Allenes. Part XXIII.[1] Mechanistic Studies on the Formation of 1-Bromoallenes from Prop-1-yn-3-ols

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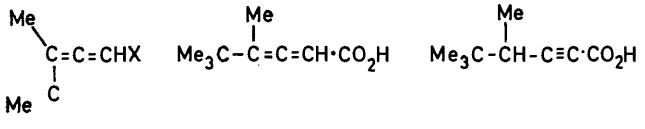
The formation of 1-bromo-3-methylpenta-1,2-diene by the action of hydrobromic acid on 3-methylpent-1-yn-3-ol in the presence of cuprous bromide has been investigated in the temperature range 0—25° and found to follow first-order kinetics. The rate constant and half-life at 0·00, 20·80, and 25·20° and the activation energy for the reaction have been determined. Evidence has been obtained to support the intermediacy of an acetylene–copper(I) π-complex from which the 1-bromoallene is formed by a stereospecific S_Ni' process in which the configuration is retained.

In a previous Part [2] it was reported that acetylenic alcohols [$R^1R^2C(OH)\cdot C{\equiv}CH$] react with hydrobromic acid (48% w/w) in the presence of a catalyst consisting of cuprous bromide, copper powder, and ammonium bromide over a temperature range of 0—35° to form the corresponding 1-bromoallenes ($R^1R^2C{=}C{=}CHBr$) as the sole product and in excellent yield (70—80%). Omission of the catalyst mixture reduces the rate of the reaction considerably, and initially gives approximately equal quantities of 1-bromoallenes and 3-bromoacetylenes.[2,3] It appears, therefore, that a mechanistic scheme for the catalysed reaction must involve a copper(I) complex as an intermediate.

We have now shown that the reaction is highly stereospecific as the optically active acetylenic alcohol, (−)-3,4,4-trimethylpent-yn-3-ol ($[\alpha]_D^{20}$ −0·70°) gave (+)-1-bromo-3,4,4-trimethylpenta-1,2-diene ($[\alpha]_D^{20}$ +31·08°); similarly the (+)-alcohol ($[\alpha]_D^{20}$ +0·78°) gave the (−)-1-bromoallene ($[\alpha]_D^{20}$ −31·93°). The optically active allenic chloride (I) and bromide (II) were converted to the same allenic acid *via* the Grignard compounds. Since the absolute configuration of allenic chloride (I) had already been determined,[4] that of the



(I) X=Cl (II) X=Br (III) (IV)

allenic bromide (II) can now be deduced from a comparison of the sign of the specific rotations of the allenic acids.

Carbonation of the Grignard compounds, followed by hydrolysis, gave in each case, a mixture of the corresponding allenic acid (III) and acetylenic acid (IV) which were separated by chromatography on silica gel and purified by recrystallisation. The results are summarised in Table 1.

TABLE 1

Specific rotation of allene halides (I) and (II) and of the corresponding allenic and acetylenic acids (III) and (IV)

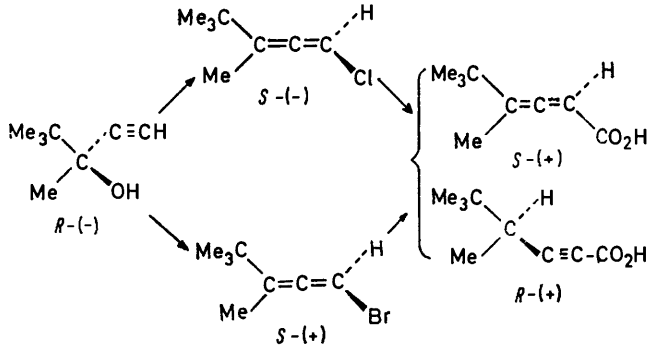
Allenic halide		Allenic acid		Acetylenic acid	
	$[\alpha]_D^{20}$	$[\alpha]_D^{20}$	Yield (%)	$[\alpha]_D^{20}$	Yield (%)
(−)-(I)	−44·25°	+0·52°	6	+12·13	3
(−)-(II)	−32·50	−0·51	7	−7·03	2
(+)-(II)	+31·08	+0·46	6	+6·51	3

From these results it can be seen that (*S*)-(+)-3,4,4-trimethylpent-1-yn-3-ol gave (−)-1-bromo-3,4,4-trimethylpenta-1,2-diene which in turn gave (−)-acids (III) and (IV), and (*R*)-(−)-3,4,4-trimethylpent-1-yn-3-ol gave (+)-1-bromo-3,4,4-trimethylpenta-1,2-diene which was converted to (+)-acids (III) and (IV). We had previously reported that (*R*)-(−)-3,4,4-trimethylpent-1-yn-3-ol gave (*S*)-(−)-1-chloro-3,4,4-trimethylpenta-1,2-diene [4] which has now been shown to give a mixture of (+)-acids (III) and (IV). Therefore the (+)-allenic bromide (II) appears to have the same configuration as the (−)-allenic chloride (I), *i.e.* the (+)-allenic bromide (II) must also have the *S*-configuration These results indicate that the allenic bromide (II) is formed from the intermediate complex by a stereospecific S_Ni' process in which the configuration is retained.

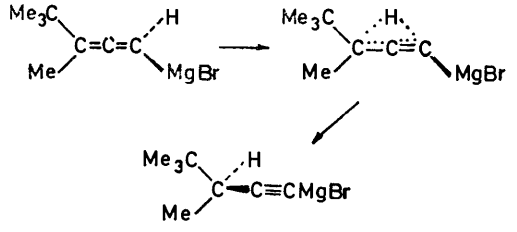
It is interesting to note that the formation of an optically active acetylenic acid in the carbonation of the

[1] Part XXII, J. S. Cowie, P. D. Landor, S. R. Landor, and N. Punja, *J.C.S. Perkin I*, 1972, 2197.
[2] S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, *J. Chem. Soc.* (*C*), 1966, 1223.
[3] D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *Tetrahedron Letters*, 1963, 843.
[4] S. R. Landor and J. Evans, *J. Chem. Soc.*, 1965, 2553.

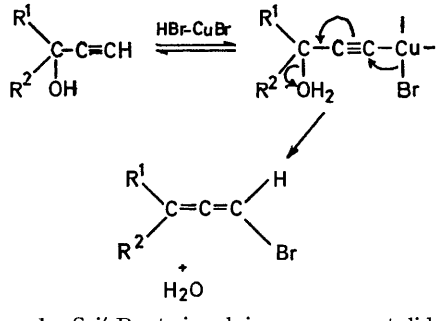
allenic Grignard reagent requires an unusual stereospecific prototropic rearrangement, probably of the Grignard reagent.



The S_Ni' mechanism suggested in an earlier publication [3] and shown in Scheme 1, which involves the transient formation of a copper acetylide intermediate, is



now discounted on the basis that deuterium is not incorporated in the product when 3-methylpent-1-yn-3-ol is converted to the allenic bromide in a solution (50%; w/w) of deuterium bromide in deuterium oxide. Furthermore, no deuterium–hydrogen exchange occurs when pure 1-deuterio-3-methylpent-1-yn-3-ol is converted to 1-bromo-1-deuterio-3-methylpenta-1,2-diene in isotopically normal aqueous hydrobromic acid.



SCHEME 1 S_Ni' Route involving copper acetylide intermediate

The mechanism outlined in Scheme 2, accounts for all the observed facts (*cf.* the formation of dihalogenoallenes [5]), therefore this Scheme depicts the most probable mechanistic pathway for 1-bromoallene formation.

[5] P. M. Greaves, M. Kalli, P. D. Landor, and S. R. Landor, *J. Chem. Soc.* (*C*), 1971, 667.

Omission of copper powder and ammonium bromide does not affect the quality, yield (*ca.* 90%), or rate of formation (Table 2) of the product. Hence, cuprous

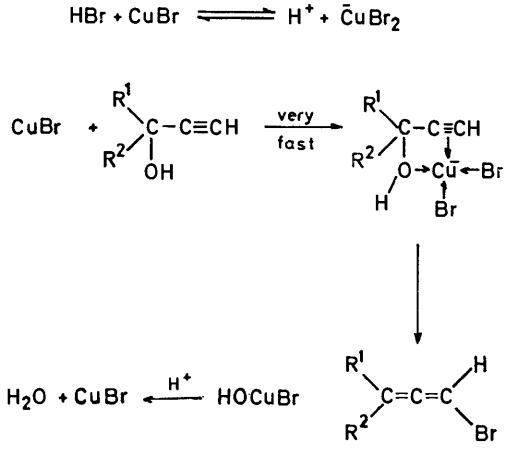
TABLE 2

Half-life and rate constants for 1-bromo-3-methylpenta-1,2-diene formation at 0·00, 20·80, and 25·20°

	With Cu–NH_4Br	Without Cu–NH_4Br		
Temp. (°C) ± 0·01°	0·00	0·00	20·80	25·20
Half-life (min)	72·2	71·5	9·65	5·77
$10^{-3}k/s^{-1}$	0·016	0·0161	0·121	0·20

The experimental error in the g.l.c. analyses of allenic bromide and unreacted alcohol was ±1%.

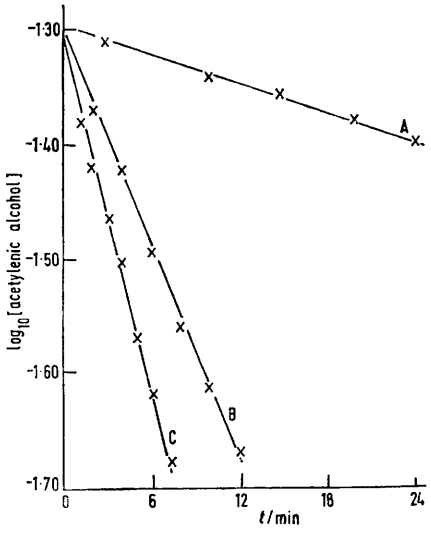
bromide is the only essential component of the catalyst mixture described earlier and the exclusion of copper powder and ammonium bromide from the suggested mechanism (Scheme 2) is justified.



SCHEME 2 S_Ni' Route involving an acetylene–copper(I) π-complex as the intermediate

This is supported further by a study of the kinetics of 1-bromoallene formation. The reaction conditions were slightly modified as it was essential to employ a homogeneous reaction mixture. It was found that the addition of a small quantity of diglyme ensured complete miscibility of the 3-methylpent-1-yn-3-ol with the aqueous phase. 1-Bromo-3-methylpenta-1,2-diene, obtained in 90% yield, separates as an upper layer during the course of the reaction and only a trace of it is detected in the aqueous phase. This modified procedure is not to be regarded as a general preparative method for 1-bromoallenes, as it is applicable only to acetylenic alcohols of low molecular weight. Higher homologues require a substantially greater quantity of diglyme for solubilisation; under these conditions the efficiency of the catalyst is greatly impaired and this results in substantially lower yields of product. A solution composed of acetylenic alcohol, concentrated hydrobromic acid, and diglyme shows a proton resonance at τ 7·1 attributable to the acetylenic proton; on addition of cuprous bromide this signal disappeared immediately which suggests that formation of the π-complex is

instantaneous. It is therefore reasonable to assume that the rate-determining step in the reaction is the conversion of the π-complex to the 1-bromoallene, and, on this basis, the reaction would be expected to follow first-order kinetics. The experimental results reported here support this view, since first-order plots are linear



Plots of [acetylenic alcohol] against time at A, 0·0; B, 20·8; and C, 25·2°

(Figure). The activation energy for the reaction was calculated to be 70·2 kJ mol^{-1}.

The half-life and the rate constants at 0·00, 20·80, and 25·20° are given in Table 2.

EXPERIMENTAL

G.l.c. was carried out with a Pye 104 instrument (with flame ionisation detector); glass columns (5 ft) were used with nitrogen as a carrier gas at a flow rate of 40 ml min^{-1}. I.r. spectra were determined for liquid films on Perkin-Elmer Infracord and 237 spectrometers. N.m.r. spectra were determined with a Perkin-Elmer R10 spectrometer for solution in deuteriochloroform, with tetramethylsilane as internal standard.

(−)-1-*Bromo*-3,4,4-*trimethylpenta*-1,2-*diene*.— (+)-3,4,4-Trimethylpent-1-yn-3-ol [4] (12·6 g, 0·1 mol), $[\alpha]_D^{20}$ +0·78°, was shaken with concentrated hydrobromic acid (23 ml, 48% w/w), cuprous bromide (11·2 g), ammonium bromide (6·0 g), and copper powder (1·1 g) for 40 h at room temperature. The mixture was filtered and the organic layer was washed several times with concentrated hydrobromic acid and dissolved in ether (100 ml). The ethereal solution was washed with aqueous sodium hydrogen carbonate and dried ($MgSO_4$). Fractional distillation gave one main fraction, b.p. 65° at 15 mmHg, (12·8 g, 67%), d_4^{20} 1·1612, $[\alpha]_D^{20}$ −31·93°, $\nu_{max.}$ 1950 (C=C=C) 1160, 825, and 725 cm^{-1}.

(+)-1-*Bromo*-3,4,4-*trimethylpenta*-1,2-*diene*. Similarly, (−)-3,4,4-trimethylpent-1-yn-3-ol, $[\alpha]_D^{20}$ −0·77°, gave the (+)-bromoallene, $[\alpha]_D^{20}$ +31·08°.

(−)-4,5,5-*Trimethylhexa*-2,3-*dienoic acids*.—A solution of (−)-1-bromo-3,4,4-trimethylpenta-1,2-diene (7·9 g, 0·042 mol), $[\alpha]_D^{20}$ −32·50°, in dry tetrahydrofuran (70 ml) was added slowly to magnesium (1·0 g) and mercuric chloride (0·1 g) stirred in dry tetrahydrofuran (50 ml) under dry nitrogen. The mixture was refluxed for 1 h, cooled to 0°, and a stream of dry carbon dioxide was then passed through the solution for 3 h, dry tetrahydrofuran (950 ml) being added to replace losses due to evaporation. The mixture was shaken with ether and dilute hydrochloric acid, and the organic layer was extracted with aqueous sodium hydrogen carbonate. The combined extracts were acidified and shaken with ether. Evaporation of the solvent from the dried ($MgSO_4$) ethereal extract left a viscous, yellow oil (2·4 g), $[\alpha]_D^{20}$ −0·77° which was chromatographed on silica gel (100—200 mesh, activated for 2 h at 350—400°). Elution with 10% ether–light petroleum gave (−)-4,5,5-*trimethylhexa*-2,3-*dienoic acid*, recrystallised from n-pentane, (0·45 g, 7%), m.p. 47—48° (Found: C, 70·0; H, 9·7. $C_9H_{14}O_2$ requires C, 70·0; H, 9·4%), $[\alpha]_D^{20}$ −0·50°, $\nu_{max.}$ 1950 (C=C=C) and 1690 (C=O) cm^{-1}. Elution with ether gave (after recrystallisation from ether–light petroleum) (−)-4,5,5-trimethylhex-2-ynoic acid monohydrate (0·17 g, 2·4%), m.p. 141° (Found: C, 63·2; H, 8·5. $C_9H_{14}O_2,H_2O$ requires C, 62·7; H, 9·3%), $[\alpha]_D^{20}$ −7·0°, $\nu_{max.}$ 3350 (OH), 2230 (C≡C), and 1700 (C=O) cm^{-1}.

Similarly, (−)-1-chloro-3,4,4-trimethylpenta-1,2-diene,[4] $[\alpha]_D^{20}$ −44·25°, and (+)-1-bromo-3,4,4-trimethylpenta-1,2-diene, $[\alpha]_D^{20}$ +31·08°, gave the (+)-allenic and (+)-acetylenic acids (Table 1).

1-*Bromo*-3-*methylpenta*-1,2-*diene*.— 3-Methylpent-1-yn-3-ol (4·9 g, 0·05 mol) containing diglyme (0·6 g) was mixed with a solution (12·5 ml) prepared by dissolving cuprous bromide (25 g) in concentrated hydrobromic acid (125 ml, 48% w/w) and allowed to stand at room temperature. 1-Bromo-3-methylpenta-1,2-diene (7·2 g, 90%), b.p. 49° at 25 mmHg, separated as the upper layer; g.l.c. showed one peak R_t 8 min (carbowax 20M; 60°).

Kinetic Procedure.—The reactions were allowed to attain the appropriate temperature (0·00 in melting ice; 20·80 and 25·20° in a ' Townson and Mercer ' thermostat); they were then mixed in relatively large flasks (250 ml) in order to dissipate any heat of mixing or reaction.

At each temperature the kinetics were studied in duplicate by carrying out a number of reactions using the following quantities of reactants: 3-methylpent-1-yn-3-ol (4·900 g, 0·05 mol), diglyme (0·56 g), and a solution of cuprous bromide in 48% w/w hydrobromide acid (12·5 ml, 20% w/w). Individual batches of reaction mixture were kept in the thermostat for different lengths of time and then quenched with ice cold ammonia (*d* 0·88) solution (20 ml). Each batch was then extracted with ether (9 × 10 ml) and the ethereal extracts were combined and made up to 100 ml in a graduated flask which also contained a known quantity of n-butanol (2 ml). The latter was employed as the internal standard in the subsequent quantitative g.l.c. analysis of allenic bromide and unreacted acetylenic alcohol which is completely regenerated from the π-complex by the ammonia solution.

The same procedure was employed (at 0·00° only) in investigating the role played in this reaction by copper powder and ammonium bromide (Table 2).

Deuterium bromide was prepared by treating a paste of red phosphorus and deuterium oxide with bromine; the resulting gas was passed through a U-tube containing a paste of deuterium oxide and red phosphorus and then absorbed in a known weight of cooled deuterium oxide until a 50% w/w solution was produced. This was then

used to prepare 1-bromo-3-methylpenta-1,2-diene as previously described.[2]

1-*Deuterio*-3-*methylpent*-1-*yn*-3-*ol* (*with* P. M. GREAVES).—3-Methylpent-1-yn-3-ol (15 g, 0·15 mol) in dry ether (30 ml) was added over 30 min to a stirred solution of ethylmagnesium bromide (0·4 mol) [prepared from ethyl bromide (43·6 g, 0·4 mol)]. When addition of the alcohol was complete the suspension was stirred under reflux for 30 min before being cooled to 20° when deuterium oxide (20 ml, 1 mol) was added over 15 min. The suspension was then vigorously stirred for 3 h before being decomposed with hydrochloric acid (10 ml, 1 : 1), filtered, extracted with (3 × 50 ml), and dried ($MgSO_4$). Distillation gave 1-deuterio-3-methylpent-1-yn-3-ol, (14 g, 87·5%), b.p. 121° at 170 mmHg. This was shown to be completely deuteriated at C-1, $\nu_{max.}$ 3400vs (OH), 2600s (C≡C–D), and 1975s (C≡C–D) cm^{-1} τ 8·95 (3H, t, CH_3CH_2, $J_{4,5}$ Hz), 8·52 (3H, s, CH_3C) 8·27 (2H, q, CH_2CH_3, $J_{5,4}$ 6·5 Hz), and 7·39 (1H, s, O*H*), g.l.c. R_t 3·1 min (silicone oil; 80°).

1-*Bromo*-1-*deuterio*-3-*methylpenta*-1,2-*diene* (*with* P. M. GREAVES).—1-Deuterio-3-methylpent-1-yn-3-ol (4 g, 0·04 mol) was added to a mixture of cuprous bromide (2·1 g, 0·014 mol), ammonium bromide (1·7 g, 0·017 mol), copper powder (0·2 g), and concentrated hydrobromic acid (48% w/w, 10·5 ml, 0·088 mol) and stirred vigorously at room temperature for 25 min when the i.r. spectrum of a small sample showed complete absence of the 3400 cm^{-1} –OH band. The mixture was filtered and separated, the aqueous portion being extracted with light petroleum. the organic layers were combined and washed with concentrated hydrobromic acid (45% w/w, 10 ml) and dried ($MgSO_4$–$Na2CO_3$). Distillation gave 1-bromo-1-deuterio-3-methylpenta-1,2-diene (4 g, 62%), b.p. 60° at 30 mmHg, $\nu_{max.}$ 2300 (=C–D), 1950 (C=C=C), 955, 870 (=C=C–D in-plane deformation), and 715 cm^{-1}, g.l.c. showed one peak R_t 15 min (silicone oil, 82°), τ 8·94 (3H, t, CH_3CH_2, $J_{5,4}$ 7·5 Hz) 8·14 (3H, s, CH_3C), and 7·87 (2H, q, CH_3CH_2).

[2/297 *Received*, 10*th February*, 1972]