gen in 8 min. The purple colored solution was poured into one liter of water and neutralized with acetic acid. The whole was then extracted with ether. Upon evaporation of the ether a yellow oil (2.0 g.) was obtained (mol. wt. 265). On chromatographing the oil (1.5 g.) over a column of alumina using benzene as solvent and eluent, the major fraction gave an orange-yellow crystalline product (0.3 g.) identified as 2,6-di-*tert*-butylbenzoquinone, melting at 67°.[17, 23] The infrared spectrum was identical with that reported by Müller and Ley.[10]

The absorption spectrum in isoöctane showed λ_{max} 252, 308, and 380 mμ; ϵ_{max} 15,800, 384, and 261 respectively.

On eluting the column with benzene containing 1% ethanol, a colorless fraction (0.43 g.) was obtained which melted at 187°. The product was shown to be identical with 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde.

Reaction of compound XVIII *with base.* Compound XVIII (0.04 g.) was suspended in a ethanolic (50 ml.) solution of sodium hydroxide (5%; 1 ml.). The air in the apparatus was replaced by nitrogen. The whole was then agitated vigorously. The color of the solution became intense purple in about 10 min. A small sample was withdrawn and its visible absorption measured at 575 mμ at different intervals. The extinction was found to be about ϵ_{max} 120,000 showing approximately half as much of XVII compared to the pure methylenequinone which has ϵ_{max} 220,000.

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[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, THE UNIVERSITY OF CHICAGO]

Bromination of Octene-1 with *N*-Bromosuccinimide*

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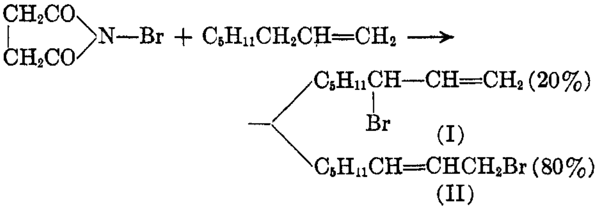
When *N*-bromosuccinimide reacts with octene-1 in light or in the presence of traces of peroxides, there is obtained a mixture consisting of 65% of monobrominated octenes, 15% of dibrominated octenes, and higher bromination products. The monobrominated octenes are *trans*-1-bromooctene-2 (80%; n_D^{20} 1.4760; b.p. 62–63°/6 mm) and 3-bromooctene-1 (20%; n_D^{20} 1.4669; b.p. 69–70°/14 mm). The dibrominated octenes contain one readily replaceable bromine atom per molecule. The reaction in question is retarded by oxygen and completely inhibited by small amounts of nitrosobenzene (0.5 mole %).

It has been claimed[1] that *N*-bromosuccinimide reacts with simple olefins containing a terminal double bond to give mixtures of allylic bromides of unknown composition. The composition of the mixture of the octenyl bromides resulting from the reaction of octene-1 with *N*-bromosuccinimide was investigated as part of an extensive study of the various mechanisms involved when *N*-bromosuccinimide reacts with a variety of organic compounds.

The bromination of octene-1 with *N*-bromosuccinimide was carried out in carbon tetrachloride in the presence of benzoyl peroxide (0.2 mole %) or in light. At 75°, in the absence of oxygen, the reaction is complete in about 1 hr. The reaction mixture was fractionated at low temperature and pressure. Two major fractions were thus obtained: (1) a mixture of monobrominated octenes (65 per cent); (2) a residue consisting of dibrominated octenes and higher bromination products.

Two fractionations of the monobrominated products through a 24-inch tantalum spiral column gave two fractions in the raio of one part to four.



$$\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array}\!\!>N{-}Br + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow \begin{cases} C_5H_{11}CH(Br){-}CH{=}CH_2\ (20\%) & \text{(I)} \\ C_5H_{11}CH{=}CHCH_2Br\ (80\%) & \text{(II)} \end{cases}$$

Structures are assigned to these two materials (I and II) on the basis of their infrared spectra.[2] The lower boiling material (n_D^{20} 1.4670) has bands with maxima at 1635 cm.$^{-1}$, 985 cm.$^{-1}$, and 920 cm.$^{-1}$ (vinyl group) and therefore has structure I (3-bromooctene-1); the higher boiling material (n_D^{20} 1.4760) has bands with maxima at 1658 cm.$^{-1}$ and 962 cm.$^{-1}$ (*trans*-disubstituted double bond) and must therefore be compound II (1-bromooctene-2).

The dibrominated octenes, which form about 15 per cent of the reaction mixture, are extremely unstable; they could be distilled, without decomposition, from the higher bromination products only in a molecular still. Unfortunately, under these conditions small amounts of succinimide (formed in the reaction) are found in each fraction. Analyses, for total bromine and bromine removable by silver nitrate, indicate that only one of the bromine atoms in these dibromides is readily replaceable. Because of the large number of dibromides (each containing only one allylic bromine atom) which would result from bromination of compounds I and II, the dibromides were not examined in detail.

Whether products I and II formed in a ratio of 1 to 4 are primary reaction products, or whether formation of the large amounts of II is due (under

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* This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

[1] K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 93 (1942); Two excellent reviews are available (up to 1951) of the reactions of *N*-bromosuccinimide with many types of organic compounds [C. Djerassi, *Chem. Revs.*, **43**, 271 (1948); T. D. Waugh, *N-Bromosuccinimide, Its Reaction and Uses*, Arapahoe Chemicals, Inc., Boulder, Colorado, 1951].

[2] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1954.

the experimental conditions) to very extensive rearrangement of compound I remains an open question.[3] Examination of the index of refraction and infrared spectrum of the initial mixture of the monobrominated products indicates the same ratio (1 to 4) of the isomers. These data indicate little or no isomerization occurs during the separation (by distillation) of the isomers. On the other hand, it was also noted that compound I when heated to 80° for 1 hr. without solvent in the absence of oxygen rearranges to give a mixture containing about 20 per cent compound II.

It should be noted here (Kharasch and Fono—unpublished work) that the decomposition of benzoyl peroxide in octene-1 gives predominantly a product corresponding to II, in which the (-$OCOC_6H_5$) group occupies the position of the bromine atom. In this connection studies of the rearrangement of type I compounds (in which a benzoyl group occupies the position of the bromine atom) to corresponding type II compounds might provide a partial answer to this interesting and vexing problem.[4]

EXPERIMENTAL

Octene-1. Octene-1 (Phillips Petroleum Co., 99% minimum purity) was refluxed over molten sodium in a nitrogen atmosphere and distilled.

Bromination of octene-1. A mixture of freshly distilled octene-1 (n_D^{20} 1.4088; 50 g.), crystallized *N*-bromosuccinimide (26.7 g.), benzoyl peroxide (0.07 g.), and carbon tetrachloride (113 ml.) was heated under gentle reflux in a nitrogen atmosphere. The reaction was complete in about 1 hr.

The reaction mixture was cooled, and the succinimide which separated was collected on a filter. It was washed several times with small portions of cold carbon tetrachloride and dried. The yield of succinimide was 13.8 g. (93%). The washings were combined with the filtrate, and the solvent and most of the unreacted octene were removed by distillation at reduced pressure (20 mm.). The residue was distilled at 35° (0.06 mm.) and the distillate consisting mostly of monobrominated products was collected in a cold trap (−70°). A non-volatile fraction (Residue I) of 6.6 g. remained. The distillate (23.3 g.) was fractionally distilled at reduced pressure (6 mm.) through a 24-in. tantalum spiral column to give the following fractions:

Fraction	B.P. at 6 Mm.	Weight	n_D^{20}
1	50–57°	2.1 g.	1.4687
2	57–60°	2.1 g.	1.4716
3	61–62°	3.7 g.	1.4746
4	62–63°	10.5 g.	1.4760

Octene-1 (3.3 g., n_D^{20} 1.4093) was recovered from the cold trap and a small amount (0.3 g.) of pot residue remained.

Fraction 4 was essentially pure 1-bromo-2-octene (II) as shown by its infrared spectrum, ν_{max} at 1658 cm.$^{-1}$ and 962 cm.$^{-1}$

Anal. Calcd. for $C_8H_{15}Br$: C, 50.27%; H, 7.91%; Br, 41.81%; mol. wt., 191. Found: C, 50.39%; H, 7.92%; Br, 41.84%; mol. wt. (cryoscopic), 185.

Fraction 1 to 3 were shown by their infrared spectra to contain 3-bromo-1-octene (I), ν_{max} at 1635 cm.$^{-1}$, 985 cm.$^{-1}$, and 920 cm.$^{-1}$ The lower boiling fractions of several runs were combined and fractionated through the same column, and a sample of pure 3-bromo-1-octene was thus obtained [b.p. 61° (9.5 mm.), 69–70° (14 mm.), n_D^{20}1.4669].

Anal. Calcd. for $C_8H_{15}Br$: C, 50.27%; H, 7.91%; Br, 41.81%; mol. wt., 191. Found: C, 50.62%; H, 8.09%; Br, 41.48%; mol. wt. (cryoscopic), 187.

It was shown that linear relationship existed between the refractive index and the percentage composition of 3-bromo-1-octene and 1-bromo-2-octene mixture. The yield of monobrominated products based on refractive indexes were: 3-bromo-1-octene (I), 3.4 g. (12%); 1-bromo-2-octene, 15.0 g. (53%).

Residue I was placed in a Hickman molecular still and distilled at 10^{-5} mm. and 95° (bath temperature), and the distillate (3.1 g.) collected. A small amount (0.5 g.) of more volatile fraction was recovered from the cold trap. Some crystals of succinimide collected on the wall of the still. A viscous brown tar (2.9 g.) remained in the still. The distillate was shown to contain 49% of bromine by analysis and had an average molecular weight of 230. The infrared spectrum indicated the presence of succinimide. Approximately half of the bromine content could be titrated with aqueous silver titrate.

The bromination proceeded without peroxide under diffused light at a slower rate (8 hr. at 75°), and a similar mixture of products was obtained. The reaction was retarded by molecular oxygen and completely inhibited by a small amount of nitrosobenzene (0.5 mole per cent).

Isomerization of I *and* II. A small amount (100 mg.) of 3-bromo-1-octene (I) was heated in a water bath at 80° (in a nitrogen atmosphere) for 1 hr. The refractive index changed from n_D^{20} 1.4670 to 1.4690. The infrared spectrum of this material was identical with a synthetic mixture of I and II in a ratio of 2:7. The index of refraction of 1-bromo-octene-2 remained unchanged when the material was heated to 80° for 1 hr.

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[3] For rearrangement of allylic bromides (similar to I) to allylic bromides (similar to II) under the action of hydrogen bromide and oxygen, see M. S. Kharasch, E. T. Margolis, and F. R. Mayo, *J. Org. Chem.*, **1**, 393 (1936); see also the excellent and comprehensive review by R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 775 (1956).

[4] For the bromination of related olefins by *N*-bromosuccinimide see the following papers: Allylbenzene to cinnamyl bromide, and non-1-en-4-yne to 1-bromo-non-2-en-4-yne [E. A. Braude and E. S. Waight, *J. Chem. Soc.*, 1116 (1952)]. Note also that in the case of methyl vinylacetate [E. J. Corey, *J. Am. Chem. Soc.*, **75**, 2251 (1953)] and vinyl acetonitrile [P. Couvreur and A. Bruylants, *Bull. soc. chim. Belg.*, 61, 253 (1952); W. Bailey and J. Bello, *J. Org. Chem.*, **20**, 525 (1955)] no methyl γ-bromocrotonate or γ-bromocrotonitrile were isolated. The reaction of vinyl acetonitrile was repeated in our laboratory. We differ, in a minor point from Bailey and Bello. The index of refraction of the β,γ-dibromobutyronitrile obtained by us was n_D^{20} 1.5485, whereas Bailey and Bello report an index of refraction at 25° of 1.5165.