1256. *Allenes. Part X.* The Claisen–Cope Rearrangement of Propargyl Vinyl Systems*

By D. K. Black and S. R. Landor

The Claisen rearrangement of propargyl vinyl ethers provides a new general method for the synthesis of allenic aldehydes. Boron trichloride-catalysed rearrangement of phenyl propargyl ethers gave only starting material and fission products. Cope rearrangement of a propargylvinylmalonic ester gave moderate yields of the allenic malonic ester together with fission products. The mechanistic implications of these reactions are discussed.

An investigation of the Claisen rearrangement[1] of propargyl vinyl ethers and the Cope[2] rearrangement of propargylvinylmalonic esters was initiated in 1958 as part of our programme on stereospecific acetylene allene-rearrangements.[3]

We had established that propargyl vinyl and isobutenyl ethers[4] gave allenic aldehydes on pyrolysis when a preliminary report of independent work by Jones, Loder, and Whiting[5] described the direct conversion of isobutyraldehyde dipropargyl and dibut-1-ynyl acetals to the corresponding allenic aldehydes without isolation of the ether; starting with optically active but-1-yn-3-ol of known absolute configuration the absolute configuration of the optically active allenic aldehyde was deduced by these authors postulating the ether as an intermediate. In view of this publication we decided to concentrate on the preparative aspect of the Claisen rearrangement.[6] The following general procedure was developed. The propargylic ether was passed in a stream of nitrogen through an electrically heated glass tube (20 × 2 cm.) lightly packed with glass wool and the product was collected in a trap cooled to $-60°$.

Conversions were effected in the vapour phase at low concentrations and unstable products quickly removed from the reaction tube. In this way rearrangements could be carried out on a small scale (0·5—2·0 g.) at temperatures up to 400°. Polysubstituted propargyl vinyl ethers were heated under reflux or prepared *in situ* from the α-chloroallyl ethers and rearranged without isolation at 120—150° to the allenic aldehydes (Table 1).

Table 1

Aldehyde	B. p./atmos.	Yield (%)	Derivative[a] (m. p.)
$CH_2=C=CH\cdot CH_2\cdot CHO$[b]	—	20—30	147—149°
$MeCH=C=CH\cdot CH_2\cdot CHO$[b]	—	10—20	133—134
$Me_2C=C=CH\cdot CH_2\cdot CHO$[b]	—	10	145—146
$CH_2=C=CH\cdot CMe_2\cdot CHO$	126—127°	70	122
$MeCH=C=CH\cdot CMe_2\cdot CHO$	139—140	60	116
$Me_2C=C=CH\cdot CMe_2\cdot CHO$	156—158	76	98—99
$PrCH=C=C=CMe_2\cdot CHO$	178	93	89—90

[a] 2,4-Dinitrophenylhydrazone. [b] The i.r. spectra of these 3,4-dienals show a band at 1690 as well as the expected band at 1730 cm.$^{-1}$. This suggests presence of 2,4-dienals but end absorption only in the u.v. spectra and one peak in the g.l.c. does not confirm this.

There is considerable evidence[7] that the Claisen rearrangement of allyl vinyl ethers involves a six-membered cyclic transition state, C–C bond formation occurring simultaneously with C–O bond fission.

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* Part IX, S. R. Landor and P. F. Whiter, *J.*, 1965, 5625.

[1] L. Claisen, *Ber.*, 1912, **45**, 3157.

[2] A. C. Cope and E. M. Hardy, *J. Amer. Chem. Soc.*, 1940, **62**, 441, and subsequent Papers.

[3] Cf. Allenes. Parts I, II, and IV, *J.*, 1956, 1015; 1959, 24; 1963, 1506.

[4] D. K. Black and S. R. Landor, *J.*, 1965, 5225.

[5] E. R. H. Jones, J. D. Loder, and M. C. Whiting, *Proc. Chem. Soc.*, 1960, 180.

[6] Cf. D. K. Black and S. R. Landor, *Proc. Chem. Soc.*, 1963, 183.

[7] C. D. Hurd and M. A. Pollack, *J. Amer. Chem. Soc.*, 1938, **60**, 1905; F. W. Schuler and G. W. Murphy, *ibid.*, 1950, **72**, 3155; S. Marcinkiewicz, J. Green, and P. Mamalis, *Tetrahedron Letters*, 1961, *No.* **14**, 208; L. Stein and G. W. Murphy, *J. Amer. Chem. Soc.*, 1952, **74**, 1041; Y. Pocker, *Proc. Chem. Soc.*, 1961, 141.

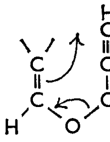
The formation of a planar, cyclic, activated complex is possible, but less favourable * with propargyl vinyl ethers as shown by the higher temperature (250°) required for rearrangement. Increased substitution leads to an easier rearrangement at lower temperature (Table 2) showing that steric hindrance in the transition state is not an important factor.

TABLE 2

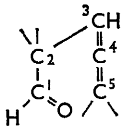
Ether	Aldehyde	Temp	Product
$CH_2=CH·O·CH_2·C≡CH$	$CH_2=C=CH·CH_2·CHO$	200°.	Unchanged ether
„	„	250	20—30% Aldehyde
„	„	250	Polymerisation
$CH_2=CH·O·CHMe·C≡CH$	$MeCH=C=CH·CH_2·CHO$	150	Unchanged ether
„	„	200	10—20% Aldehyde
„	„	250	Polymerisation
$CH_2=CH·O·CMe_2·C≡CH$	$Me_2C=C=CH·CH_2·CHO$	200	Unchanged ether
„	„	250	10% Aldehyde
„	„	300	Rapid polymerisation
$Me_2C=CH·O·CH_2·C≡CH$	$CH_2=C=CH·CMe_2·CHO$	140	4 hr. reflux 70%
$Me_2C=CH·O·CMe_2·C≡H$	$Me_2C=C=CH·CMe_2·CHO$	140	15 min. reflux 76%

Increasing methyl substitution of the propargyl vinyl ether should not favour a two electron shift (I) → (II) and the results are perhaps best explained by a mechanism involving a one-electron shift as in structure (III).[8]

Partial radical formation at C_2 and C_5 (viz. (IV)) is helped by increasing substitution at these points.†



(I)



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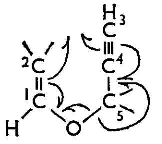

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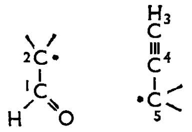

(IV)

Rearrangement products could not be isolated from 2-chlorovinyl and 2,2-dichlorovinyl propargyl ethers at temperatures between 150 and 350°. At 150—250° unreacted ethers were isolated; at 250—350° only polymers were obtained. These chlorovinyl ethers are electronically and sterically unfavourable and the high activation energy of the cyclic transition state may lead to preferential fission.

A number of attempts at pyrolytic rearrangement of propargyl phenyl ethers have been described in the literature;[9] most resulted in polymers but a small number of furanoid or pyranoid products have been described which might have been formed by ring closure either of the allenic phenol or of the propargylic ether. As the conditions used by previous workers (high temperatures and prolonged reaction times) are not favourable for the isolation of *o*-allenylphenols, the boron trichloride-catalysed rearrangement was investigated.[10] Phenyl propargyl ether and boron trichloride in methylene chloride at

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* The rigid, linear propargyl group is sterically less favourable than the flexible allyl group.

† Partial bond formation would have to precede bond fission for the reaction to be intramolecular (as shown by Jones, Loder, and Whiting [5] and Evans, Landor, and Regan, *Chem. Comm.*, 1965, 397, but the extent of the specificity has not yet been established).

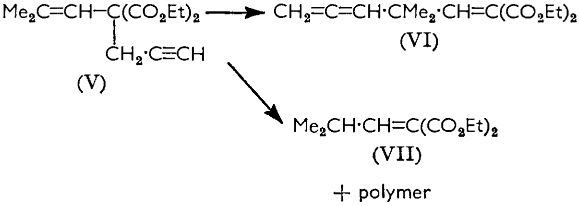
[8] Cf. W. N. White, C. D. Slater, and W. K. Fyfe, *J. Org. Chem.*, 1961, **26**, 627.

[9] S. G. Powell and R. Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 654; C. D. Hurd and F. L. Cohen, *ibid.*, 1931, **53**, 1068; R. Gaertner, *ibid.*, 1951, **73**, 4400; Y. Okajima and I. Ide, *Chem. and Pharm. Bull.* (*Japan*), 1962, **10**, 926; B. S. Thyagarajan, K. K. Balasubramanian, and R. B. Rao, *Tetrahedron Letters*, 1963, 1398.

[10] W. Gerrard, M. F. Lappert, and A. Silver (*Proc. Chem. Soc.*, 1957, 19) reacted allyl phenyl ether in n-pentane at −80° with boron trichloride and, on fractionation, obtained 73% of tri-*o*-allylphenyl borate. In our hands allyl phenyl ether, allyl 2,6-dimethylphenyl ether and allyl 2,4,6-trimethylphenyl ether with boron trichloride first at 0° and then at room temperature gave 58, 61, and 80% yields of *o*-allylphenol, 4-allyl-2,4-dimethylphenol and 3-allyl-2,4,6-trimethylphenol respectively. Independent and more detailed results by A. Habich and H. Schmidt, *Helv. Chim. Acta*, 1960, **56**, 448, are in agreement with this work.

—40° and then at 0° gave only polymeric products. No reaction had taken place after 15 min. at —40° as shown by infrared spectra.

In pentane at —60° a white solid was formed which on warming to 0° gave a red-brown oil, $\nu_{\text{max.}}$ 1360 (B–O stretching), 3300 ($C\equiv CH$) and 2110 cm.$^{-1}$ ($C\equiv CH$) but no $C=C=C$ bonds suggesting it to be the intermediate borate; the ultraviolet spectrum showed only phenyl absorption. Similar reactions with 1-phenylpropargyl phenyl ether and 3-methylbut-1-yn-3-yl phenyl ether gave only polymers; extraction with ice-cold 10% sodium hydroxide solution gave only phenol. Similarly 2,6-dimethylphenyl propargyl ether gave 2,6-dimethylphenol as the only isolatable product.

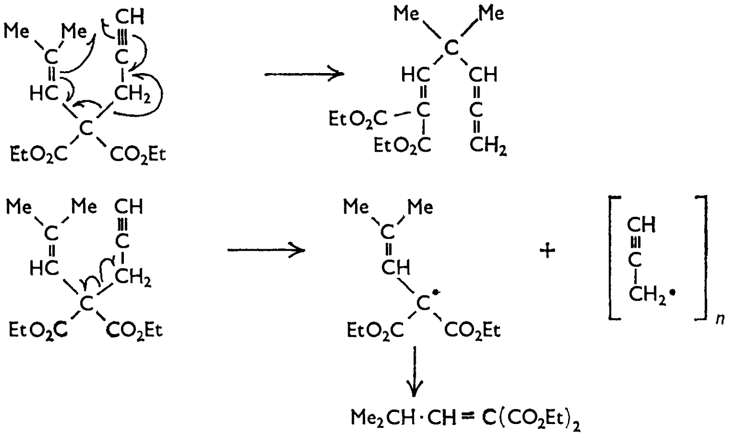


$$Me_2C=CH-\underset{\displaystyle CH_2\cdot C\equiv CH}{C}(CO_2Et)_2 \longrightarrow CH_2=C=CH\cdot CMe_2\cdot CH=C(CO_2Et)_2$$

(V) (VI)

$$\longrightarrow Me_2CH\cdot CH=C(CO_2Et)_2 \text{ (VII)} + \text{polymer}$$

A Cope type rearrangement [2] of diethyl isobutenylpropargylmalonate (V) at 270—280° gave a mixture containing 35% of diethyl 2,2-dimethylpenta-3,4-dienylidenemalonate (VI) which on careful fractionation gave 20% of the pure allenic material. Twelve per cent of the isobutylidenemalonate (VII) [resulting from the fission of the isobutenylpropargylmalonate—the names are those used by Cope (*J. Amer. Chem. Soc.*, 1941, **63**, 1851, 3452)] was also isolated together with 50% polymer. At lower temperatures only traces of rearranged products are obtained while at temperatures of 300° or higher only the fission product, diethyl isobutylidenemalonate (VII) and polymer, could be isolated.



Presumably the activation energy of the cyclic transition state in the Cope rearrangement of propargylic vinylmalonates is only marginally lower than the activation energy necessary for bond fission.

EXPERIMENTAL

Infrared spectra were determined by a Perkin-Elmer Infracord spectrometer on liquid films, and ultraviolet spectra by a Unicam S.P. 500 and a Bausch and Lomb Spectronic 505 spectrometer on solutions in absolute ethanol.

*Penta-*3,4-*dienal.*—Propargyl vinyl ether [4] (0·8 g., 0·098 mole) was passed dropwise, in a stream of nitrogen, through a glass tube (10 cm. × 2 cm.) heated electrically to 250° and packed with glass wool, the system being previously flushed with nitrogen. The product was collected in a trap cooled to —60°, ether added, and the solution dried ($MgSO_4$). Removal of ether *in vacuo* gave a yellow liquid (0·6 g., 75% recovery), $\nu_{\text{max.}}$ 1950s (C=C=C), 845s ($>$C=CH$_2$), 1740m (C=O), 1690 (C=C–C=O), 2700w (CHO), 3280 cm.$^{-1}$ w (C≡CH) but no absorption in the ultraviolet region. G.l.c. (dinonyl phthalate, 77°, N$_2$ 2·0 l./hr.) showed a main component with retention time (*t* 31 min.) with a minor component (*t* 7 min.) corresponding to unchanged propargyl vinyl ether. The product gave a 2,4-dinitrophenyldrazone, yellow needles, m. p. 147—149°, $\nu_{\text{max.}}$ 1950s (C=C=C) (Found: C, 49·1; H, 3·8; N, 21·2. $C_{11}H_{10}N_4O_4$ requires C, 50·4; H, 3·8; N, 21·4%).

2,2-*Dimethylpenta*-3,4-*dienal*.—(*a*) 1-Chloroisobutyl propargyl ether[4] (19 g., 0·13 mole), heated under reflux (bath temperature 150°) in the presence of hydroquinone (20 mg.) for 6 hr., gave 2,2-dimethylpenta-3,4-dienal (8·0 g., 56%), b. p. 126—127°/760 mm. (Found: C, 76·4; H, 8·9. $C_7H_{14}O$ requires C, 76·4; H, 9·1%), $\nu_{\text{max.}}$ 1950vs (C=C=C), 850s (C=CH$_2$), 1740vs (C=O) and 2700 cm.$^{-1}$ (CHO). G.l.c. (dinonyl phthalate, 90°, N$_2$ 1·8 l./hr.) gave a single peak (*t* 12 min.). The product gave a 2,4-dinitrophenylhydrazone, orange needles, m. p. 122° (Found: C, 53·3; H, 4·8; N, 19·7. $C_{13}H_{14}N_4O_4$ requires C, 53·8; H, 4·8; N, 19·3%) and a semicarbazone, colourless plates, m. p. 133° (Found: C, 57·6; H, 7·6; N, 25·0. $C_8H_{13}H_3O$ requires C, 57·5; H, 7·8; N, 25·0%).

(*b*) Propargyl 2,2′-dimethylvinylether (11·6 g., 0·106 mole) was heated under reflux (bath temperature 140°) in a nitrogen atmosphere in the presence of hydroquinone (20 mg.) and NN-dimethylaniline (30 ml.) as a diluent for 4 hr. Distillation gave 2,2-dimethylpenta-3,4-dienal (8·0 g., 70%), b. p. 126—130°/760 mm. It gave a diethyl acetal, b. p. 40°/0·9 mm. (Found: C, 71·7; H, 10·9. $C_{11}H_{20}O$ requires C, 71·7; H, 10·9%), $\nu_{\text{max.}}$ 1960s (C=C=C), 842m ($>$C=CH$_2$) and 1110 cm.$^{-1}$ (C–O–C).

Rearrangement of But-1-*yn*-3-*yl Vinyl Ether*.—But-1-yn-3-yl vinyl ether[4] (1·0 g., 0·01 mole) was passed, in a stream of nitrogen, through a glass tube (20 cm. × 2 cm.) filled with glass wool and heated electrically to 250°. The product, collected in a trap cooled at −60°, was taken up in ether and treated with 10% ammoniacal silver nitrate solution until no further precipitation took place. The silver salt was filtered, washed with ether, and the aqueous phase of the filtrate extracted with ether (2 × 20 ml.). The combined organic fractions were dried (MgSO$_4$) and solvent removed *in vacuo* giving a residue (0·4 g.), $\nu_{\text{max.}}$ 1950s (C=C=C), 850s ($>$C=CH$_2$), 1750ms (C–O), 2700m (CHO), 3290w (C≡CH), and a strong band at 1680 cm.$^{-1}$. The ultraviolet spectrum showed only end absorption. G.l.c. (dinonyl phthalate, 86°, N$_2$ 2·1 litres/hr.) showed three components (*t* 11 min. 10%, *t* 13 min. 60%, and *t* 34 min. 20%).

The product in ether (20 ml.) after being shaken with ammoniacal silver nitrate solution gave a yellow liquid having no C=C bands in the infrared and showing no component with *t* 11 min. in the g.l.c. The product gave a 2,4-dinitrophenylhydrazone derivative as orange needles, m. p. 133—134° (Found: C, 52·1; H, 4·3; N, 19·6. $C_{12}H_{12}N_4O_4$ requires C, 52·2; H, 4·4; N, 19·8%).

2,2-*Dimethylhexa*-3,4-*dienal*.—1-Chloroisobutyl but-1-yn-3-yl ether[4] (7·8 g., 0·049 mole) was heated under reflux (bath temperature 150—160°) for 90 min. and distilled, giving crude aldehyde 42—60°/7 mm. (5·3 g.), $\nu_{\text{max.}}$ 1950m (C=C=C), 3300w (C=CH), 2700m (CHO) and 1720—1740 cm.$^{-1}$ vs (C=O). G.l.c. (dinonyl phthalate, 112°, N$_2$ 1·9 l./hr.) showed 3 components (*t* 3, 9·5, and 12·5 min.). Treatment with 10% ammoniacal silver nitrate solution (20 ml.) removed the component *t* 3 min. (unchanged ether) and distillation of the residue gave 2,2-dimethylhexa-3,4-dienal (3·7 g., 60%), b. p. 139—140°/760 mm. (Found: C, 76·9; H, 9·7. $C_8H_{12}O$ requires C, 77·4; H, 9·7), $\nu_{\text{max.}}$ 1950ms (C=C=C), 1740vs (C=O) 2700m (C=O) and 1360s (C–Me). It gave a 2,4-dinitrophenylhydrazone derivative as yellow needles, m. p. 116° (Found: C, 55·2; H, 5·2; N, 18·3. $C_{14}H_{16}N_4O_4$ requires C, 55·3; H, 5·3; N, 18·4%) and a semicarbazone as colourless plates, m. p. 129° (Found: C, 60·2; H, 8·1; H, 23·4. $C_9H_{15}N_3O$ requires C, 59·7; H, 8·3; N, 23·2%).

The Rearrangement of 3-*Methylbutynyl Vinyl Ether*.—3-Methylbut-1-yn-3-yl vinyl ether[4] (2·0 g., 0·018 mole) was passed dropwise in a stream of nitrogen through a glass tube (10 cm. × 2 cm.) heated electrically to 200° and packed with glass wool. The product was collected in a trap cooled to −60°. It showed infrared bands at 3280vs (C=CH), 2110m (C=C), 1740m (C=O) and 1955 cm.$^{-1}$ vw (C=C=C) indicating that little conversion had been effected. The product gave the 2,4-dinitrophenylhydrazone derivative of 5-methylhexa-3,4-dienal in very low yield, as orange needles, m. p. 145—146° (Found: C, 53·6; H, 4·6; N, 19·2. $C_{13}H_{14}N_4O_4$ requires C, 53·8; H, 4·8; N, 19·3%).

2,2,5-*Trimethylhex*-3,4-*dienal*.—1-Chloroisobutyl 3-methylbut-1-yn-3-yl ether[4] (2·0 g., 0·0115 mole) was refluxed for 15 min. Evolution of hydrogen chloride ceased after 10 min. and distillation gave 2,2,5-trimethylhex-3,4-dienal, 156—158°/755 mm. (1·2 g., 76%) (Found: C, 78·2; H, 10·0. $C_9H_{14}O$ requires C, 78·3; H, 10·1%), $\nu_{max.}$ 1960m (C=C=C), 3300w (C≡CH), 1740vs (C=O), 2700s (CHO) and a doublet at 1360/1380 cm.$^{-1}$ m ($-CMe_2-$); 2,4-dinitrophenylhydrazone derivative, orange needles, m. p. 98—99° (Found: C, 53·0; H, 6·1; N, 19·0. $C_{15}H_{18}N_4O$ requires C, 53·1; H, 6·1; N, 19·1%) and a semicarbazone, colourless plates, m. p. 124° (Found: C, 61·7; H, 8·5; N, 20·9. $C_{10}H_{17}N_3O$ requires C, 61·5; H, 8·7; N, 21·5%). G.l.c. (silicone oil, 123°, N_2 2·0 l./hr.) gave one component (*t* 14 min.) with a trace of the acetylenic ether as impurity.

2,2-*Dimethylocta*-3,4-*dienal*.—1-Chloroisobutyl hex-1-yn-3-yl ether [4] (4·0 g., 0·0212 mole) was refluxed for 20 min. and distilled giving 2,2-dimethylocta-3,4-dienal (3·0 g., 93%) b. p. 90°/30 mm. (Found: C, 78·3; H, 10·7. $C_{10}H_{16}O$ requires C, 78·9; H, 10·5%), $\nu_{max.}$ 1960vs (C=C=C), 880s ($>C=CH_2$), 1740vs (C=O), 2700s (CHO) and a doublet at 1360/1380 cm.$^{-1}$ m ($-CMe_2-$); 2,4-dinitrophenylhydrazone, orange needles, m. p. 89—90° (Found: C, 57·7; H, 6·3; N, 16·8. $C_{16}H_{20}N_4O_4$ requires C, 57·8; H, 6·0; N, 16·9%); semi-carbazone, colourless plates, m. p. 85—86° (Found: C, 63·6; H, 9·2; N, 20·0. $C_{11}H_{19}N_3O$ requires C, 63·2; H, 9·1; N, 20·1%).

Diethyl Isobutenylpropargylmalonate.—Diethyl isobutylidenemalonate (25·6 g., 0·12 mole, $\lambda_{max.}$ 209, ε 13020) was added dropwise to a stirred solution of sodium (2·8 g., 0·11 g.-atom) in absolute ethanol (100 ml.). As the sodium salt precipitated out, ethanol (100 ml.) was added, then propargyl bromide (14·8 g., 0·124 mole) over 15 min. at 0° and the reactants heated under reflux for 15 min., allowed to cool, ether (150 ml.) and water (150 ml.) added, the aqueous layer separated and extracted with ether (3 × 40 ml.), and the combined organic layer dried ($MgSO_4$). Distillation gave a fore-run of unreacted diethyl isobutylidenemalonate followed by diethyl isobutenylpropargylmalonate (18 g., 60%), b. p. 90—92°/0·08 mm. (Found: C, 65·6; H, 8·2. $C_{14}H_{20}O_4$ requires C, 66·6; H, 8·2%), $\nu_{max.}$ 3280vs (C≡CH) 2120 (C≡C), 1740vs (C=O), 1650m (C=C), 1360vs and 1380 cm.$^{-1}$ vs (CMe_2 doublet). G.l.c. (silicone oil, 174°, N_2 2·8 l./hr.) showed a single component (*t* 25 min.).

Diethyl 2,2-*Dimethylpenta*-4,5-*dienylidenemalonate*.—(With N. PUNJA). Diethyl isobutenylpropargylmalonate (15 g., 0·06 mole) was refluxed at 270—280° for 30 min. in an atmosphere of N_2. Fractionation gave (i) mainly diethyl isobutylidenemalonate and recovered starting material, b. p. 84—96°/0·8 mm. (3·5 g.), $\nu_{max.}$ 3300, 2120, 1750, s, 1650 cm.$^{-1}$. G.l.c. (silicone oil 176°, N_2 3 l./hr. gave two main components (*t* 19 min. 50%, *t* 34 min. 40%) and (ii) diethyl 2,2-dimethylpenta-4,5-dienylidenemalonate (3·5 g., 23%) (Found: C, 66·6; H, 8·0. $C_{14}H_{20}O_4$ requires: C, 66·64; H, 7·99%), b. p. 128—130°/0·8 mm., $\nu_{max.}$ 1960m (C=C=C), 1750s (C=O), and 1650 cm.$^{-1}$ s (C=C), $\lambda_{max.}$ 204 mμ, ε 8500. G.l.c. (silicone oil 176°, N_2 3 l./hr.) gave one component (*t* 51 min.). A polymeric residue (7·5 g.) gave $\nu_{max.}$ 1759 cm. (C=O) but no bands for acetylenic or allenic groups.

An experiment in which diethyl isobutenylpropargylmalonate (0·5 g.) was heated under reflux under N_2 at 300—320° for 15 min. gave a thick, polymeric red-brown product, $\nu_{max.}$ 1750m, 1650 cm.$^{-1}$ s, no bands for acetylene or allene groups. G.l.c. (silicone oil, 176°, N_2 3 l./hr.) gave one volatile component only (*t* 19 min.) which was shown to be diethyl isobutylidenemalonate.

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WOOLWICH POLYTECHNIC, LONDON S.E.18.
FOURAH BAY COLLEGE, FREETOWN, SIERRA LEONE.

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