519. *Kinetics and Mechanisms of Nucleophilic Displacement in Allylic Systems. Part IX.* Bimolecular Substitution with Rearrangement in the Reaction of* 1-tert.-*Butylallyl Chloride with Ethoxide Ion.*

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From 3-*tert.*-butylallyl alcohol (4 : 4-dimethylpent-2-en-1-ol) has been prepared 1-*tert.*-butylallyl chloride (3-chloro-4 : 4-dimethylpent-1-ene), together with its anionotropic isomer, from which it has been separated by fractional distillation. It has been characterised kinetically, and has been shown to give, on bimolecular reaction with ethoxide ions in ethanol, exclusively the product of substitution with anionotropic rearrangement, 3-*tert.*-butylallyl ethyl ether (4 : 4-dimethylpent-2-en-1-yl ethyl ether).

Early searches [1,2,3] for bimolecular substitution with anionotropic rearrangement (the S_N2' reaction), by using alkyl-substituted allyl chlorides and simple anions as the reactants, showed that the main and nearly exclusive product of such reaction was that of normal substitution. England and Hughes,[4] by using a tracer technique, showed, however, that the S_N2' reaction of 1-methylallyl bromide with bromide ions was slower than the corresponding S_N2 process by a factor of only about 40. From this it became clear that quite small structural changes might be sufficient to render dominant the reaction involving rearrangement, and for this reason the reaction of 1-*tert.*-butylallyl chloride, $CH_2{:}CH{\cdot}CHCl{\cdot}CMe_3$, was examined. In this compound, normal bimolecular substitution is impeded by steric factors analogous to those rendering this mode of substitution very slow in *neo*pentyl bromide.

Experimental

1- *and* 3-tert.-*Butylallyl Bromide.*—4 : 4-Dimethylpent-1-ene, prepared as described by Whitmore and Homeyer,[5] had b. p. 71·8°/756 mm., n_D^{25} 1·3892. This was treated in dry carbon tetrachloride with *N*-bromosuccinimide and benzoyl peroxide. When reaction was complete, succinimide was removed and the filtrate was fractionally distilled. Fractions, b. p. 60—62·5°/30 mm. (79% yield), from several experiments were combined and refractionated, giving material of b. p. 61·5—62°/28 mm., 53°/14 mm., n_D^{25} 1·4668, d_{25}^{25} 1·152. This was a mixture of 1- and 3-*tert.*-butylallyl bromide (3-bromo-4 : 4-dimethylpent-1-ene and 1-bromo-4 : 4-dimethylpent-2-ene) (Found: C, 47·9; H, 7·4; Br, 45·1. Calc. for $C_7H_{13}Br$: C, 47·5; H, 7·3; Br, 45·2%); there was no indication of separation during fractional distillation, but kinetic analysis, using excess of sodium ethoxide in ethanol, showed that the mixture contained 84% of 3-*tert.*-butylallyl bromide (k_2 at 24·9°, 0·138 l. mole^{-1} min.$^{-1}$) and 16% of the much more slowly reacting 1-*tert.*-butylallyl bromide.

1- *and* 3-tert.-*Butylallyl Alcohol.*—The mixture of bromides (100 g.) was hydrolysed by heating it under reflux for 3 hr. with water (2 l.), dioxan (3 l.), and potassium hydroxide (40 g.). Sodium chloride was then added to the cooled mixture; the organic layer was removed, dried (K_2CO_3), and fractionally distilled. The main products were two fractions: (*a*) b. p. 77·5°/152 mm. (60 g.) and (*b*) b. p. 85—86°/28 mm. (9 g.). Intermediate fractions were combined and worked up in successive experiments; the total overall yield of alcohols was about 90%. Refractionation gave the following materials; (a) 3-tert.-*butylallyl alcohol* (4 : 4-*dimethylpent-2-en-1-ol*), b. p. 77·5°/28 mm., 156—157°/760 mm., n_D^{25} 1·4360 (Found: C, 73·8; H, 12·7. $C_7H_{14}O$ requires C, 73·7; H, 12·3%) [α-*naphthylurethane*, m. p. 92·5° (Found: C, 76·9; H, 7·5; N, 5·1. $C_{18}H_{21}O_2N$ requires C, 76·3; H, 7·4; N, 5·0%); 3 : 5-dinitrobenzoate, m. p. 87·5°];

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* Part VIII, *J.*, 1954, 4462.

[1] Roberts, Young, and Winstein, *J.*, 1942, **64**, 2157.

[2] Catchpole and Hughes, *J.*, 1948, 4; Catchpole, Hughes, and Ingold, *J.*, 1948, 8.

[3] Hughes, *Trans. Faraday Soc.*, 1941, **37**, 627.

[4] England and Hughes, *Nature*, 1951, **168**, 1002.

[5] Whitmore and Homeyer, *J. Amer. Chem. Soc.*, 1933, **55**, 4555.

and (b) 1-*tert*.-butylallyl alcohol (4 : 4-dimethylpent-1-en-3-ol), b. p. 85·5°/152 mm., 131°/760 mm., n_D^{25} 1·4282, still impure even after being dried (K_2CO_3) (Found: C, 71·0; H, 11·9%), [*α-naphthylurethane*, m. p. 111·5° (Found: C, 75·8; H, 7·5; N, 4·8%)].

1- *and* 3-tert.-*Butylallyl Chloride*.—The properties of these materials have been outlined elsewhere,[6] but their preparation has not been described. 3-*tert*.-Butylallyl alcohol (50 g.) was cooled to 0°, and thionyl chloride (35 ml.) was added dropwise. The mixture was then stirred successively for 30 min. at 0°, for 1 hr. at room temperature, and for 1 hr. at 60°. The product was then treated with aqueous sodium carbonate and extracted with ether. After being dried, the ether layer was fractionated. The crude chloride, b. p. 53—64°, n_D^{25} 1·4373, was subjected to kinetic analysis. Samples of solution in 0·0963N-sodium ethoxide (0·0505N with respect to organic chloride, as determined by heating an aliquot part in a sealed tube with excess of aqueous nitric acid and silver nitrate) were heated at 64·0°, and at intervals the acid liberated was determined by titration, as follows:

Time (min.)	0	20	48	70	90	120	182	1120
Titre (ml. of 0·01656N-KOH)	10·83	13·25	15·88	16·85	17·83	18·71	19·60	20·34
x	—	2·42	5·05	6·02	7·00	7·88	8·77	9·51
k_2 (l. mole^{-1} min.$^{-1}$)	—	0·160	0·181	0·169	0·180	0·185	0·184	—

Here values of k_2 were calculated by using the value (9·51) of x at 1120 min. (about 25 half-lives) as the infinity for complete destruction of the rapidly reacting chloride. Further solvolysis was too slow to affect such a calculation. The total acid liberated on treatment with excess of silver nitrate was equivalent to x = 16·31 ml., so the material contained 60% of the more rapidly reacting 3-*tert*.-butylallyl chloride.

The mixture of chlorides obtained from several experiments was fractionally distilled under reduced pressure at high reflux ratio, through a helix-packed jacketed column. The separation was followed by b. p. (rising from 53° to 63·5° at 59 mm.) and refractive index (n_D^{25} rising from 1·4335 to 1·4390). A large quantity of material intermediate in properties was obtained. Suitable early and late fractions were combined and refractionated. The following materials were obtained: (a) 3-tert.-*butylallyl chloride* (1-*chloro*-4 : 4-*dimethylpent*-2-*ene*), b. p. 63·4°/58 mm., n_D^{25} 1·4389. Its reaction with sodium ethoxide went to completion (k_2 = 0·171 l. mole^{-1} min.$^{-1}$; 0·0977N-NaOEt, 65°) (Found: C, 63·3; H, 10·0; Cl, 26·3. $C_7H_{13}Cl$ requires C, 63·4; H, 9·8; Cl, 26·8%); (b) 1-tert.-*butylallyl chloride* (3-*chloro*-4 : 4-*dimethylpent*-1-*ene*), b. p. 54·7°/58 mm., n_D^{25} 1·4340 (Found: C, 64·2; H, 9·7; Cl, 26·4%). The latter material was shown by kinetic analysis to contain less than 3% of the more reactive isomer, which with 0·1N-sodium ethoxide at 65° reacted about 680 times more rapidly.

3-tert.-*Butylallyl Ethyl Ether*.—(a) *From* 3-tert.-*butylallyl chloride and sodium ethoxide*. The product, isolated in the usual way and distilled several times from molten potassium, had b. p. 152°/760 mm., n_D^{25} 1·4169.

(b) *From* 1-tert.-*butylallyl chloride and sodium ethoxide*. 1-*tert*.-Butylallyl chloride (10 g.) was allowed to react in sealed tubes for 2 hr. at 120° with saturated sodium ethoxide in ethanol. There were obtained 9 g. of 3-tert.-*butylallyl ethyl ether* (4 : 4-*dimethylpent*-2-*en*-1-*yl ethyl ether*), b. p. 152°/760 mm., n_D^{25} 1·4170 (Found: C, 75·6; H, 12·8. $C_9H_{18}O$ requires C, 76·2; H, 12·7%).

These two materials were characterised kinetically by reaction with bromine in acetic acid. The technique of measurement has been described elsewhere;[7] the rates were identical within experimental error, and about ten times faster than that for allyl ethyl ether.

(c) *By solvolysis of* 1-tert.-*butylallyl chloride*. 1-*tert*.-Butylallyl chloride (10 g.) and ethanol (250 ml.) were heated under reflux with precautions against ingress of water. The solution was prevented from becoming more than slightly acid by frequent addition of 0·3N-sodium ethoxide (lacmoid end-point). After 162 hr., reaction had virtually ceased. The product, recovered in the usual way, was 3-*tert*.-butylallyl ethyl ether (7 g.), n_D^{25} 1·4169, b. p. 147—148°/755 mm. (Found: C, 75·2; H, 12·7%).

1-tert.-*Butylallyl Ethyl Ether*.—To 1-*tert*.-butylallyl alcohol (8·3 g.) in diethyl ether (10 g.) a slight excess of finely powdered potassium was added. The mixture was heated under reflux for 4 hr., then cooled, and to it was added excess of ethyl iodide. The diethyl ether was removed by distillation, and the residue heated under reflux for 6 hr., after which time much potassium iodide had separated. The products were extracted with pentane and fractionally

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[6] Vernon, *J.*, 1954, 423.

[7] de la Mare and Robertson, *J.*, 1945, 888.

distilled to remove all the ethyl iodide. To the residue was added pyridine and phthalic anhydride; the mixture was heated for 8 hr. The hydrogen phthalate of any unchanged alcohol was then removed by extraction from pentane into aqueous alkali. The pentane extract was washed with acid and with water, dried, and fractionally distilled. The appropriate fractions of the product were distilled from metallic potassium and again fractionally distilled. The fraction, b. p. 121°, had n_D^{25} 1·3981 (Found: C, 77·8; H, 13·4%).

The infrared spectra of the various samples of ether were examined with a Grubb-Parsons double-beam recording infrared spectrophotometer. Those of the 3-*tert*.-butylallyl ether obtained in the three ways described above were identical, with a strong band at 976 cm.$^{-1}$, as is generally characteristic of *trans*-, but not of *cis*-1 : 2-disubstituted ethylenes, and weak or very weak bands at 996, 939, and 913 cm.$^{-1}$. That of the 1-ether was generally similar, though different in detail, but markedly different between 1000 and 900 cm.$^{-1}$, with strong bands at 1000, 973, and 923 cm.$^{-1}$; strong bands near 990 cm.$^{-1}$ and 910 cm.$^{-1}$ are generally characteristic [8] of monosubstituted ethylenes, $R\cdot CH\dot{:}CH_2$. Furthermore, groupings *trans*-$R\cdot CH{=}CHR$ and $R\cdot CH{=}CH_2$ can usually be distinguished by the presence of weak bands near 1670 cm.$^{-1}$ and 1640 cm.$^{-1}$ respectively; [8] on the spectra which we have recorded, the 3-isomer had a weak band at 1678 cm.$^{-1}$, and the 1-isomer a band at 1639 cm.$^{-1}$.

Kinetics of Reaction of 1-tert.-*Butylallyl Chloride with Sodium Ethoxide*.—This reaction was of the first order with respect to organic chloride, and also with respect to ethoxide ions at high concentrations of sodium ethoxide; with 2·7M-NaOH, this kinetic form contributed *ca.* 90% to the total reactivity. The rate coefficients, corrected for the concomitant solvolysis, were k_2 (l mole^{-1} min.$^{-1}$) = $1{\cdot}6 \times 10^{-3}$ at 101°, $0{\cdot}037 \times 10^{-3}$ at 65·0°; *E*, 26 kcal. mole^{-1}.

DISCUSSION

1- and 3-*tert*.-Butylallyl alcohol could be recognised and separated readily by fractional distillation. The halides were not easily separated but pure fractions could be recognised and characterised readily by kinetic methods. The formation of an equilibrium mixture of anionotropically related bromides is not unexpected,[9] in view of the great ease with which the corresponding methylallyl bromides undergo isomerisation.[10]

The reaction of 1-*tert*.-butylallyl chloride with sodium ethoxide is of the first order with respect to ethoxide ions provided that the concentration of ethoxide ions is sufficiently high. The reaction is very slow, as would be expected from the *neo*pentyl-like structure. However, the ratio of reactivities, 1-*tert*.-butylallyl chloride : 1-methylallyl chloride,[11] is *ca.* 1 : 100 at 65°, whereas the similar ratio for *neo*pentyl bromide to ethyl bromide is considerably larger (*ca.* 1 : 100,000 at 65°).[12] This agrees with the view that the reaction of 1-*tert*.-butylallyl chloride is not at the 1-carbon atom (S_N2) but involves attack on the less hindered olefinic 3-carbon atom (S_N2'), for otherwise differences resulting from steric hindrance should be, if anything, greater in the allyl than in the saturated system.

In accordance with this view, the product of the reaction is entirely that of abnormal substitution, and agrees in properties with that of authentic material prepared by reaction of ethoxide ions on 3-*tert*.-butylallyl chloride. We conclude that the reaction is of the S_N2' type.

The total rate [13] of the bimolecular reaction of sodium ethoxide with 3 : 3-dichloropropene at 65° is $0{\cdot}84 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$, and roughly half of the reaction proceeds by the S_N2' route. The S_N2' reaction of 1-*tert*.-butylallyl chloride has a corresponding rate of $0{\cdot}037 \times 10^{-3}$ l. mole^{-1} min.$^{-1}$. Hence the 1-chloro-substituent in the former compound has a facilitating effect on the reaction, as compared with the 1-*tert*.-butyl group in the latter. This accords with the view that an important factor affecting such situations [14,15] is that a substituent may in some cases influence the rate of the S_N2' reaction

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[8] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954.
[9] Cf. Djerassi, *Chem. Rev.*, 1948, **43**, 271.
[10] England, *J.*, 1955, 1615.
[11] Vernon, *J.*, 1954, 4462.
[12] Dostrovsky and Hughes, *J.*, 1946, 157.
[13] de la Mare and Vernon, *J.*, 1953, 3325.
[14] Hughes and Ingold, *J. Chim. phys.*, 1949, **45**, 236.
[15] de la Mare and Vernon, *J.*, 1953, 3555.

by attracting or repelling the π-electrons of the double bond and thereby facilitating or impeding the approach of a nucleophilic reagent to the unsaturated carbon atom.

The solvolysis of 1-*tert.*-butylallyl chloride also gives a product from which the recovered *tert.*-butylallyl ethyl ether is entirely the 3-isomer (as far as can be seen from its spectrum). This result differs from that obtained in the solvolysis of 1-methylallyl chloride; the latter reaction gives only 82% of 3-methylallyl ethyl ether.[3] The observation suggests that either (*a*) the solvolysis is bimolecular, or (*b*) steric congestion about the 1-carbon atom is sufficiently large even in the mesomeric carbonium ion as it is incipiently produced in the reaction to divert attack by solvent molecules predominantly to the 3-position.

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