers, and G. F. Wright, *Can. J. Res.*, **B27**, 520 (1949).

(4) G. S. Myers and G. F. Wright, *Can. J. Res.*, **B27**, 489 (1949).

(5) W. J. Chute, D. C. Downing, A. F. McKay, G. S. Myers, and G. F. Wright, *Can. J. Res.*, **B27**, 218 (1949).

(6) Nitramide in excess formalin is believed to exist largely as dimethylolnitramide, *ref. 5*.

(7) A. H. Lambertson, C. Lindley, and J. C. Speakman, *J. Chem. Soc.*, 1650 (1949).

TABLE I  
PROPERTIES OF THE CONDENSATION PRODUCTS OF METHYLENEDINITRAMINE, ALKANEDIAMINES, AND FORMALDEHYDE

II, O <sub>2</sub> N—N(CH <sub>2</sub> ) <sub>n</sub> —N(CH <sub>2</sub> ) <sub>n</sub> —N(CH <sub>2</sub> ) <sub>n</sub> —CH <sub>2</sub> —CH <sub>2</sub> —R	M.P., °C.	Yield, %	Formula	Analysis						Cryoscopic Mol. Wt. <sup>a</sup>	
				Calcd.			Found			Calcd.	Found
				C	H	N	C	H	N	C	N
IIa, n = 1, R = H	165° dec.	74 <sup>b</sup>	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub> O <sub>2</sub>	41.85	7.03	32.54	41.99	7.19	32.70	172	178
IIb, n = 2, R = H	135° dec.	56	C <sub>7</sub> H <sub>14</sub> N <sub>4</sub> O <sub>2</sub>	45.15	7.58	30.09	45.24	7.80	29.70	186	181
IIc, n = 2, R = CH <sub>3</sub>	125° dec.	51	C <sub>9</sub> H <sub>18</sub> N <sub>4</sub> O <sub>2</sub>	50.45	8.47	26.15	50.61	8.60	26.22	214	208
IId, n = 5, R = H	170° dec.	5	C <sub>10</sub> H <sub>20</sub> N <sub>4</sub> O <sub>2</sub>	52.61	8.83	24.54	52.33	8.99	24.70	228	230
IIe, n = 6, R = H	78-80°	20	C <sub>11</sub> H <sub>22</sub> N <sub>4</sub> O <sub>2</sub>	54.52	9.17	23.12	54.88	9.48	23.33	242	235
IIIf, n = 7, R = H	94-95°	28									
III, [CH <sub>2</sub> —N(CH <sub>2</sub> )CH <sub>2</sub> —N(NO <sub>2</sub> )CH <sub>2</sub> —N(CH <sub>2</sub> ) <sub>n</sub> —N(NO <sub>2</sub> )CH <sub>2</sub> —N(CH <sub>2</sub> ) <sub>n</sub> —N(CH <sub>2</sub> ) <sub>n</sub> —CH <sub>2</sub> —CH <sub>2</sub> —R] <sub>2</sub>											
IIIa, n = 4	128° dec.	60	C <sub>10</sub> H <sub>20</sub> N <sub>10</sub> O <sub>8</sub>	29.41	4.94	34.30	29.39	5.04	33.95	408	398
IIIb, n = 5	125° dec.	40	C <sub>11</sub> H <sub>22</sub> N <sub>10</sub> O <sub>8</sub>	31.28	5.25	33.17	31.36	5.37	32.99	422	431

<sup>a</sup> Nitrobenzene was employed as the solvent. <sup>b</sup> A compound previously prepared from nitramide, ethylenediamine, and formalin, *ref. 5*.

butane yielded the 1,4-bis(3,5-dinitro-1,3,5-triazacyclohexyl)butane (IIIa); the 1,5-diaminopentane produced an analogous derivative, *i.e.*, 1,5-bis(3,5-dinitro-1,3,5-triazacyclohexyl)pentane (IIIb). The 1,6-diaminohexane, 1,7-diaminoheptane, and 1,8-diaminooctane yielded 3-nitro-1,3,5-triazabicyclo[6.3.1]dodecane (IIc), 3-nitro-1,3,5-triazabicyclo[7.3.1]tridecane (IId), and 3-nitro-1,3,5-triazabicyclo[8.3.1]tetradecane (IIe), respectively, although in low yields; the major reaction was the formation of a rubbery insoluble polymer of the amine and formaldehyde which contained only a few nitramino groups. The 1,9-diaminononane produced solely polymer. The latter derivatives IIc, IId, and IIe, represent ring enlargements of the bicyclic system obtained with ethylenediamine, 1,3-diaminopropane, or 1,3-diaminobutane.

The formation of the derivatives II and III is analogous to the production of the 1,3-dialkyl-5-nitro-1,3,5-triazacyclohexanes<sup>2</sup> and 1-alkyl-3,5-dinitro-1,3,5-triazacyclohexanes,<sup>2</sup> respectively, from primary amines. In no case was there any evidence for the formation of more than one condensation product even when a two-fold excess of amine or I was employed. The cyclic derivatives were slowly soluble in dilute mineral acid with the formation of the dihydrochloride of the amine, and in the case of the two derivatives of III, methylenedinitramine. Warm alkali rapidly degraded the derivatives II or III with the formation of the diamine and formaldehyde; in addition III yielded disodium methylenedinitramine. All of the condensation products slowly decomposed on storage at room temperature; the odor of formaldehyde and the diamine became noticeable after 2–4 weeks.

#### EXPERIMENTAL<sup>8</sup>

The formation of 3-nitro-1,3,5-triazabicyclo[3.2.1]octane (IIa) is representative of a condensation using the free amine, formalin, and I. To a solution of 4.08 g. (0.0300 mole) of methylenedinitramine<sup>9</sup> (I) (m.p. 100–101°) in 72 ml. (0.86 mole) of 36% formalin maintained at 0°, was added (dropwise) 1.80 g. (0.0300 mole) of ethylenediamine. The mixture was allowed to stand 4 hr. at 0°. The fine needles which had deposited were filtered to yield 5.14 g. (74%) of IIa, m.p. 160° dec.; m.p. 165°, dec., depending on rate of heating (reported 130° by Wright<sup>8</sup>) after recrystallization from acetone. No methylenedinitramine was isolated in several alkaline degradations of IIa; only ethylenediamine (isolated as the diacetyl derivative, m.p. 174–175°, reported 172° by Hofmann<sup>10</sup>) and formaldehyde were recovered. Similar results were obtained with the other derivatives of II. All derivatives of II were soluble in 3*N* hydrochloric acid; no methylenedinitramine could be isolated from the solutions.

The formation of 1,4-bis(3,5-dinitro-1,3,5-triazacyclohexyl)butane (IIIa) is typical of a run employing an amine hydro-

chloride and potassium carbonate. To a solution of 4.08 g. of I in 72 ml. of 36% formalin was added 10 ml. of a solution containing 2.64 g. (0.0300 mole) of 1,4-diaminobutane which had been neutralized by 6*N* hydrochloric acid. To the resulting solution which was maintained at 0°, was added finely powdered potassium carbonate until the reaction mixture was alkaline to nitrazine test paper. The reaction mixture, which contained precipitated IIIa, was allowed to stand 1 hr. at 0° and then filtered to yield 7.30 g. (60%) of crude IIIa, m.p. 120° dec.; m.p. 135° dec. after recrystallization from acetone. Alkaline decomposition of the two derivatives of III produced 1,4-diaminobutane from IIIa (isolated as the diacetyl derivative, m.p. 136°, reported 137° by Haga<sup>11</sup>) and 1,5-diaminopentane from IIIb (isolated as the dibenzoyl derivative, m.p. 134–135°, reported as 132° by Braun<sup>12</sup>) as well as formaldehyde. The alkaline solution was acidified and extracted with ether; evaporation of the ether left methylenedinitramine in 85% yield. Dilute hydrochloric acid, 3*N*, dissolved III with the formation of formaldehyde, the corresponding diamine dihydrochloride, and methylenedinitramine (I).

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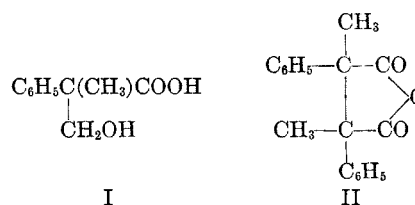
- (11) T. Haga and R. Majima, *Ber.*, **36**, 338 (1903).  
(12) J. Braun and S. W. Pirkernelle, *Ber.*, **67**, 1056 (1934).

### An Ivanov Reaction with the Use of $\alpha$ -Phenylpropionic Acid

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The renewed interest in the Ivanov reaction lately exhibited in several laboratories<sup>1–3</sup> prompts us to report the results of an Ivanov reaction of  $\alpha$ -phenylpropionic acid with formaldehyde. When a procedure, adapted from that reported by Blicke, Raffelson, and Barna<sup>4</sup> for the preparation of tropic acid in 80% yield from phenylacetic acid and formaldehyde, was applied to  $\alpha$ -phenylpropionic acid,  $\alpha$ -methyltropic acid (I) was obtained in only trace amounts. Also isolated in poor yield was a somewhat larger quantity of *sym.* dimethyldiphenylsuccinic anhydride (II), m.p. 157–159°,



- (1) F. F. Blicke and H. Zinnes, *J. Am. Chem. Soc.*, **77**, 5399, 6051, 6247 (1955) and previous papers.  
(2) H. E. Zimmerman and M. D. Traxler, *J. Am. Chem. Soc.*, **79**, 1920 (1957).  
(3) A. W. Weston and R. W. DeNet, *J. Am. Chem. Soc.*, **73**, 4221 (1951).  
(4) F. F. Blicke, H. Raffelson, and B. Barna, *J. Am. Chem. Soc.*, **74**, 253 (1952).

(8) All melting points are corrected. The combustion analyses were performed by Mr. Everett Bens of this laboratory.

(9) R. C. Brian and A. H. Lamberton, *J. Chem. Soc.*, 1633 (1949).

(10) A. W. Hofmann, *Ber.*, **21**, 2332 (1888).