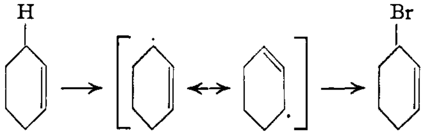
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY OF NUCLEAR SCIENCE AND ENGINEERING OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

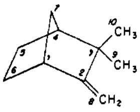
The Reaction of N-Bromosuccinimide with Camphene and α-Pinene[1,2]

BY JOHN D. ROBERTS AND E. R. TRUMBULL[3]

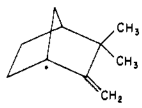
The reaction of N-bromosuccinimide (NBS) with olefins or aromatic hydrocarbons has been used for the substitution of bromine for hydrogen at a carbon atom attached to an unsaturated group.[4a,b,c] These reactions, frequently designated as "allylic brominations," are often catalyzed by peroxides or ultraviolet light and have been formulated as involving allyl-type free radicals stabilized by the contribution of resonance forms involving the double bond or aromatic system.[4c]



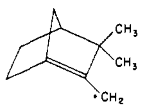
Camphene (I), whose only allyl hydrogen atom is located at a bridgehead carbon of the bicyclic ring system provides an interesting test of the scope of this method of bromination. With camphene, the free radical intermediate (II) would not be expected to be stabilized by resonance contributions of forms involving a bridgehead double bond such as III. If such resonance stabilization of an intermediate radical is an essential feature of the NBS reaction, the allylic bromination of I by this method should be expected to be difficult or impossible. In this connection it should be mentioned that Bartlett, Ryan and Cohen[5] were unable to chlorinate triptycene with sulfuryl chloride using a peroxide catalyst and Bartlett and Lewis[6] were unable to prepare the 9-triptycyl free radical from 9-bromotriptycene.



I



II



III

In the present work, I was found to react with NBS in the presence of benzoyl peroxide or on irradiation with ultraviolet light but the reaction required twenty hours at the temperature of refluxing carbon tetrachloride as compared with the one-half to three hours required with most olefins.[4c] Distillation of the reaction mixture gave about a 35% yield of material with the composition of a monobromocamphene. The product appeared to be a mixture of reactive and unreactive bromides since it gave only a slight precipitate of silver bromide with alcoholic silver nitrate at room temperature. An approximate analysis of the bromination product was obtained from reaction rate curves (Fig. 1) with sodium methoxide in methanol at different temperatures. At 25°, 15% of the material reacted rapidly at which point there was a sharp break in the rate curve and subsequent reaction proceeded slowly. At 55°, 35% of the bromide reacted rapidly whereupon no further reaction occurred. At 100°, a slow reaction of the remaining 65% of the bromide was noted. These results can be interpreted as indicating that the monobromide fraction contained 15% of very reactive (possibly allylic type), 20% of less reactive and 65% of unreactive (probably vinyl type) bromides.

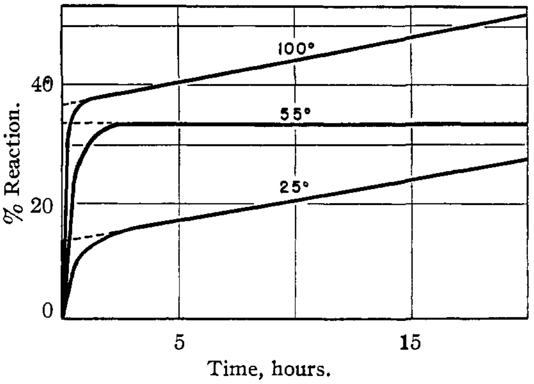


Fig. 1.—Bromocamphene reaction with NaOCH₃.

Although the bromide mixture could not be separated by distillation, the unreactive material was obtained by reduction of the active components with zinc in ethanol. The physical properties and the infrared absorption curve[7] (Fig. 2) of the unreactive material were similar to those of a sample of 8-bromocamphene prepared by the method of Langlois.[8] The identity of these materials was established by conversion to camphene-8-carboxylic acid. No attempt was made to establish the structures of the more reactive bromides. It is considered unlikely that any of the reactive bromides could contain 1-bromocamphene because of the very low reactivity of halides of this type.[6,9] The possibility exists that through the operation of a Wagner–Meerwein type rear-

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[2] Presented at the St. Louis Meeting of the American Chemical Society, September 7, 1948.

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[4] (a) Ziegler, Spaeth, Schaaf, Schumann and Winkelmann, *Ann.*, **551**, 80 (1942); (b) Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946); (c) Djerassi, *Chem. Revs.*, **43**, 271 (1948).

[5] Bartlett, Ryan and Cohen, THIS JOURNAL, **64**, 2649 (1942).

[6] Bartlett and Lewis, unpublished work, presented by P. D. Bartlett at the Organic Symposium at Boston, June, 1947.

[7] The peak at 3400 cm.$^{-1}$ in the infrared curve probably indicates the presence of some hydroxylic compound formed by hydrolysis during the reduction process.

[8] Langlois, *Ann. chim.*, [9] **12**, 193 (1919).

[9] Bartlett and Knox, THIS JOURNAL, **61**, 3184 (1939).

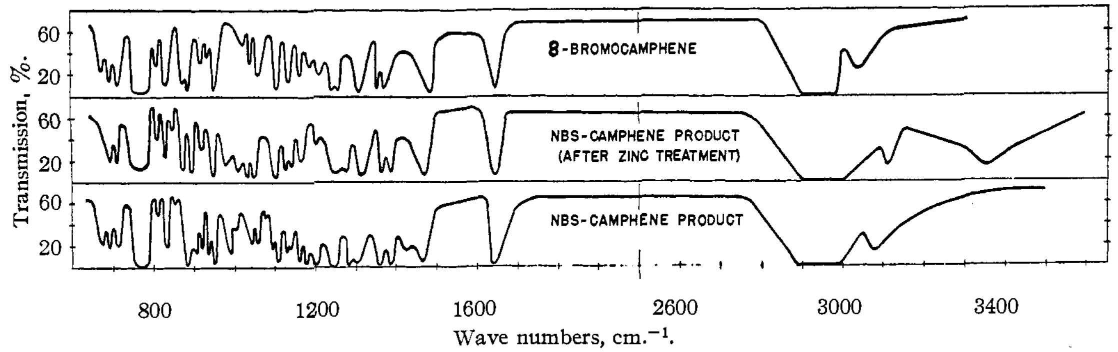
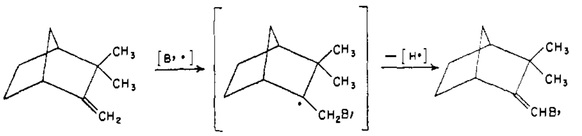


Fig. 2.

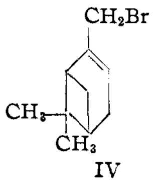
rangement the reactive halides do not have the camphene carbon skeleton.

The free-radical character of the camphene bromination was indicated by the failure of the reaction to proceed in the dark in the absence of peroxides even after twenty-four hours of heating. Hydrogen bromide was also without catalytic effect. The reaction mechanism for the bromination in the 8-position is probably best formulated as involving the attack of a bromine atom or a species capable of donating a bromine atom at the 8-position followed by removal of a hydrogen atom by a hydrogen-acceptor.

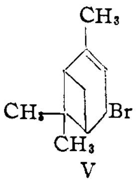


In connection with this type of substitution it is of interest that camphene reacts with lead tetraacetate to give 8-acetoxycamphene.[10]

The reaction of N-bromosuccinimide with α-pinene has been studied by Ziegler,[4a] Buu-Hoi[11] and their co-workers. This reaction proceeds much more easily than that with camphene and is complete in two hours without using a catalyst. Of the two possible isomeric monobromides (assuming no allylic rearrangement) which might be obtained from α-pinene, myrtenyl bromide (IV) and verbenyl bromide (V), Buu-Hoi and co-



IV



V

workers[11] reported only one product with different properties from myrtenyl bromide. We have analyzed the NBS bromination product of α-pinene by its reaction rates with sodium methoxide in methanol (Fig. 3) at different temperatures and have found it to be a mixture of at least two and possibly three (or more) bromides of different reactivities. It seems likely that this reaction is not as simple as has been previously formulated and that allylic or even Wagner–Meerwein rearrangements may be involved.

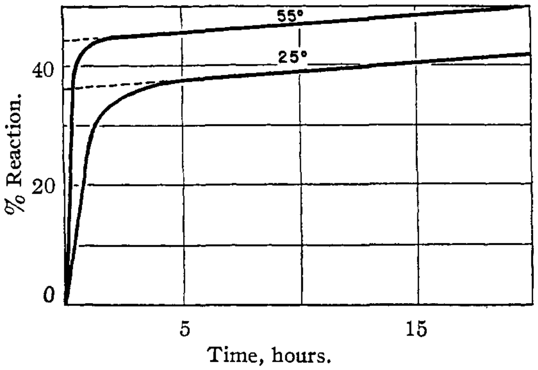


Fig. 3.—Bromopinene reaction with $NaOCH_3$.

Acknowledgment.—The aid of Dr. R. C. Lord, Jr., and Mr. R. S. MacDonald with the infrared curves and of Miss Winifred Bennett with the rate runs is gratefully acknowledged.

Experimental

Camphene with N-Bromosuccinimide.—A mixture of 40 g. (0.29 mole) of camphene,[12] 40.0 g. (0.225 mole) of NBS, 1.0 gram of benzoyl peroxide and 150 ml. of carbon tetrachloride were heated under reflux with stirring for eighteen hours. During the first six hours the reaction mixture was irradiated with a General Electric RS Sunlamp. The solid (21.8 g.) was removed by filtration and the liquid products distilled. The monobromide, b. p. 91-93° (10 mm.), amounted to 16.8 g. (35%) and after redistillation had the following physical constants: $n^{25}_{\rm D}$ 1.5172, d^{25}_{4} 1.2502.

Anal. Calcd. for $C_{10}H_{15}Br$: C, 55.83; H, 7.01; Br, 37.16. Found: C, 55.32; H, 6.83; Br, 36.7.

The product gave an immediate precipitate with alcoholic silver nitrate solution and reacted slowly with permanganate in acetone.

Partial Reduction of Monobromination Product.—The monobromination product (6.3 g.) was added dropwise to a boiling stirred suspension of 5.0 g. of powdered zinc in 50 ml. of 80% ethanol. The mixture was refluxed for five minutes, cooled and filtered. Most of the alcohol was removed by distillation, water was added and the

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(10) Hückel and Hartmann, *Ber.*, **70**, 959 (1937).

(11) Buu-Hoi, Hiong-Ki-Wei, Lecomte and Royer, *Bull. soc. chim. France*, 148 (1946).

(12) Kindly furnished by the Hercules Powder Company.

suspension extracted with chloroform. Distillation of the extract gave 1.9 g. of impure bromide; b. p. 92-95° (14 mm.), n^{25}_{D} 1.5147 and d^{25}_{4} 1.2228. The product gave no precipitate with silver nitrate and did not react with sodium methoxide in methanol at 55°.

8-Bromocamphene.—From 50.0 g. of camphene and 60.0 g. of bromine was obtained by the method of Langlois[8] 45.8 g. (58%) of 8-bromocamphene; b. p. 92-94° (14 mm.), n^{25}_{D} 1.5207 and d^{25}_{4} 1.2679.

Camphene-8-carboxylic Acid.—The unreacted bromide from the zinc reduction was converted to a Grignard reagent on refluxing overnight with 1.0 g. of magnesium and 0.1 g. of ethyl bromide. The reaction mixture was cooled in an ice-salt-bath and an excess of dry carbon dioxide bubbled through. The resulting pasty mixture was acidified with dilute hydrochloric acid and the ether layer separated. The acidic product was extracted from the ether layer by shaking with sodium carbonate solution. Acidification of the carbonate solution gave a solid which was crystallized from ethanol, m. p. 122-123°. This material did not depress the melting point (123°) of a sample of camphene-8-carboxylic acid prepared from 8-bromocamphene.

Bromopinene.—α-Pinene (50 g.) was brominated with 25 g. of NBS by the previously described procedure.[11] The yield of bromopinene after two distillations was 9.1 g. (23%); b. p. 89-90° (13 mm.), n^{25}_{D} 1.5120, d^{25}_{4} 1.2400.

Rate Determinations.—The reaction rates of the bromides with sodium methoxide in methanol solution were determined at 25° by titration with standard acid of samples withdrawn from a flask held in a thermostat at 25.0 ± 0.1°. For 50 and 100° rates, 5-ml. samples were sealed in individual test-tubes to avoid loss of the solvent.

Summary

The reaction of N-bromosuccinimide with camphene gave a mixture of monobromides of which the principal component (65%) was 8-bromocamphene.

The bromination with N-bromosuccinimide of α-pinene was shown to give a mixture of monobromides.

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[CONTRIBUTION FROM DEPARTMENT OF PHYSICS, DUKE UNIVERSITY]

Vapor Pressures of Naphthalene, Anthracene and Hexachlorobenzene in a Low Pressure Region[1]

BY G. W. SEARS[2] AND E. R. HOPKE

In line with a program of securing vapor pressure data on spectroscopically interesting compounds the vapor pressures of naphthalene, anthracene and hexachlorobenzene have been measured in the region 0.01–1.0 mm. The vapor pressure of naphthalene has previously been studied over a wide range. The vapor pressures of anthracene and hexachlorobenzene have only been determined in the region 10–760 mm.

Compounds.—The naphthalene was Eastman Kodak Co. highest purity compound. The material was purified by vacuum sublimation and the center fraction was used. The melting point range was 79.9 to 80.2°. The hexachlorobenzene was Eastman Kodak Co. best grade product. It was twice recrystallized from 95% ethyl alcohol and was dried at 115° for one hour. Its melting point range was 229.5 to 229.8°. The anthracene was also of the highest purity obtainable from Eastman Kodak Company. It was three times recrystallized from benzene and was dried at 100 for one hour. Its melting point range was 216.9 to 217.3°.

Experimental

The vapor pressure data were measured with a Rodebush gage.[3] The calibration and experimental procedure have been previously described by the authors.[4,5] Earlier measurements have all involved compounds having vapor pressures in the operating range of the gage at temperatures below room temperature. In this investigation none of the compounds were sufficiently volatile to have a vapor pressure in the gage range below room temperature.

Consequently, the experimental procedure of earlier investigations was modified. The entire gage was placed in an asbestos box, which was heated by a pair of 500-watt heating cones supplied by a one-kilowatt variac. As in earlier work the sample chamber was placed in a cold-bath. In this case the bath was cold only with respect to the interior of the box.

The cold-bath consisted of a 400-ml. beaker filled with water in the case of naphthalene and with paraffin oil for the other two compounds. The temperature of the box was maintained at about 30° above the temperature of the bath. The temperature of the bath rose about 0.1° per minute.

To avoid error caused by local temperature differences in the bath a copper cylinder 3″ in diameter and 2″ long was supported in the bath so that its surface lay at the surface of the bath. The cylinder was provided with a hole into which the sample tube fitted and with a thermometer hole of the same depth. The experimental proof that the bath was the cold spot of the gage was the repeated observation that condensed sample was never observed elsewhere than in the sample chamber.

In the case of naphthalene a calibrated 0 to 50° mercury-in-glass thermometer was used for temperature measurement. The temperature was read directly to the nearest 0.1°. The precision of the pressure measurements did not justify any closer temperature measurements. The temperatures of the hexachlorobenzene and anthracene were measured with respect to a finely ground ice-bath using a calibrated copper–constantan thermocouple. The thermal e. m. f. was measured to 1 microvolt with a Leeds and Northrup Type K-2 potentiometer. Temperatures were then calculated from the calibration chart to the nearest 0.1°.

When hexachlorobenzene and anthracene escaped from the vapor enclosure during a pressure measurement, they condensed on the walls of the high vacuum side and effectively degraded the vacuum. To avoid this a collar of Dry Ice was placed on the vacuum walls at the point

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[1] This investigation was assisted by the Office of Naval Research under Contract N6ori-107, Task Order I, with Duke University.

[2] Present address: Research Laboratory, General Electric Co., 1 River Road, Schenectady, N. Y.

[3] Rodebush and Henry, THIS JOURNAL, **52**, 3159 (1930).

[4] Sears and Hopke, *J. Phys. Chem.*, **52**, 1137 (1948).

[5] Hopke and Sears, THIS JOURNAL, **70**, 3801 (1948).