

tion was 380 g. (12.3 moles). The solution was refrigerated overnight. Distillation at reduced pressure through a column 45 cm. long packed with Berl saddles gave 675 g. (81%) of a colorless liquid, collected at 66–68° (50 mm.). The foreruns were refluxed under a water separator with 200 ml. of benzene to give 159 ml. of water. By distillation, an additional 96 g. (11.5%) of product was obtained.

α -Allylaminoacetonitrile.—Commercial formalin (249 g., 36.2%, 3 moles) was added to aqueous allylamine (419 g., 40%, 3 moles) at 15–20° in 30 minutes. After stirring one hour, hydrogen cyanide (81 g., 3 moles) was added at 20°. The mixture was stirred for three hours, then saturated with salt. The oil layer was separated and the brine layer was extracted with benzene. The combined extract and oil were distilled to give 147 g. of a faintly yellow liquid, b.p. 97–108° (30 mm.), n_D^{20} 1.4503, d_4^{20} 0.9221. Further distillation gave 35 g. of somewhat less pure material.

Acknowledgments.—Robert W. Faulkner, Jr., and Rita Cerruti assisted in much of the experimental work. Individual experiments were provided by Martin J. Culver, Gerard E. Gantert and John O. Van Hook. Analyses were performed under the direction of Thomas Callan.

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The Reaction of N-Bromosuccinimide with 2-Heptene

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RECEIVED MARCH 6, 1953

In their classic paper on allylic bromination by the use of N-bromosuccinimide (NBS) Ziegler, *et al.*,¹ made the statement that an allylic methylene group undergoes substitution much more readily than an allylic methyl group. The evidence for this statement was that 2-methyl-2-hexene reacted with NBS much more rapidly than did 2-methyl-2-butene, and that 1,1-diphenyl-1-butene reacted much more rapidly than 1,1-diphenyl-1-propene. The alkenes were prepared by dehydration of tertiary alcohols, and no structure work was carried out with the bromides resulting from the NBS reactions. The above conclusion on the relative reactivity of allylic methylene and allylic methyl groups may not be justified. The observed results may be due to individual differences in the various compounds. That this could be the case is suggested by the finding of Bateman and Cunneen² that 1-octene reacted with NBS much more readily than did 1,5-hexadiene. Also, in the present work it was found that the reaction of NBS and 2-heptene was unsuccessful in the absence of benzoyl peroxide.

Instances in the literature of the reaction of NBS with compounds containing both allylic methylene and methyl groups and where structure work was carried out on the reaction product are rather few. Buu-Hoi, *et al.*,³ have compared the monobromopinene from the pinene-NBS reaction with the bromide resulting from the reaction of 1-myrtanol with phosphorus tribromide. The physical constants of the two compounds were quite similar and the ultraviolet spectra were similar, but not identical.

(1) K. Ziegler, A. Spaeth, E. Schaaf, W. Schumann and E. Winkelmann, *Ann.*, **551**, 80 (1942).

(2) L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 941 (1950).

(3) Buu-Hoi, Hiong-Ki-Wei, J. Lecomte and R. Royer, *Bull. soc. chim. France*, **148** (1948).

They concluded the monobromopinene had the structure of myrtenyl bromide. Mousseron, *et al.*,⁴ have reported on the reaction of some methylcyclohexenes and methylcyclopentenes with NBS. The products of these reactions on oxidation by a method used by Courtot and Pierron⁵ gave ketones, and hence it was concluded that bromination had occurred in the ring. Bateman, *et al.*,⁶ have found 2,6-dimethyl-2,6-octadiene to give a complex mixture of isomeric bromides.

The work of Buchman and Howton⁷ and of Bateman and Cunneen² indicates that one cannot neglect the possibility of allylic rearrangement in NBS reactions. There is disagreement between Bateman⁸ and Karrer⁹ as to the occurrence of an allylic rearrangement in the reaction of 1,5-hexadiene with NBS.

4-Bromo-2-heptene was desired for some synthetic work, and the synthesis of this compound by the reaction of 2-heptene with NBS was proposed. This reaction presented a clear case to test the relative reactivity of allylic methylene and methyl groups. The product of the reaction would also indicate whether or not allylic rearrangement had occurred during the reaction. 2-Heptene was prepared by a Boord-type synthesis, and this was reacted with NBS in the presence of benzoyl peroxide. The product was distilled *in vacuo* and had an amazingly narrow boiling range (0.5°). Analysis of the material showed it to be monobromoheptene. The infrared curves of the 2-heptene and monobromoheptene were quite similar, and in neither curve was there any indication of terminal carbon-carbon unsaturation. 1-Bromo-2-heptene has been prepared by Young, *et al.*,¹⁰ and found to have n_D^{25} 1.4745. Our bromoheptene had n_D^{25} 1.4712. Young, *et al.*,¹¹ have shown that allylic halides can be ozonized without rearrangement, and this method of structure proof was chosen for the bromoheptene. The bromoheptene was carefully ozonized and the ozonide decomposed with hydrogen peroxide. Acetic acid was isolated in nearly quantitative yield from the decomposition mixture, and α -bromovaleric acid was also isolated. These data would indicate that in the reaction of 2-heptene with NBS the allylic methylene group does react in preference to the allylic methyl group, that there is no significant allylic rearrangement and that the product is 4-bromo-2-heptene.

Experimental

Chemicals.—For exploratory experiments 2-heptene (pure grade, Phillips Petroleum Company, Bartlesville, Oklahoma) was used. The material was distilled through a Fenske column (18 theoretical plates) and practically all of the

(4) M. Mousseron, F. Winternitz and R. Jacquin, *Compt. rend.*, **224**, 1062 (1947).

(5) C. Courtot and J. Pierron, *Bull. soc. chim. France*, [4] **45**, 286 (1929).

(6) L. Bateman, J. I. Cunneen and H. P. Koch, *J. Chem. Soc.*, 3045 (1950).

(7) E. R. Buchman and D. R. Howton, *THIS JOURNAL*, **70**, 2517 (1948).

(8) L. Bateman, J. I. Cunneen, J. M. Fabran and H. P. Koch, *J. Chem. Soc.*, 936 (1950).

(9) P. Karrer and S. Perl, *Helv. Chim. Acta*, **33**, 36 (1950).

(10) W. G. Young, L. Richards and J. Azorlosa, *THIS JOURNAL*, **61**, 3070 (1939).

(11) W. G. Young, A. C. McKinnis, J. D. Webb and J. D. Roberts, *ibid.*, **68**, 293 (1946).

material had b.p. 98.5° (770 mm.) and n_D^{25} 1.4050. Our final experiments were carried out with 2-heptene which was prepared by a method similar to that used by Wibaut and Gitsels¹² for the preparation of 3-octene. The alkene was distilled through the Fenske column and had b.p. 98.5° (766 mm.) and n_D^{25} 1.4043. The infrared spectrograms of the two samples of 2-heptene were identical except for minor differences in intensity of absorption. Carbon tetrachloride was purified according to Fieser.¹³ N-Bromosuccinimide (Arapahoe Chemicals, Inc., Boulder, Colo.) was used as purchased.

4-Bromo-2-heptene.—The influence of the following factors on the reaction was studied: ratio of reactants, time of refluxing, light and benzoyl peroxide. The procedure described below gave consistently good results. In a 500-ml., three-necked flask fitted with a stirrer, reflux condenser and nitrogen inlet tube were placed 40 g. (0.41 mole) of synthetic 2-heptene, 48.1 g. (0.27 mole) of NBS, 250 ml. of carbon tetrachloride and 0.2 g. of benzoyl peroxide (Distillation Products, Rochester, N. Y.). The mixture was stirred and refluxed in a nitrogen atmosphere for two hours. The reaction mixture was cooled, the succinimide removed by filtration and washed with two 15-ml. portions of carbon tetrachloride. The succinimide weighed 26.5 g. (99%). The volatile material was removed from the carbon tetrachloride solution by distillation *in vacuo* through a 20-cm. column filled with glass helices. The residue was then distilled from a Claisen flask. Both distillations were carried out in a nitrogen atmosphere. There was a forerun of 1.2 g., b.p. 31–71.5° (37 mm.), n_D^{25} 1.4650; then 36.3 g. (76%) of 4-bromo-2-heptene was collected, b.p. 71.5–72° (37 mm.), n_D^{25} 1.4712, d_4^{25} 1.151; 6.6 g. of high boiling material, n_D^{25} 1.5174, remained in the distilling flask. This represents our best yield; the yield was usually 60–70%.

Anal. Calcd. for C₇H₁₃Br: C, 47.5; H, 7.2; Br, 45.2. Found¹⁴: C, 47.3; H, 7.4; Br, 45.3; active bromine (determined by a five-minute reflux of the compound with alcoholic silver nitrate), 44.9.

The infrared spectrogram of the 4-bromo-2-heptene had absorption maxima at the same wave lengths as the 2-heptene, and one additional peak at 8.5 μ . In neither curve was there any evidence of terminal carbon-carbon unsaturation.

Ozonation of 4-Bromo-2-heptene.—A solution of 17.5 g. (0.1 mole) of 4-bromo-2-heptene in 150 ml. of purified *n*-pentane¹⁵ was ozonized in an apparatus which has been described elsewhere.¹⁵ The reaction mixture was kept at –45 to –38° during the ozonation. The ozonizer was producing 395 mg. of ozone per hour (gas flow, 11.4 l. per hour; 1.64 volume % of ozone). The ozone-oxygen solution was led into the reaction flask for 12.15 hours in order to introduce 0.1 mole of ozone. The effluent gas from the reaction flask first contained ozone 9.79 hours after the start of the ozonation, but between this time and the conclusion of the reaction only 4 mg. of ozone was unabsorbed by the reaction mixture.

Decomposition of Ozonide and Identification of Products.—The ozonide-pentane solution was transferred to a one-liter, three-necked flask which was in an ice-bath. The flask was kept in the ice-bath and the pentane removed *in vacuo*. The flask was then fitted with a stirrer, dropping funnel, reflux condenser and thermometer well. The ice-bath was replaced by a salt-ice-bath, and 250 ml. of aqueous hydrogen peroxide (2.76% hydrogen peroxide) was added dropwise to the reaction flask during 1.25 hours. The addition of the hydrogen peroxide was regulated such that the temperature of the reaction mixture never rose above 0°. The mixture was allowed to stand at room temperature for two days, stirred at room temperature for 12 hours, refluxed for one hour, cooled, a spatula tip of Adams platinum oxide added and the mixture allowed to stand overnight. After refluxing for one hour the reaction mixture gave a negative test for peroxide with potassium iodide. The platinum oxide was removed by filtration, and the

aqueous layer extracted with five 25-ml. portions of ether. The combined ether extracts were dried over freshly heated sodium sulfate.

The aqueous layer was neutralized to a phenolphthalein end-point with 1 *N* sodium hydroxide. The solution was evaporated to dryness *in vacuo*, and after drying in a vacuum desiccator over phosphorus pentoxide the residue weighed 7.8 g. The theoretical amount of sodium acetate would be 8.2 g. Fusion of a portion of the residue with sodium and subsequent testing for bromide gave a negative result. Were α -bromoacetic acid or α -bromopropionic acid formed during the ozonolysis procedure, one might expect some of these acids to remain in the aqueous layer. Two-tenths of a gram of the residue gave 0.38 g. of *p*-bromophenacyl ester, m.p. 83–84.5°; the same amount of residue also gave 0.16 g. of *p*-nitrobenzyl ester, m.p. 75–77°. Authentic sodium acetate (0.20 g.) gave 0.41 g. of *p*-bromophenacyl ester, m.p. 83.5–84°, and 0.19 g. of *p*-nitrobenzyl ester, m.p. 76–77°; mixed m.p. 83–84° and 76–77°, respectively.

The ether layer was filtered from the sodium sulfate and the ether removed through a column filled with glass helices. The lachrymatory residue was vacuum distilled to give a forerun and then three fractions (combined weight 5.4 g.) having n_D^{25} 1.4467, 1.4578 and 1.4580 were collected at 70–80° (9 mm.). Two-tenths of a gram of this material gave 0.20 g. of *p*-bromophenacyl ester, m.p. 71–73°, mixed m.p. 72–73°. Authentic α -bromovaleric acid was prepared according to Marvel¹⁶ and had b.p. 132–136° (28 mm.) and n_D^{25} 1.4592. The authentic bromoacid (0.20 g.) gave 0.23 g. of *p*-bromophenacyl ester, m.p. 72–73°.

Acknowledgments.—We are indebted to Samuel P. Sadtler and Son, Inc., and to Dr. Gordon Evans for the infrared spectrograms. For a Frederick Gardner Cottrell grant that made this work possible we wish to express our gratitude to the Research Corporation of New York.

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Some Nitro- and Aminodibenzofurans

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RECEIVED MAY 13, 1953

The announcement by Barry¹ of the high antituberculous activity of 2-chloro-7-aminodibenzofuran emphasized the desirability of additional research upon dibenzofuran derivatives. Since dibenzofuran may be regarded as a "closed model" of diphenyl ether, information concerning the activity of the diphenyl ether series was reviewed.

One of the more active diphenyl ethers is 2-chloro-4'-aminodiphenyl ether.¹ Evidence indicates that for high activity the chlorine atom must be either ortho or para to the ether linkage and that additional halogen substitution in either ring results in a marked increase in activity. Barry also found the brominated derivative to be equally as active as the chloro compound. These findings indicated that the preparation and testing of an aminodihalodibenzofuran would be valuable. 2,8-Dibromo-3-aminodibenzofuran was synthesized by the bromination and subsequent hydrolysis of 2-bromo-7-acetaminodibenzofuran. The positions of the bromine atoms were verified by deamination to yield 2,8-dibromodibenzofuran. The results of pharmacological tests will be reported elsewhere.

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