

189. The Reaction of Hexa-1 : 5-diene with N-Bromosuccinimide.

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By analytical application, qualitative and approximately quantitative, of infra-red spectroscopy, and by conversion into known derivatives by reactions along well established structural routes, it has been demonstrated, contrary to the conclusions of Karrer and Schneider (*Helv. Chim. Acta*, 1948, **31**, 395), that the monobromide isolated from the reaction named in the title consists mainly of 1-bromohexa-2 : 5-diene, mixed with about 10% of the 3-bromo- $\Delta^{1:5}$ -isomer.

DURING an investigation of certain allylic terpenoid bromides it became of interest to attempt the preparation of the bromide (I; X = Br) and to see whether dehydrobromination yielded hexa-1 : 3 : 5-triene. In view of the investigations of Winstein and Young (*J. Amer. Chem. Soc.*, 1936, **58**, 104), of Kharasch, Margolis, and Mayo (*J. Org. Chem.*, 1936, **1**, 393), and of Young, Richards, and Azorlosa (*J. Amer. Chem. Soc.*, 1939, **61**, 3070) into the isolation and interconversion of related allylic bromides, it was apparent from the outset that this bromide would generally co-exist with its allylic isomer (II; X = Br) and that its preparation substantially pure would present much difficulty. It was, therefore, surprising that Karrer and Ringli (*Helv. Chim. Acta*, 1947, **30**, 863) reported the preparation of (I; X = Br) by treatment of hexa-1 : 5-diene (diallyl) with N-bromosuccinimide in boiling carbon tetrachloride. Further bromination by the same method yielded a crystalline dibromide formulated as (III). A



second, correcting paper (*idem, ibid.*, 1947, **30**, 1771) reported the dibromide to be the conjugated compound (IV; X = Y = Br) (Farmer, Larria, Switz, and Thorpe, *J.*, 1927, 2937), and doubt was expressed concerning the correctness of the structure assigned to the monobromide. This doubt was quickly resolved in favour of the original assignment by Karrer and Schneider (*ibid.*, 1948, **31**, 395), who condensed the monobromide with acetophenone in the presence of magnesium and ether, ozonised the resulting *tert.*-alcohol, and measured the liberation of 1.44 g.-mols. of

formaldehyde; no acetaldehyde was detected. The last observation was significant since Karrer and Schneider had found that mild hydrolysis of the acetate obtained from the bromide by silver acetate produced an unsaturated alcohol which yielded *n*-hexanol on catalytic reduction. An ω -bromide structure therefore became a possibility and consideration was mainly given to (IV; X = H; Y = Br) rather than to (II; X = Br), presumably because of analogy with the dibromide structure. However, the ozonolysis apparently serves to eliminate this possibility, and requires that the formation of the primary alcohol be attributed to rearrangement occurring during its synthesis from the bromide.

The identification of diallyl monobromide * as (I; X = Br) is so contrary to expectation based on the behaviour of similar bromides (Young *et al.*, *loc. cit.*) as to provoke critical examination of the supporting evidence. Three unsatisfactory features are then evident. First, the absence of any mention of interconversion (I; X = Br) \rightleftharpoons (II; X = Br) suggests that Karrer and Schneider overlooked the controlling influence on the composition of the product likely to be exerted by this ready isomerisation. Secondly, it seems that no isomerisation occurs during the monobromination stage and yet two double-bond displacements and the migration of the initially substituted bromine atom occur on further reaction. Thirdly, the presumed diagnostic criterion afforded by ozonolysis is almost certainly valueless since, in the case of the closely similar 1-methylallyl and 3-methylallyl bromides, Roberts and Young (*J. Amer. Chem. Soc.*, 1945, **67**, 148, 319; 1946, **68**, 1472) established that, irrespective of the isomeric nature of the original halide, reaction of the derived Grignard complex with carbonyl compounds yields almost pure secondary allylic derivatives.

The ever-present possibility of allylic isomerisation accompanying reaction militates severely against the successful application of purely chemical methods to solve this structural problem.† Accordingly, our investigations (which date from the appearance of Karrer and Ringli's first paper) have sought to make full use of infra-red and ultra-violet spectroscopy (cf. especially Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland, *J.*, 1950, 915).

The Composition of Diallyl Monobromide.—We find that analytically pure diallyl monobromide boiling over the temperature range reported by Karrer and Ringli and prepared either according to these authors' directions or by the modified procedures referred to later is neither (I; X = Br) nor (IV; X = H; Y = Br) but is *essentially* (II; X = Br). Its infra-red absorption spectrum exhibits a strong band at 965 cm^{-1} , characteristic of the presence of the CHR:CHR grouping and absent in diallyl, as well as bands at 918 and 990 cm^{-1} caused by CH_2 :CHR groups. The intensity of the latter band is approximately half that of the same absorption in diallyl. The ultra-violet absorption spectrum confirms the absence of diene conjugation.

With carbon dioxide the Grignard complex derived from the bromide yields the secondary allylic *hexa-1 : 5-diene-3-carboxylic acid* (I; X = CO_2H) (*p*-bromophenacyl ester, m. p. 32—33°), whose infra-red absorption differs markedly from the bromide but closely resembles that of the parent olefin between 900 and 1000 cm^{-1} . This practically quantitative change from primary allylic type has been incontrovertibly demonstrated by Young and Roberts (*loc. cit.*) to be a general characteristic of carbonyl compound-butenylmagnesium halide reactions, and therefore we can confidently assert that while Karrer and Schneider's structure for the bromide is wrong their formulation of the *tert.*-alcohol prepared from acetophenone as (I; X = $-\text{CPhMe}\cdot\text{OH}$) is right. When the bromide is converted into an ether by a hot concentrated solution of sodium ethoxide in ethyl alcohol, the product exhibits intense ultra-violet absorption at 2250 A ., indicative of its conjugated nature and, in conformity, its infra-red absorption spectrum reveals the presence and absence of $\text{CH}:\text{CH}$ and $\text{CH}:\text{CH}_2$ groups, respectively. The ether must therefore be either 1-ethoxyhexa-2 : 4-diene (IV; X = H; Y = OEt) or the 3-ethoxy-isomer. The location of the ultra-violet absorption maximum affords strong evidence favouring the former. This indication has been verified completely by catalytic reduction and identification of the product as *n*-hexyl ethyl ether by cleavage with hydriodic acid and conversion into *n*-hexylisothiuronium picrate, m. p. 156°. Since it is now well authenticated that bimolecular ($\text{S}_{\text{N}}2$) replacement reactions of allylic halides with ethoxyl ions lead wholly to attachment of the entrant group at the site of the displaced group (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 627; Catchpole and Hughes, *J.*, 1948, 4; Roberts, Young, and Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157; Young and

* Throughout this paper, "diallyl monobromide" designates the isolated *substitution* product irrespective of its isomeric constitution.

† It should be noted that ozonolysis of allylic compounds possessing α -methylene functional groups can provide particularly untrustworthy information (Young, McKinnis, Webb, and Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 293).

Andrews, *ibid.*, 1944, **66**, 421), combination of the ethoxyl group at a terminal carbon atom under the drastic S_N2 conditions employed provides independent and specific information concerning the location of the original bromine atom. The double-bond shift accompanying alcoholysis exemplifies the well-known lability of 1:4-dienes to such isomerisation under proton-transfer conditions. We have not repeated Karrer and Ringli's bromide \longrightarrow acetate \longrightarrow alcohol sequence since the tendency to S_N1 replacement (and therefore to isomeric mixtures) in the first stage (see, *e.g.*, Catchpole, Hughes, and Ingold, *J.*, 1948, 8) introduces ambiguity into any structural deductions. The procedure employed for isolation by the Swiss workers would hardly be likely to determine whether the alcohol said to be (IV; X = H; Y = OH) was free from (I; X = OH), and the mild hydrolytic conditions used in the second stage suggest that (II; X = OH) may also have been present.

No uncertainty attaches to the data and conclusions so far presented, but the normal existence of similar allylic bromides as isomeric mixtures containing *ca.* 15% of the secondary allylic form (Young *et al.*, *loc. cit.*), together with the fact that the bromination conditions and the subsequent isolation of the product both strongly facilitate interconversion (*cf.* following paper), indicate that the possibility of isolating a homogeneous diallyl monobromide as the reaction product is negligible. An immediate and affirmative indication of isomeric heterogeneity is afforded by the observation that analytically pure monobromide boils over a range of about five degrees (*cf.* Karrer and Ringli, *loc. cit.*). More significantly, the infra-red spectra of head and of tail fractions showed small but readily detectable variations corresponding to a higher concentration of the secondary allylic isomer (I; X = Br) in the lower-boiling material. In agreement with the work of Young *et al.* (*loc. cit.*), this partial isomeric separation on distillation was also reflected in substantial differences in refractive index. The difficult and tedious problem of accurate isomeric analysis, necessitating the separate physical characterisation of both components, is beyond the scope of the present work, but an approximate estimation can be deduced by comparing the absolute extinction coefficients of the infra-red absorption frequencies due to the CHR:CHR and CH₂:CHR groups in the bulked monobromide product. Such analysis (see the Experimental section) is complicated by the occurrence of *cis*- and *trans*-forms of the 1-bromo- Δ^2 -isomer, but it is estimated that 5–15% of (I; X = Br) is present in a typical monobromide preparation.

Secondary Products of Reaction.—As reported by Karrer and Ringli (*loc. cit.*), a minor product of the diallyl-*N*-bromosuccinimide reaction is the crystalline, conjugated dibromide (IV; X = Y = Br), which is better prepared by further bromination of the monobromide and displays spectroscopic characteristics in full accord with its established molecular structure. We have also isolated a second dibromide—a liquid in which the elements of hydrogen bromide have added to the CH:CH centre of the monobromide. This compound has not been specially investigated, but its spectral properties together with knowledge of the orientation of hydrogen bromide addition to allyl bromide under similar conditions suggest fairly definitely that it is 4:6-dibromohex-1-ene. Small quantities of hydrogen bromide are often evolved during bromination with *N*-bromosuccinimide; larger quantities are to be expected only when spontaneous dehydrobromination is occurring simultaneously (see, *e.g.*, Dorée, McGhie, and Kurzer, *J.*, 1949, 570). Under the conditions of reaction, the bromide (II; X = Br) shows little tendency to liberate hydrogen bromide (*e.g.*, during further bromination), as might be expected from its structure, but the isomer (I; X = Br) may well do so very readily, and in doing so may provide the source of the polymeric tar which is formed in considerable quantity. Kharasch, Nudenberg, and Sternfeld (*J. Amer. Chem. Soc.*, 1940, **62**, 2032) have actually stated that a tendency to just this behaviour is exhibited by the corresponding chloride even at room temperature. Adequate quantities of (I; X = Br) are likely to be available for dehydrobromination on the scale required, for there is reason to believe (following paper) that (I; X = Br) and (II; X = Br) are formed in somewhat comparable amounts in the primary bromination process, although the former cannot survive isolation in amounts greater than its thermodynamic equilibrium proportion.

The Reactivity of Diallyl towards N-Bromosuccinimide.—Bromination proceeds far less readily with diallyl than with the singly unsaturated Δ^1 -olefin, oct-1-ene (following paper), and the isoprenic diene, 2:6-dimethylocta-2:6-diene (unpublished). Our experience is that the use of the olefin in excess rather than in equimolecular proportion to the brominating agent (*cf.* Karrer and Ringli, *loc. cit.*) expedites reaction and lessens contamination of the monobromide with by-products. However, under conditions such that reaction with the last two olefins is complete within 15 minutes, reaction with diallyl is incomplete after two hours. Irradiation with ultra-violet light produces a small acceleration, but this is offset by an increase in secondary

decomposition, shown by a marked darkening of the reaction mixture. If one accepts as a reasonable assumption, in the absence of positive evidence, that a rate-determining step in the bromination is the detachment of an α -methylene hydrogen atom (Bloomfield, *J.*, 1944, 114; cf. following paper), then the enhanced reactivity of 2 : 6-dimethylocta-2 : 6-diene compared with diallyl can readily be associated with the increased mesomerism of the methylallyl as compared with the allyl radical. The rate difference between oct-1-ene and diallyl is much less obvious, especially as Bolland (*Trans. Faraday Soc.*, in the press) has found that peroxide radicals abstract α -methylene hydrogen atoms from both molecules with practically the same efficiency—a result which should be general for any similar hydrogen exchange.

Added in proof. On the basis of ozonolysis results, Karrer and Perl (*Helv. Chim. Acta*, 1950, 33, 36) have rejected our conclusions as presented in a preliminary note (*Nature*, 1949, 164, 242), and identify the isolated monobromide as essentially $\text{CHMe}\cdot\text{CH}\cdot\text{CHBr}\cdot\text{CH}\cdot\text{CH}_2$ (V). The analytical data supporting this view are, however, inherently uncertain (cf. *J.*, 1950, 915), and it is opposed by the diverse and fully consistent evidence reported in this and the following paper, and the facts that it involves unusual prototropic changes [*e.g.*, the conversion of (V) into (I; $\text{X} = \text{CO}_2\text{H}$) during an ordinary Grignard reaction], and that 3-bromo-1 : 4-dienes do not normally exist because the lability of the bromine atom allows full rein to the conjugative tendency of the 1 : 4-diene unit [*e.g.*, attempted preparations of 1-phenylallyl bromide and linaloyl bromide always yield the isomeric cinnamyl and geranyl compounds, respectively, and diallyl dibromide is obtained as (IV; $\text{X} = \text{Y} = \text{Br}$) for the same reason].

EXPERIMENTAL.

Hexa-1 : 5-diene, prepared from allyl bromide (Cortese, *J. Amer. Chem. Soc.*, 1929, 51, 2267), had b. p. $59\cdot6^\circ/758$ mm. Its infra-red spectrum reflects unambiguously the absence of any but $\text{CH}_2\cdot\text{CHR}$ -type unsaturation (cf. Barnard *et al.*, *loc. cit.*).

Purchased and synthesised batches of N-bromosuccinimide varied greatly in efficacy. Recrystallisation from water was found to yield consistently active material.

Reaction of Hexa-1 : 5-diene with N-Bromosuccinimide.—(a) *Karrer and Ringli's conditions.* The olefin (50.5 g., 0.62 mole), N-bromosuccinimide (89 g., 0.5 mole), carbon tetrachloride (300 ml.), and benzoyl peroxide (0.2 g.)* were refluxed for 8 hours. Removal of the insoluble succinimide and the solvent, and distillation of the liquid residue gave the following fractions of 1-bromohexa-2 : 5-diene admixed with a little 3-bromohexa-1 : 5-diene: (1) 1 g., b. p. $39\text{--}40^\circ/11$ mm., n_D^{16} 1.4963 (Found: C, 44.2; H, 5.7; Br, 50.2. $\text{C}_6\text{H}_9\text{Br}$ requires C, 44.7; H, 5.6; Br, 49.7%); (2) 2.1 g., b. p. $40\text{--}41^\circ/11$ mm., n_D^{16} 1.4985; and (3) 9.5 g., b. p. $41\text{--}44^\circ/11$ mm., n_D^{16} 1.5005 (Found: C, 44.5; H, 5.7; Br, 50.1%).

(b) *Large excess of olefin.* The olefin (131 g., 1.6 moles), N-bromosuccinimide (100 g., 0.56 mole), carbon tetrachloride (230 ml.), and benzoyl peroxide (0.2 g.) were refluxed for 4 hours. Fractionation of the product gave (1) 2.9 g., b. p. $39\text{--}40^\circ/10$ mm., n_D^{16} 1.4970 (Found: C, 44.5; H, 5.7; Br, 50.0%), (2) 11 g., b. p. $40\text{--}41\cdot5^\circ/10$ mm., n_D^{16} 1.4996, and (3) 12.3 g., b. p. $41\cdot5\text{--}44^\circ/11$ mm., n_D^{16} 1.5009 (Found: C, 44.4; H, 5.7; Br, 49.7%).

(c) *Irradiation with ultra-violet light.* The olefin (70.5 g., 0.86 mole), N-bromosuccinimide (178 g., 1.0 mole), carbon tetrachloride (300 ml.), and benzoyl peroxide (0.2 g.) were irradiated with a Hanovia S. 500 mercury-arc lamp 15 cm. distant and refluxed for 2.5 hours. Two fractions of the distilled product were collected: (1) 4.2 g., b. p. $39\text{--}40^\circ/10$ mm., n_D^{16} 1.4980 (Found: C, 44.5; H, 5.7; Br, 50.2%), and (2) 13.9 g., b. p. $40\text{--}43^\circ/10$ mm., n_D^{16} 1.4990 (Found: C, 44.5; H, 5.7; Br, 49.9%).

Ultra-violet Spectrographic Examination of Diallyl Monobromide.—The bulked distillate from (a) displayed no selective absorption between 2200 and 3400 Å.

Infra-red Spectrographic Examination of Diallyl Monobromide.—The bulked distillate from (a) exhibited strong infra-red absorption at 965, 918, and 990 cm^{-1} . Comparison with diallyl (much stronger absorption at 913 and 990 cm^{-1} , no absorption at 965 cm^{-1}) and allyl bromide (strong absorption at 927 and 990 cm^{-1} , no absorption at 965 cm^{-1}) indicated that the product was essentially (II; $\text{X} = \text{Br}$).

For the reason given in the next paragraph, the ratio of the observed molecular extinction coefficient at 965 cm^{-1} to that exhibited by a pure reference compound does not afford an absolute measure of the concentration of $\text{CH}_2\cdot\text{CH}$ units. However, comparison of the relative variations at 918 and 965 cm^{-1} in the several fractions yields a *relative* measure of the proportion of $\text{CH}_2\cdot\text{CHR}$ and $\text{CHR}\cdot\text{CHR}$ groups. The following optical densities (determined immediately after isolation of the fractions, using *ca.* 4% solutions in carbon tetrachloride and the same absorption cell throughout) reveal that an increase in b. p. and refractive index reflects an increase in the proportion of the primary allylic isomer (cf. Young, Richards, and Azorlosa, *loc. cit.*):

Bromide fraction.	a1.	b1.	c1.	c3.	a3.	b3.
n_D^{16}	1.4963	1.4970	1.4980	1.4990	1.5003	1.5009
$\log (I_0/I)_{918}/\log (I_0/I)_{965}$	1.90	1.64	1.51	1.08	1.11	1.01

In principle, two independent, absolute estimations of the isomeric composition of the bromide product are obtainable by the comparison of its extinction coefficients (i) at 918 or 990 cm^{-1} and (ii) at

* On the scale described, Karrer and Ringli would have added 2.08 g. The essential features of the reaction are obviously insensitive to the use of an amount more in keeping with the catalytic rôle of the peroxide.

965 cm^{-1} with standard values determined from appropriate reference compounds. Since the former dual absorption is common to both isomers whereas the latter absorption is due solely to the presence of the $\Delta^{2:5}$ -isomer, the second comparison is potentially the more sensitive. However, absorption at 965 cm^{-1} originates in the *trans*-form of the CHR:CHR' grouping only, and hence the occurrence of both *cis*- and *trans*-forms of the latter isomer would obviously vitiate this simple analysis. That this situation actually prevails was evident first from the much lower proportion of the $\Delta^{2:5}$ -isomer thus estimated as compared with the proportion derived from method (i), and secondly from the occurrence of absorption at 680 cm^{-1} attributable to the *cis*-CHR:CHR' grouping (Kilpatrick and Pitzer, *J. Res. Nat. Bur. Stand.*, 1947, **38**, 191; Sheppard and Sutherland, *Proc. Roy. Soc., A*, 1949, **196**, footnote p. 203). Since a standard value of the extinction coefficient at 965 cm^{-1} of a *trans*-dialkylethylene is available (Hart and Meyer, *J. Amer. Chem. Soc.*, 1949, **71**, 1980),* comparison at this frequency serves to determine the concentrations of *trans*-1-bromohexa-2 : 5-diene. Technical difficulties, as well as the absence of a satisfactory standard, prohibit a corresponding quantitative determination of the *cis*-form. It is only possible, therefore, to estimate the chemical isomeric composition of the bromide mixture by method (i); as the data collected in the following table show, the results have limited accuracy. Since the

Compound.	Absorbing unit.	Frequency (cm^{-1}).	Molecular extinction coefficient (per absorbing unit).	Composition of diallyl monobromide.	
				3-Bromohexa-1 : 5-diene (%).	1-Bromohexa-2 : 5-diene (% <i>trans</i> -).
Hexa-1 : 5-diene	CH ₂ :CHR	{ 913	107		
		{ 990	45		
Allyl bromide ...	CH ₂ :CHR	{ 927	126		
		{ 983	45		
<i>trans</i> -Hex-2-ene ...	CHR:CHR	965	157 †	—	—
		Bulked sample from preparation (a) } CH ₂ :CHR	{ 918	113	5
			{ 990	50	11
	<i>trans</i> -CHR:CHR	965	100	—	67

† From Hart and Meyer, *loc. cit.*

absorption at 990 cm^{-1} appears to be insensitive to substitutional changes in the reference compounds, comparison at this frequency is considered to provide the more reliable estimate, correct to $\pm 5\%$. By difference, *cis*-1-bromohexa-2 : 5-diene must be present to the extent of about 22%.

4 : 6-Dibromohex-1-ene.—Fractionation of the liquid remaining after fraction 3 from preparation (a) had distilled gave: (4) a mixture of increasing bromine content, b. p. 53—86°/14 mm., n_D^{20} 1.5121 (2.6 g.); and (5) a dibromide, b. p. 86—87°/14 mm., n_D^{20} 1.5215 (Found: C, 30.1; H, 4.2. C₆H₁₀Br₂ requires C, 29.8; H, 4.1%) (6.3 g.). Infra-red spectroscopic examination of the dibromide established the presence of CH₂:CHR groups and the absence of CHR:CHR groups; this material therefore results from the addition of hydrogen bromide either non-terminally to (II; X = Br) or terminally to (I; X = Br). In the latter case, addition is possible at the double bond nearer to, or further from, the initially substituted bromine atom. No attempt has been made to determine the structure of the product formally, but the following deductions appear to be virtually conclusive. No selective absorption occurs between 2200—3400 μ , and the general absorption (*e.g.*, $\log \epsilon = 3.0$ at 2200 μ) is much less than that of the specimen of diallyl monobromide referred to above (*e.g.*, $\log \epsilon = 3.7$ at 2200 μ). This difference can only mean that allylic bromide absorption has been replaced by alkyl bromide absorption, *i.e.*, hydrogen bromide addition may have occurred at the nearer, but not at the further, double bond in (I; X = Br). In accordance with the orientation of peroxide-catalysed hydrogen bromide addition to allyl bromide (Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2468), the resulting product will be the same as that obtainable from (II; X = Br), *viz.*, 4 : 6-dibromohex-1-ene.

1 : 6-Dibromohexa-2 : 4-diene (IV; X = Y = Br).—The residue left after isolating the diallyl monobromide from preparation (c) gave on further fractionation: (3) a monobromide-dibromide mixture, b. p. 49—87°/12 mm. (8 g.); (4) an isomeric dibromide mixture, b. p. 40—60°/0.03 mm. (14 g.); (5) 1 : 6-dibromohexa-2 : 4-diene, b. p. 60—65°/0.03 mm., m. p. 86° from light petroleum (b. p. 40—60°) (Found: C, 30.1; H, 3.4. Calc. for C₆H₈Br₂: C, 30.0; H, 3.3%). This dibromide exhibited typical conjugated-diene light absorption in the ultra-violet region (λ_{max} , 2550 μ , $\epsilon = 20,000$); the infra-red spectrum showed no absorption at 915 and 990 cm^{-1} , but very strong absorption at 965 cm^{-1} . A better synthesis is: diallyl monobromide (2 g.), *N*-bromosuccinimide (2.1 g.), carbon tetrachloride (12 ml.), and benzoyl peroxide (0.01 g.) are refluxed for 6 hours; removal of volatile material under reduced pressure leaves a residue (1.6 g.) which solidifies on cooling and then has m. p. 86° (after crystallisation from light petroleum) (Found: C, 30.4; H, 3.6%).

Hexa-1 : 5-diene-3-carboxylic Acid (I; X = CO₂H).—Diallyl monobromide (10 g.) in dry ether (60 ml.) was added during 2.5 hours to a well-stirred mixture of magnesium turnings (5 g.) and ether (30 ml.). Reaction proceeded readily after initiation with a crystal of iodine. The solution of the Grignard derivative so obtained was poured quickly on powdered, solid carbon dioxide. After hydrolysis with ice and hydrochloric acid and isolation in the usual way through its sodium salt, hexa-1 : 5-diene-3-carboxylic acid was obtained (3.5 g.), b. p. 101—102°/12 mm. (Found: C, 66.9; H, 8.1%; equiv., 126.5. C₇H₁₀O₂ requires C, 66.7; H, 7.9%; equiv., 126). Its infra-red spectrum exhibits strong absorption at 915 and 990 cm^{-1} , but no absorption at 965 cm^{-1} (contrast the parent bromide, p. 939). *p*-Bromophenacyl hexa-1 : 5-diene-3-carboxylate had m. p. 32—33° after crystallisation from aqueous ethanol (Found: C, 55.7; H, 4.9; Br, 24.6. C₁₅H₁₅O₃Br requires C, 55.8; H, 4.7; Br, 24.8%).

* We are indebted to these authors for an advance copy of their publication.

1-Ethoxyhexa-2:4-diene (IV; X = H, Y = OEt).—Diallyl monobromide (15 g.), sodium ethoxide (48 g.), and ethanol (240 ml.) were refluxed together for 3 hours. Most of the alcohol was then distilled off, water (450 ml.) added, and the mixture extracted with ether. The product isolated from the ethereal extract was 1-ethoxy-2:4-diene (43%), b. p. 48—49°/9 mm., n_D^{20} 1.4615 (Found: C, 75.9; H, 11.2. $C_8H_{14}O$ requires C, 76.1; H, 11.2%). The ultra-violet spectrum is characterised by: λ_{max} , 2250 Å., $\epsilon = 25,000$ (in ethanol). The infra-red spectrum shows strong absorption at 965 cm^{-1} , but no absorption at 915 and 990 cm^{-1} . When the alcoholysis of the bromide was carried out under rather milder conditions (refluxing for 2 hours and addition of water without distilling off the alcohol), an incompletely conjugated ether was obtained, having b. p. 48—52°/15 mm., n_D^{20} 1.4572 (Found: C, 76.0; H, 11.2%).

Degradation of 1-Ethoxyhexa-2:4-diene.—The fully conjugated ether (5 g.) in ethanol (100 ml.) containing Adams's catalyst (0.5 g.) was shaken with hydrogen at 30 lb. per sq. inch.; ca. 2.3 l. of gas were absorbed in a few minutes, and no further absorption occurred during 4 hours. Isolation of the product in the usual way gave ethyl *n*-hexyl ether (4 g.), b. p. 143—145°/761 mm., n_D^{19} 1.4016 (Found: C, 73.4; H, 13.9. Calc. for $C_8H_{18}O$: C, 73.8; H, 13.9%). An authentic sample of ethyl *n*-hexyl ether had n_D^{19} 1.4017.

The hydrogenated ether (3 ml.) was refluxed with hydriodic acid (57%; 20 ml.) for 3 hours. After dilution of the cooled mixture with water, the product was recovered by ether-extraction and identified as *n*-hexyl iodide, b. p. 178°/753 mm. (2.1 g.), by conversion into *n*-hexylisothiuronium picrate, m. p. alone or mixed with an authentic specimen 156° (from ethanol) (Found: C, 40.2; H, 5.2; S, 8.0. Calc. for $C_{13}H_{19}O_7N_3S$: C, 40.2; H, 4.9; S, 8.2%).

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