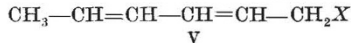
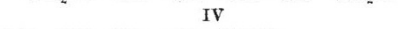
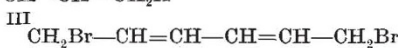
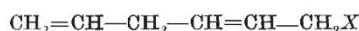
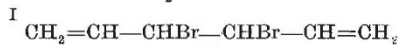
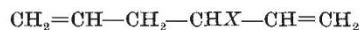


### Bromination of $\Delta^1$ Olefins with *N*-Bromosuccinimide

IN connexion with a re-investigation of the preparation, structure and reactivity of the bromo compound prepared from 2:6-dimethyloctadiene-2:6 and *N*-bromosuccinimide<sup>1</sup>, an examination of the analogous reactions with some simple  $\Delta^1$  olefins has been undertaken. A recent theoretical discussion<sup>2</sup> of the reaction mechanism operative in the latter systems prompts us to present a summary of our findings.

Karrer and Ringli<sup>3</sup>, using 1:5-hexadiene (diallyl) with *N*-bromosuccinimide, obtained mono- and dibromo derivatives which were formulated as (I;  $X = \text{Br}$ ) and (II) respectively. In a second paper<sup>4</sup>, the crystalline dibromide was recognized as the known conjugated dibromide (IV), and doubt was



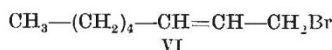
V

expressed as to whether the liquid monobromide was (I), (III) or (V) ( $X = \text{Br}$ ). Shortly afterwards, however, Karrer and Schneider<sup>5</sup> claimed to have confirmed the original structural assignment for the monobromide by condensing it with acetophenone in the presence of magnesium and diethyl ether and submitting the resulting *tert.*-alcohol to ozonolytic degradation: *c.* 1.44 moles of formaldehyde were liberated, but no acetaldehyde. Two features of this work are questionable: (a) the actual isolation of what is undoubtedly the most labile isomeric monobromide; on further reaction, re-arranged derivatives are apparently produced with extreme ease (further bromination gives (IV), and the alcohol (V;  $X = \text{OH}$ ) is obtained via the acetate<sup>6</sup>); (b) the presumed decisiveness of the structural conclusion derived from the degradation experiment, since the investigations of Young and Roberts<sup>6</sup> make it virtually certain that the addendum in the Grignard reaction would combine at the  $\gamma$ - rather than at the  $\alpha$ -carbon atom irrespective of whether the bromide were primary (as in III or V) or secondary (as in I).

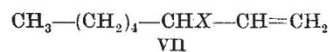
With the aid of infra-red and ultra-violet spectrographic technique, this structural problem is readily resolved. We find that the liquid monobromide possessing the physical properties reported by the Swiss authors is essentially III ( $X = \text{Br}$ ), admixed with a small amount (*c.* 10 per cent) of I ( $X = \text{Er}$ ). Its infra-red spectrum displays strong absorption at 965  $\text{cm}^{-1}$ , characteristic of  $-\text{CH}=\text{CH}-$  groupings, and absent in diallyl, as well as other bands at 915 and 990  $\text{cm}^{-1}$ , due to the presence of  $-\text{CH}=\text{CH}_2$  groups. The intensity of the latter band is of the order of one half that of the same absorption in the parent olefin, and the relative intensities at 990 and 965  $\text{cm}^{-1}$ , correspond to comparable amounts of the two types of double bond, as present in structure III ( $X = \text{Br}$ ). The ultra-violet spectrum of this monobromide confirms the absence of conjugation. Treatment of the derived diallyl magnesium bromide with carbon dioxide yields the acid I ( $X = \text{CO}_2\text{H}$ ), the infra-red absorption of which is markedly different from the bromide but closely

similar to that of diallyl between 900 and 1,000  $\text{cm}^{-1}$ . The bromide reacts with a concentrated solution of sodium ethoxide in ethyl alcohol—that is, under  $\text{S}_{\text{N}}2$  conditions leading to ethoxide substitution at the original position of the bromine atom<sup>7,8</sup>—to produce the conjugated 2:4-hexadiene ethyl ether V ( $X = \text{OEt}$ ), which has intense ultra-violet absorption at 2,250 Å and exhibits no infra-red bands attributable to  $-\text{CH}=\text{CH}_2$  groups. The facile prototropic re-arrangement occurring in this reaction is in keeping, of course, with the 1:4-olefinic character of the parent bromide.

Similar reactivity is evidenced by 1-octene; and the presence of only one unsaturated centre renders the infra-red structural diagnosis more strictly quantitative. The analytically pure octene monobromide isolated was a liquid mixture containing about 80 per cent of VI and 20 per cent of VII ( $X = \text{Br}$ ), which are partly separable by fractional distillation.



VI



VII

Carbonation of the derived Grignard complex yielded the structurally homogeneous acid VII ( $X = \text{CO}_2\text{H}$ ).

Full experimental details and further discussion will shortly be submitted for publication elsewhere; but we would add here that we do not accept Dewar's suggestion that these data have a critical bearing on the elucidation of the mechanism of the bromination reaction.

This work forms part of a programme of fundamental research undertaken by the Board of the British Rubber Producers' Research Association.

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<sup>1</sup> Bloomfield, *J. Chem. Soc.*, 114 (1944).

<sup>2</sup> Dewar, "The Electronic Theory of Organic Chemistry", 273 (Oxford, 1949).

<sup>3</sup> Karrer and Ringli, *Helv. Chim. Acta*, **30**, 863 (1947).

<sup>4</sup> Karrer and Ringli, *Helv. Chim. Acta*, **30**, 1771 (1947).

<sup>5</sup> Karrer and Schneider, *Helv. Chim. Acta*, **31**, 395 (1948).

<sup>6</sup> Roberts and Young, *J. Amer. Chem. Soc.*, **67**, 148, 319 (1945).

Young and Roberts, *J. Amer. Chem. Soc.*, **68**, 1472 (1946).

<sup>7</sup> Roberts, Young and Winstein, *J. Amer. Chem. Soc.*, **64**, 2157 (1942).

Young and Andrews, *J. Amer. Chem. Soc.*, **66**, 421 (1944).

<sup>8</sup> Catchpole and Hughes, *J. Chem. Soc.*, 4 (1948).

### Estimation of Non-Ionic Detergents

ALTHOUGH satisfactory methods are available<sup>1,2</sup> for the determination of anionic and cationic active agents, no method has hitherto been found for surface-active agents which do not ionize in solution. Compounds of this type are prepared by the action of ethylene oxide on organic bodies containing OH-groups and have the basic structure,  $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ , in which *R* may be an aliphatic and/or hydrocarbon residue. Since these compounds are achieving growing importance as detergents, wetting agents and emulsifying agents, the need for a method of determination has become urgent.

Several methods have been examined in our laboratories, and a phosphomolybdic acid precipita-