291. *The Bromination of Allylbenzene.*

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The reaction between 1-phenylallyl alcohol and hydrogen bromide takes place with rearrangement, cinnamyl bromide being obtained instead of 1-phenylallyl bromide. In order to obtain the latter we have studied the reaction of *N*-bromosuccinimide with allylbenzene; the physical constants of the product and of its acetate are practically identical with those corresponding to the cinnamyl derivatives.

Ozonolysis of the carbinol obtained by the Grignard reaction of acetophenone with the bromo-derivative, and direct ozonolysis of the bromo-derivative, point to rearrangement in the action of *N*-bromosuccinimide on allylbenzene, cinnamyl bromide being obtained, with 1-phenylallyl bromide as an impurity. This result is confirmed by the infra-red spectrum of the bromide. The spectrum of the bromination product of diallyl showed that also in this case rearrangement accompanies bromination.

IN the reaction of 1-phenylallyl alcohol with hydrogen bromide cinnamyl bromide

$$C_6H_5\cdot CH{:}CH\cdot CH_2Br$$

is obtained instead of 1-phenylallyl bromide $C_6H_5\cdot CHBr\cdot CH{:}CH_2$ (Moureu and Gallagher, *Bull. Soc. chim.*, 1921, [iv], **29**, 1009; Meisenheimer and Link, *Annalen*, 1930, **479**, 213; Lora-Tamayo and Perez Ossorio, *Anal. Fís. Quím.*, 1948, **44**, *B*, 981). Bouis (*Ann. Chim.*, 1928, **9**, **407**), in experiments with various arylvinylcarbinols, established as a general rule that the transformation of secondary carbinols into bromo-derivatives is accompanied by rearrangement to give primary bromides. As we wished to prepare 1-phenylallyl bromide, we have studied the reaction of allylbenzene with *N*-bromosuccinimide, which Ziegler has proposed

(Ziegler, Späth, Schaaf, Schumann, and Winkelmann, *Annalen*, 1942, **551**, 80) as a reagent for the bromine-substitution of allyl compounds in the α-position to the double bond.

Among the numerous recent applications of *N*-bromosuccinimide (Ruzicka *et al.*, *Helv. Chim. Acta*, 1943, **25**, 1235; 1945, **28**, 1360; 1946, **29**, 473; Buu-Hoï, *Annalen*, 1944, **556**, 1; Buu-Hoï and Lecocq, *Compt. rend.*, 1946, **222**, 1441; *J.*, 1946, 830; Lecocq, *Ann. Chim.*, 1948, [xii], **3**, 62) including those which involve the use of catalysts (Karrer *et al.*, *Helv. Chim. Acta*, 1946, **29**, 573), few cases are mentioned where bromination is accompanied by rearrangement. Karrer and Ringli (*Helv. Chim. Acta*, 1947, **30**, 863, 1771) considered this possibility when they studied the bromination of diallyl, but concluded that the normal halogenation product, $CH_2{:}CH{\cdot}CH_2{\cdot}CHBr{\cdot}CH{:}CH_2$, is formed. Very recently, Braude and Waight, and Bateman, Cuneen, and Koch, in preliminary communications (*Nature*, 1949, **164**, 241), have reported conclusions which agree with those now reached, *viz.*, that allylbenzene and diallyl undergo rearrangement on monobromination with *N*-bromosuccinimide.

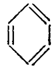
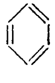
We carried out the bromination according to the method of Ziegler and Lecocq and with a time of heating and molar relations similar to those adopted in the case of propenylbenzene. The brominated product, b. p. 132°/17 mm., resembled cinnamyl bromide. For its initial identification, we prepared the acetate by treating it with silver acetate in benzene and this had constants practically identical with those of cinnamyl acetate.

	B. p.	n_D^{22}.
Ester obtained	140—141°/10 mm.	1·5480
Cinnamyl acetate	139—140°/10 mm.	1·5464 *
1-Phenylallyl acetate	111°/16 mm.	1·5092 †

* Bouis, *Ann. Chim.*, 1928, **9**, 407. † Dureen and Kenyon, *J.*, 1939, 1697.

For the reaction product of diallyl with *N*-bromosuccinimide Karrer and Schneider (*Helv. Chim. Acta*, 1948, **31**, 395) ascertained the structure by treating the bromo-derivative with magnesium and acetophenone and ozonizing the alcohol so produced. Using this method with our bromide from allylbenzene, we obtained a carbinol, m. p. 82°, which on ozonolysis yielded no formaldehyde, thereby showing that the bromide did not react as 1-phenylallyl bromide. Somewhat more direct evidence was obtained by ozonizing the bromo-compound directly. This gave benzoic acid in very small amounts (1·5% of the theoretical quantity), formaldehyde, and an unidentified reducing residue containing bromine. However, if the original product does not undergo rearrangement during the process, the results allow us to regard it as cinnamyl bromide, with 1-phenylallyl bromide as an impurity.

The infra-red spectrum of the bromo-derivative can undoubtedly disclose its structure with greater certainty. Thanks to the kindness of Mr. Henry Cohn of University College, London, we were able to obtain and interpret these spectra (see table).

Frequency, cm.$^{-1}$.	Intensity.	Probable assignment.
Bromo-derivative of allylbenzene.		
1598	strong	C═C bond
1202	very strong	C—Br bond
1077	strong	
965	very strong	$R_1{\cdot}CH{:}CH{\cdot}R_2$
747	very strong	 monosubstitution
Bromo-derivative of diallyl.		
1203	very strong	C—Br bond
994	strong	$R{\cdot}CH{:}CH_2$
967	very strong	$R_1{\cdot}CH{:}CH{\cdot}R_2$
917	very strong	$R{\cdot}CH{:}CH_2$

Thompson (*Trans. Faraday Soc.*, 1945, 249) showed that compounds of the types

$$R_1{\cdot}CH{:}CH{\cdot}R_2 \text{ and } R{\cdot}CH{:}CH_2$$

could be distinguished, inasmuch as the former give an intense band at 965 cm.$^{-1}$, and the latter bands at 909 and 990 cm.$^{-1}$. In our bromination product a very strong band occurs at 965 cm.$^{-1}$, which indicates the presence of the former grouping and weak bands at 998 and 985 cm.$^{-1}$, which can be attributed to a terminal double bond in very small quantity. The other bands, entered in the table, correspond, as indicated, to the C–Br bond, to the monosubstitution, and also to the conjugation $C{:}C{\cdot}C_6H_5$.

The conclusion we reach is that the product examined is mostly, if not entirely,

$$C_6H_5{\cdot}CH{:}CH{\cdot}CH_2Br,$$

which confirms the occurrence of rearrangement in the bromination of allylbenzene with *N*-bromosuccinimide.

In view of this, the infra-red spectrum (see table) was obtained of the bromination product of diallyl, assumed by Karrer to be $CH_2{:}CH{\cdot}CHBr{\cdot}CH_2{\cdot}CH{:}CH_2$. The presence of strong bands at 994 and 917 cm.$^{-1}$ indicates the existence of the grouping $R{\cdot}CH{:}CH_2$, and the band at 967 cm.$^{-1}$ points to the existence of $R_1{\cdot}CH{:}CH{\cdot}R_2$. The compound concerned may be

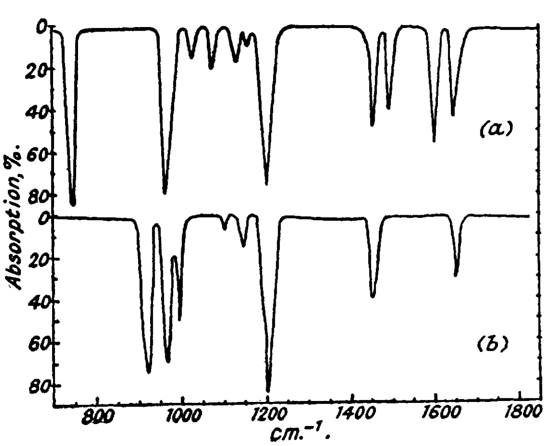
$$CH_2Br{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2,$$

or a mixture of $CH_2Br{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2$ and $CH_2{:}CH{\cdot}CHBr{\cdot}CH_2{\cdot}CH{:}CH_2$, or another. Whichever it is, the spectrum shows that in the bromination of diallyl partial rearrangement occurs. This does not agree with conclusions derived from chemical transformations.

EXPERIMENTAL.

Preparation of Allylbenzene.—Herschberg's technique (*Helv. Chim. Acta*, 1934, **17**, 353) was followed but, instead of bromobenzene and allyl bromide, the corresponding iodine derivatives were used.

Reaction of Allylbenzene with N-*Bromosuccinimide.*—A solution of allylbenzene (22 g.) and *N*-bromosuccinimide (25 g.) in dry carbon tetrachloride (100 c.c.) was refluxed for 20 hours. The succinimide formed was separated, the solvent removed under reduced pressure, and the residue fractionated. After a small fraction of unchanged allylbenzene, the bromo-derivative, b. p. 118—120°/6 mm. (45—50%), passed over, and there remained a residue not yet investigated. The strongly coloured distillate was washed with a solution of sodium carbonate and redistilled in presence of anhydrous potassium carbonate. It then had b. p. 98°/1·5 mm. and, on addition of bromine, formed $C_6H_5{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$, m. p. 128°.



Transformation of the Bromo-derivative into the Acetoxy-derivative.—The bromo-derivative (7 g.), crystallized silver acetate (4 g.), and anhydrous benzene (60 c.c.) were refluxed for 2 hours, then another 2 g. of silver acetate were added, and another 2 g. after 10 hours. Boiling was continued for 30 hours. The silver bromide and the acetate residues were then separated, the benzene evaporated off, and the residue distilled under reduced pressure (b. p. 115/2·5 mm.; n_D^{22} 1·5480).

Condensation of the Bromo-derivative with Acetophenone.—To 1·1 g. of magnesium shavings, a solution of 9 g. of the bromo-derivative in 30 c.c. of anhydrous ether was added. When addition was complete, heating under reflux was carried out for 1—1·5 hours, followed by cooling in an ice-bath. 5 g. of acetophenone dissolved in 15 c.c. of anhydrous ether were then added dropwise. When the reaction was complete, heating was continued for another 2 hours, with stirring. The magnesium compounds were decomposed with aqueous ammonium chloride and the mixture extracted with ether; the ethereal solution was washed with water and dried (Na_2SO_4) : the solvent was removed, and the residue was distilled *in vacuo*. The unchanged acetophenone fraction was separated and the residue allowed to crystallize in a freezing mixture. It was then collected and recrystallized from alcohol. A white *product* was obtained (small nacreous laminae), m. p. 82° (Found : C, 85·6; H, 7·7. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%).

Ozonolysis of the Carbinol.—In all experiments we employed an ozonizer which produces 5—7 mg. of ozone per hour at a speed of passage of 90—100 bubbles per minute. The temperature of the solution to be ozonized was –15°.

The carbinol (0·254 g.) in pure carbon tetrachloride was ozonized until no more ozone was absorbed. Water (50 c.c.) was added to the solution, which was then refluxed for 3 hours, the end of the condenser being connected by a glass tube to a vessel containing 20 c.c. of water (*A*) cooled in ice (Sorm and Urbanek, *Coll. Trav. chim. Tchécosl.*, 1948, **13**, 425). The aqueous layer and the water (*A*) were distilled, 0·2 g. of dimedon was added, and the whole boiled for 10 minutes and set aside for 24 hours. No crystallization was observed.

The solvent was evaporated from the carbon tetrachloride layer, the residue was dissolved in ether, extracted several times with a 15% sodium carbonate solution and washed with water, and the ether was evaporated off. The residue then gave a semicarbazone, m. p. 209° (from methanol). The m. p. of benzaldehyde semicarbazone is 210°; mixed m. p. was 209°.

Ozonolysis of the Original Bromo-derivative.—In the same way 0·3880 g. of the bromo-derivative was ozonized. The ozonide formed was decomposed by Batt and Slater's technique (*J.*, 1949, 838), and three solutions were obtained; (*A*) aqueous solution, (*B*) ethereal extract of neutral products, and (*C*) fraction soluble in aqueous sodium carbonate.

(*A*) treated as above, gave 0·0060 g of a product, m. p. 187° (from alcohol) (the formaldehyde-dimedon complex has 187°; mixed m. p., 187°).

(*C*) was acidified with hydrochloric acid and extracted with ether. When the solvent had evaporated, the residue, recrystallized from water, melted at 122°; it was benzoic acid.

(*B*) gave, after removal of the solvent, a thick yellow liquid which contained bromide and readily reduced Fehling's solution. This liquid decomposed on distillation *in vacuo*, and neither a semicarbazone nor a crystalline 2 : 4-dinitrophenylhydrazone could be obtained.

Infra-red Spectra.—A D209 Hilger spectrometer for infra-red was used. The compounds were studied as liquids, between rock-crystal plates of 0·005—0·1 mm. thick. The spectra comprised the range 5—15 μ. and the frequency accuracy was at least $\pm$ 2 cm.$^{-1}$. The figure shows the spectrograms of the bromo-derivatives of allylbenzene (*a*) and diallyl (*b*) obtained with *N*-bromosuccinimide.

Diallyl.—This was prepared, either by the action of the zinc–sodium alloy on allyl iodide, or according to Turk and Chanan (*Org. Synth.*, 1947, **27**, 7), allyl iodide being used instead of the chloride. Bromination was effected with *N*-bromosuccinimide, according to Karrer and Ringli (*loc. cit.*), the monobromo- (b. p. 40—45°/10 mm.) being fractionated from the dibromo-product (b. p. 115—120°/40 mm.).

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