EXPERIMENTAL[5,6]

Nitration of 2-nitro-2-butene. Nitric acid, 150 ml. of 70%, was warmed to 40° and 25 g. (0.25 mole) of 2-nitro-2-butene[7] was added dropwise in 90 min. The temperature was maintained at 39 to 41° by intermittent cooling during the addition and for 1 hr. after the addition was completed.[8] At the end of this time, the temperature began to drop, indicating that the reaction was completed. The mixture was cooled to 5°, causing a white solid to separate, and poured onto ice. The white solid was collected, washed thoroughly with water, and dried *in vacuo* over potassium hydroxide. The yield of 2,2,3-trinitrobutane was 12.1 g. (25.3%), m.p. 42–45°. Recrystallization from isopropyl ether raised the melting point to 46–48°. A Liebermann test for the nitrite group was negative.

Anal. Calcd. for $C_4H_7N_3O_6$: C, 24.88; H, 3.65; N, 21.76; mol. wt., 193. Found: C, 24.85; H, 3.75; N, 22.00; mol. wt., 211.

Proof of structure of 2,2,3-trinitrobutane. A solution of 19.3 g. (0.10 mole) of 2,2,3-trinitrobutane in 150 ml. of ether was cooled to 18–20° and a solution of 4.0 g. (0.10 mole) of sodium hydroxide in 50 ml. of water was added dropwise with stirring. The yellow ether layer was separated and the orange aqueous layer was extracted with ether. The combined ether extracts were dried and concentrated leaving 13.3 g. (91.2%) of yellow liquid. A sample was distilled from a Claisen flask, b.p. 102–103° (2.5 mm.), n_D^{25} 1.4830, m.p. 26°.[9]

Anal. Calcd. for $C_4H_6N_2O_4$: C, 32.86; H, 4.12; N, 19.17. Found: C, 32.69; H, 4.19; N, 18.79.

When treated with ammonia it produced 2-amino-3-nitro-2-butene, m.p. 159–160°, identical to the product previously obtained from the reaction of 2,3-dinitro-2-butene with ammonia.[10]

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[5] All melting points are uncorrected.

[6] Microanalyses by Elek Microanalytical Laboratories, Los Angeles, Calif.

[7] H. B. Hass, *J. Org. Chem.*, **15**, 8–14 (1950).

[8] When 2-nitro-2-butene and 70% nitric acid were mixed at 5–10° and then allowed to warm up, a fume off occurred.

[9] E. M. Nygaard and T. T. Noland, U. S. Patent **2,396,282**, March 12, 1946, reported 2,3-dinitro-2-butene to have a boiling point of 97–100° (1–2 mm.) and a melting point of 25.9°.

[10] L. B. Clapp, J. F. Brown, Jr., and L. Zeftel, *J. Org. Chem.*, **15**, 1043 (1950).

Amount of β-Isomer Formed in the Bromination of Naphthalene[1]

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In connection with a recent study of the kinetics of bromination of naphthalene in 50% aqueous acetic acid,[2] it seemed important to determine the amount of β-bromonaphthalene formed under these conditions. The extent of β-bromination has not previously been determined in solution, but its presence could be inferred from other data. Wibaut and co-workers have determined the amount of α- and β-bromonaphthalene in uncatalyzed *liquid phase* bromination in the temperature range 85–215°, and in the gas phase.[3] In the gas phase above 300° the reaction follows a free-radical course, but in the liquid phase a polar reaction occurs, and the amount of β-isomer varies with temperature from 3% to 6.8%. Small amounts of β-isomer are formed in nitration,[4] and apparently also in chlorination[5] and iodination.[6] More significant amounts are obtained in the Friedel-Crafts acylation[7] and alkylation,[8] and in sulfonation,[9] although, at least in the last two cases, the proportions of isomers are determined by their equilibrium concentrations, rather than their rates of formation.[10]

The amount of β-bromination of naphthalene at 25° in 50% aqueous acetic acid was determined by the isotopic dilution method, using molecular bromine containing the isotope Br^{82} as the substituting agent and adding an excess of inactive β-bromonaphthalene to the completed reaction mixture. From the amount and the activity of the recovered pure β-bromonaphthalene, the extent of β-bromination could be calculated. The percentages of β-isomer in three different runs, each $0.01M$ in naphthalene, $0.1M$ in potassium bromide, and approximately $0.005M$ in bromine, were 1.07 ± 0.056, 0.981 ± 0.024, and 0.992 ± 0.032. The weighted average[11] is 1.00 ± 0.02, and this represents the percent. β-bromonaphthalene in the total bromination products.

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[1] Taken from the senior honors thesis of F. J. Ochs, 1957.

[2] E. Berliner and M. C. Beckett, *J. Am. Chem. Soc.*, **79**, 1425 (1957).

[3] (a) J. F. Suyver and J. P. Wibaut, *Rec. trav. chim.*, **64**, 65 (1945); (b) G. M. Badger, *The Structure and Reactions of the Aromatic Compounds*, Cambridge University Press, Cambridge, 1954, pp. 259–262.

[4] See M. J. S. Dewar and T. Mole, *J. Chem. Soc.*, 1441 (1956) for the most recent determination and for previous references.

[5] Quoted by R. W. Beattie and F. C. Whitmore, *J. Chem. Soc.*, 50 (1934); for iodine-catalyzed vapor phase chlorination, see J. P. Wibaut and G. P. Bloem, *Rec. trav. chim.*, **69**, 586 (1950).

[6] A. Edinger and P. Goldberg, *Ber.*, **33**, 2875 (1900).

[7] Ref. 3b, Chapter 7; L. F. Fieser and M. Fieser, *Organic Chemistry*, Third Edition, D. C. Heath and Co., Boston, Mass., 1956, Chapter 31. G. Baddeley, *J. Chem. Soc.*, S99 (1949).

[8] C. C. Price in *Org. Reactions*, **Vol. III**, pp. 1–82 (1946).

[9] C. M. Suter and A. W. Weston in *Org. Reactions*, **Vol. III**, pp. 141–197 (1946).

[10] For the view that acylation of naphthalene is also a reversible reaction see P. H. Gore, *Chem. Revs.*, **55**, 229 (1955).

[11] A. G. Worthing and J. Geffner, *Treatment of Experimental Data*, John Wiley and Sons, Inc., New York, N. Y., Sixth Printing, 1950, Chapter VIII.

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°.[3] It is also consistent with the values of 5–10% of β-isomer reported in nitration,[4] because nitration is known to be a less selective reaction than bromination by molecular bromine.[12]

EXPERIMENTAL

Materials. The 50% aqueous acetic acid was prepared from purified acetic acid as described before.[2] The recrystallized naphthalene sample melted at 80.0–80.4°,[13] and β-bromonaphthalene was prepared by the method of Newman and Wise.[14] 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 β-isomer. In one of the three runs, about 3 mc of 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 ± 0.02°, 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 β-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 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 γ-activity was counted and the discriminator was set to accept only the higher energy γ-particles. Samples of β-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 γ 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 β-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, corrected 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 4.29×10^4 counts per second. Because of the immediate establishment of the tribromide equilibrium, the 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 3.850×10^3 counts per second. One half of that amount, or 1.925×10^3 counts per second, has entered the naphthalene molecules. Corrected for 15 ml. of solution withdrawn for counting and titration, the total counts for α- plus β-bromonaphthalene are 1867 counts per second. The amount of β-bromonaphthalene recovered was 31.44%, and hence the activity for the total β-isomer is 5.85/0.3144, or 18.61 counts per second, neglecting the weight of the very small amount of β-isomer formed during substitution. The fraction of β-isomer is therefore 18.61/1867 or 0.997%. After counting, the β-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 β-isomer, or an average of 0.992%.

In order to obtain some information about the depression of the melting point of pure β-bromonaphthalene on admixture with possible contaminants, artificial mixtures were prepared and their melting points determined by the usual capillary method. Mixtures of pure β-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 β- and 5% of α-bromonaphthalene melted at 44.2–52.2°. All of the purified samples of the β-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[1]

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

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(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.