315. *The Carbonylation of Allylic Chlorides.*

By W. T. Dent, R. Long, and G. H. Whitfield.

π-Allylic palladium chloride complexes catalyse reaction between allylic halides and carbon monoxide to give high yields of alk-3-enoyl chlorides. The carbonylation in methanol is a highly exothermic reaction, giving a complex mixture of products in low yield, including methyl but-3-enoate.

A synthesis of but-3-enoic acids and their esters from allylic chlorides, carbon monoxide, water or an alcohol, and nickel carbonyl has been described by Chiusoli.[1] The method has the disadvantage that more than 0·5 mole of nickel carbonyl per mole of allylic chloride is required and that the yields were less than 40%. The low reaction efficiencies are due in part to the dimerisation of allylic chlorides, shown by Webb and Borcherdt [2] to be promoted by nickel carbonyl. We have now shown that when allylic chlorides are heated under pressure with carbon monoxide in the presence of small quantities of π-allylic palladium chloride complexes, *e.g.*, 3 × 10^{-4} mole per mole of allylic chloride, alk-3-enoyl chlorides are formed in high yield (cf. Table 1; the analytical results quoted were obtained by quantitative g.l.c.). But-3-enoyl chloride was the sole product when the reaction times were short (experiments 5 and 8). In the other experiments longer times were required and small amounts of crotonoyl chloride were observed which were presumably formed by the isomerisation of the major product. In addition to the use of π-allylic palladium chloride complexes as catalysts, palladium chloride and even palladium

---

[1] Chiusoli, *Chimica e Industria*, 1959, **41**, 503.
[2] Webb and Borcherdt, *J. Amer. Chem. Soc.*, 1951, **73**, 2654.

TABLE 1.

The carbonylation of allyl chloride.

Expt. no.	Allyl chloride (g.)	Catalyst (g.)		Temp.	Absorption of CO (Atm.)	Reaction time [1] (min.)	Product discharge (g.)	Products (w/w %; ±3%) Allyl chloride	But-3-enoyl chloride	Crotonoyl chloride	Solid by-product (g.)
1	37·7	PdCl$_2$	5·0	150°	220	60	44·2 [2]	—	—	—	— [3]
2	37·9	PdCl$_2$	5·0	110	170	60	46·0	7	81	4	1·1
3	37·9	PdCl$_2$	0·5	110—120	190	165	46·4	5	89	6	— [3]
4	37·7	PdCl$_2$	0·1	110—130	140	180	46·4	9	84	8	— [3]
5	37·7	(π-Allyl-PdCl)$_2$	1·0	110	230	15	49·3	3	96	—	0·2
6 [4]	19·2	(π-Allyl-PdCl)$_2$	0·5	110	80	20					
	19·3			110	140	45	47·8	3	93	2	— [3]
7	38·1	(π-Allyl-PdCl)$_2$	0·1	110—130	140	120	46·2	10	87	4	— [3]
8	37·7	(π-But-2-enyl-PdCl)$_2$	1·0	110	205	15	48·4	3	94	—	0·35
9	18·3	PdO [5]	2·0	120—130	110	120	31·4 [6]	6	28	4	1·8
10	34·7	—		110	—	30	30·4	100	—	—	—

[1] The reaction was considered to have ended when the gas absorption ceased.
[2] The product was used for qualitative examination, see Experimental section.
[3] Solid by-product was present but not isolated.
[4] Experiment conducted in two parts to demonstrate the preservation of catalyst activity.
[5] Palladium oxide was suspended in hexane (13·6 g.) and reduced with hydrogen before addition of allyl chloride.
[6] Product contained hexane which was not estimated.

TABLE 2.

The carbonylation of methyl substituted allyl chlorides.

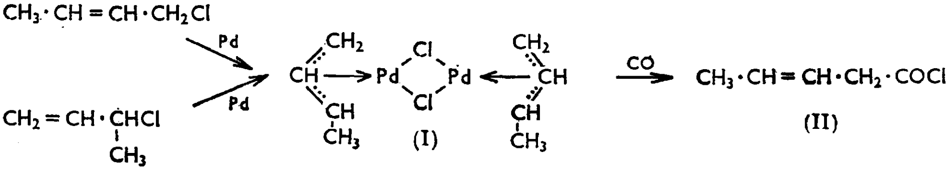
Expt. no.	Allylic chloride (g.)		Catalyst (g.)		Temp.	Absorption of CO (Atm.)	Re-action time [1] (min.)	Product discharge (g.)	Product (w/w %; ±3%) 3-Chlorobut-1-ene	1-Chlorobut-2-ene		Pent-3-enoyl-chloride
1	1-Chlorobut-2-ene	38·6	(π-Allyl-PdCl)$_2$	1·0	100°	150	25	44·1 [2]	—	—		—
2	1-Chlorobut-2-ene	37·8	(π-Allyl-PdCl)$_2$	1·0	100	160	30	46·3	3	8		81
3	3-Chlorobut-1-ene	37·8	(π-Allyl-PdCl)$_2$	1·0	100	180	60	46·0	1	3		84
4	1-Chloro-2-methylprop-2-ene	38·0	PdCl$_2$	0·1	110—140	50	295	39·5 [2]	—	—		—
5	1-Chloro-2-methylprop-2-ene	37·5	(π-Methallyl PdCl)$_2$	0·5	120	100	120	42·7	1-Chloro-2-methylprop-2-ene	t-Butyl chloride	3-Methylbut-2-enoyl chloride	3-Methylbut-3-enoyl chloride
									16	1	7	77·5

[1] The reaction was considered to have ended when the gas absorption ceased.
[2] The product was used for qualitative examination, see Experimental section.

metal promoted the reaction whereas nickel chloride, cuprous chloride, dicobalt octacarbonyl, and iron pentacarbonyl were completely inactive.

The solid by-product from experiment 2, in which a relatively large quantity of palladium chloride was used as catalyst, has an infrared spectrum in which all the absorption frequencies are assignable to a terminal metal carbonyl group. The stretching frequency observed at 1972 cm.$^{-1}$ is very similar to the value of 1976 cm.$^{-1}$ reported by Irving and Magnusson[3] for $[Pd(CO)Cl_2]_2$. The by-products from experiments 5 and 8 show infrared absorption frequencies identical to those of the product[4] obtained by the action of carbon monoxide on a mixture of di-μ-chloro-di-π-allyldipalladium and palladium chloride in methanol.

The three monomethyl-allyl chlorides reacted similarly with carbon monoxide (Table 2). 1-Chlorobut-2-ene and 3-chlorobut-1-ene both gave high yields of pent-3-enoyl chloride (II); explicable if it is assumed that π-allylic palladium chloride complexes are intermediates in the reaction because either 1-chlorobut-2-ene or 3-chlorobut-1-ene would give the same complex (I), which evidently carbonylates exclusively at the primary carbon atom.



The carbonylation of 1-chloro-2-methylprop-2-ene required longer reaction times than was found necessary with other allylic chlorides under comparable conditions and this probably accounts for the greater complexity of the product, the composition of which varied in a series of experiments although the main product was always 3-methylbut-3-enoyl chloride. With palladium chloride as catalyst (experiment 4) a temperature of 140° was required and, in addition to the products obtained in experiment 5, 1-chloro-2-methylprop-1-ene and 1,2-dichloro-2-methylpropane were detected. Both these products are derivable from the starting material; 1-chloro-2-methylprop-1-ene by double-bond isomerisation and 1,2-dichloro-2-methylpropane by addition of hydrogen chloride.

To determine whether this carbonylation was specific to allylic chlorides we examined the behaviour of the following chlorides under similar conditions; isopropyl chloride, t-butyl chloride, ethylene chlorohydrin, 1,2-dichloropropane, β-chloropropionyl chloride, 1-chloroprop-1-ene, *p*-chlorotoluene, and benzyl chloride. In no case was carbon monoxide absorbed and the starting materials were recovered unchanged except in the case of benzyl chloride where a tar was formed.

Reactions in Methanol.—It was of interest to study the carbonylation in an alcohol to achieve a direct preparation of the esters of but-3-enoic acids as might be expected from the work of Chiusoli.[1] However, we found that the reaction of carbon monoxide with allyl chloride dissolved in methanol in the presence of di-μ-chloro-di-π-allyldipalladium as catalyst was very exothermic, that the recovery of products (60—70%) based on the weight of the starting materials was only moderate, and that the products were complex mixtures. At least nine components were shown (by g.l.c.) to be present and of these one was water and three were high-boiling substances which were not identified. The remaining five components were characterised and the percentage of each present in the products was determined (Table 3).

The results, which display considerable variation between experiments, indicate that methyl but-3-enoate is one of the initial products, for on isomerisation it will yield methyl

---

[3] Irving and Magnusson, *J.*, 1958, 2283.

[4] Dent, Long, and Wilkinson, preceding paper.

crotonate and by the addition of hydrogen chloride it will give methyl 3-chlorobutyrate. The absence, even of traces, of methyl methacrylate was demonstrated (g.l.c.). The gaseous products were shown (by mass spectrographic analysis) to contain methyl chloride as main component.

Whilst this work was in progress, Fischer and Bürger[5] reported that methyl methacrylate was obtained in 50% yield from reaction of carbon monoxide with allyl chloride in methanol in the presence of nickel carbonyl, contrary to Chiusoli's findings.[1] Accordingly, we repeated the work of Fischer and Bürger[5] and demonstrated conclusively that methyl but-3-enoate was the main product and that methyl methacrylate was not present. Additionally, we found allyl methyl ether and hexa-1,5-diene, neither being referred to by Fischer and Bürger.[5] Table 4 records the products from two experiments.

TABLE 3.

Products from the carbonylation of allyl chloride in methanol with di-μ-chloro-di-π-allyldipalladium as catalyst.

Component	Amount present (w/w %; ±3%) Expt. 1	Expt. 2	Component	Amount present (w/w %; ±3%) Expt. 1	Expt. 2
Methanol	16	21	Methyl Crotonate	4	8
Methyl Isobutyrate	11	7	Methyl 3-Chlorobutyrate	7	7
Methyl But-3-enoate	27	13			

TABLE 4.

Products from the carbonylation of allyl chloride in methanol with nickel carbonyl as catalyst.

Component	Amount present (w/w %; ±3%) Expt. 1	Expt. 2	Component	Amount present (w/w %; ±3%) Expt. 1	Expt. 2
Methanol	1	4	Hexa-1,5-diene	22	12
Allyl Methyl Ether	13·5	7	Methyl But-3-enoate	52	60
Allyl Chloride	—	8			

The recoveries of liquid products (30—40%) based on the starting materials were even lower than was the case with di-μ-chloro-di-π-allyldipalladium as catalyst and the composition of the products showed variation between experiments. The major gaseous product was methyl chloride.

Chiusoli and Merzoni[6] have since confirmed that methyl but-3-enoate is the initial carbonylation product of allyl chloride in methanol, with nickel carbonyl as catalyst.

EXPERIMENTAL

Melting points were determined on the Kofler block.

Infrared spectra in the range 2—15 μ were measured on a Grubb-Parsons GS2 instrument and those in the range 15—35 μ on a Grubb-Parsons DM2. N.m.r. spectra were recorded on an A.E.I. RS2 spectrometer at 60 Mc./sec. G.l.c. was carried out with various instruments and conditions, specified below where appropriate. The examination of liquid products was frequently accomplished with a gas chromatograph (capacity 100 mg.) constructed from a Griffen and George instrument, having a 6 ft. column ($\frac{3}{16}$ in. I.D.) of dinonyl phthalate on Celite, to split the material into fractions which were

---

[5] Fischer and Bürger *Z. Naturforsch.*, 1962, **17***b*, 484.
[6] Chiusoli and Merzoni, *Z. Naturforsch.*, 1962, **17***b*, 850.

collected by cooling the column effluent to −78°. The fractions were then identified by comparison of the retention times and of the i.r. spectra of authentic samples prepared by synthesis. This method of qualitative analysis is referred to in the following description as "g.l.c./i.r. comparison." The method used for the quantitative analysis of the products was based on g.l.c. The components of each product were synthesised during the process of qualitative identification thus providing standard reference samples. Mixtures of known quantities of the synthetic components approximately corresponding to the composition of each product were then prepared in an inert material (1 ml.) chosen to act as a marker and possessing a retention time similar to but not identical with the retention times of any of the components. Gas–liquid chromatograms were then obtained for each synthetic mixture and the ratios of the peak heights of the components relative to that of the marker were obtained. These peak height ratios were plotted against the weights of components per 1 ml. of marker to give a calibration graph. By dissolving a given weight of product in 1 ml. of marker, running the gas–liquid chromatogram and determining the peak height ratios, the amounts of each component present could be calculated from the calibration graph.

The Carbonylation of Allylic Chlorides in the Absence of Solvent.—General procedure. A known weight of the allylic chloride (*ca.* 0·5 mole), together with the catalyst, was introduced into a glass liner which fitted the well of a 100-c.c. chrome-steel autoclave. A glass-sheathed stirrer impelled by an induction coil was provided. Temperature measurements were made by means of a thermocouple housed in a glass-sheathed metal tube dipping into the reaction mixture. The electrical heating was carefully controlled by a Kelvin-Hughes regulator. The vessel was flushed with carbon monoxide and then pressurised to 500 atm. The temperature was slowly raised until reaction commenced. More carbon monoxide was compressed into the vessel to maintain the pressure at ∼500 atm. Details are recorded in Tables 1 and 2.

The Carbonylation Products of Allyl Chloride (*Table* 1).—The product from experiment 1 was distilled at atmospheric pressure giving: a forerun (1·2 g.), b. p. 48—80°; a main fraction (25·4 g.), b. p. 80—110°, mostly distilling at 99°; and a third cut (9·2 g.), b. p. 110—126°. The main fraction was identified as but-3-enoyl chloride containing a small amount of crotonoyl chloride by g.l.c./i.r. comparison with a sample of but-3-enoyl chloride, b. p. 99°, synthesised according to Jeffery and Vogel's method [7] (they quote b. p. 98—99°/774 mm.), and with a commerical sample of crotonoyl chloride, b. p. 126°. The absence of methacryloyl chloride was established by adding a sample, b. p. 40—41·5°/100 mm., prepared from methacrylic acid and thionyl chloride (cf. Rehberg, Dixon, and Fischer [8]), to the product and demonstrating that the gas–liquid chromatogram exhibited a new peak solely due to methacryloyl chloride which was not previously present. Although experiment 1 served to identify the components it was untypical in that a relatively large quantity of palladium chloride was used as catalyst and that the reaction temperature was higher than in the other experiments so that considerable quantities of crotonoyl chloride were formed. Accordingly, a portion (32·0 g.) of the product from experiment 8 was distilled at atmospheric pressure giving a forerun (2·7 g.), b. p. 70—97°, and but-3-enoyl chloride (20·8 g.), b. p. 98—101°, containing a trace of crotonoyl chloride.

The quantitative analysis was carried out with a Griffen and George chromatograph having a 6-ft. glass column $\frac{3}{16}$ in. I.D.) packed with 30% vaseline on 30—60 grade Celite operated at 81°. The carrier gas was nitrogen passed at 2·5 l./hr. with an exit pressure of 95 mm. The bridge current of the katharometer detector was 165 mA. Under these conditions the retention times of the components relative to n-octane, which was used as the marker, were allyl chloride (0·11), but-3-enoyl chloride (0·39), and crotonoyl chloride (0·64).

Solid by-products (*Table* 1). Buff-coloured solids were obtained as by-products from experiments 2, 5, and 8. These were insoluble in the usual organic solvents and consequently purification, apart from washing with light petroleum (b. p. 40—60°), was not possible. Analytical infrared spectral data were as follows: Solid from experiment 2 (Found: C, 8·1; H, 0·3; Cl, 19·0; Pd, 59·8%); ν 2003w, 1972vs, 1942sh, 617vs, 588s, 434m, and 385m. Solid from experiment 5 (Found: C, 11·7; H, 1·4; Cl, 20·3; Pd, 58·8%). Solid from experiment 8 (Found: C, 11·9; H, 1·4; Cl, 20·1; Pd, 59·2%). These last two solids had identical infrared absorptions at 1980w, 1934vs, 1460m, 1387s, 1235w, 1027w, 995m, 957m, 931m, 751w, 645s, 615m, 510w, 444w, 397w, and 377w.

---

[7] Jeffery and Vogel, *J.*, 1948, 661.

[8] Rehberg, Dixon, and Fischer, *J. Amer. Chem. Soc.*, 1945, 67, 208.

The Carbonylation Products of 1-*Chlorobut*-2-*ene and* 3-*Chlorobut*-1-*ene* (*Table* 2).—The product from experiment 1 was examined by g.l.c.; it consisted of three components, the third in large excess. The two minor peaks were due to 3-chlorobut-1-ene and 1-chlorobut-2-ene. A portion (34·8 g.) of the product from experiment 1 was distilled giving a fraction (27·8 g.), b. p. 32—35·5°/20 mm. which was shown to be pent-3-enoyl chloride by g.l.c./i.r. comparison with an authentic sample, b. p. 40°/30 mm. (cf. b. p. 53—54°/55 mm.,[9] b. p. 46°/23 mm.[10]) prepared [11] from thionyl chloride and pent-3-enoic acid.

Pent-3-enoyl chloride (major component), 3-chlorobut-1-ene, and 1-chlorobut-2-ene were also shown (by g.l.c./i.r. comparison with authentic samples) to constitute the product from the carbonylation of 3-chlorobut-1-ene (experiment 3, Table 2). The absence of 2-methylbut-3-enoyl chloride was confirmed by comparison with synthetic sample.[12] Quantitative analysis of the products was carried out as for carbonylation products of allyl chloride. Under these conditions the retention times of the components relative to n-octane, which was employed as the marker, were 3-chlorobut-1-ene (0·20), 1-chlorobut-2-ene (0·35), and pent-3-enoyl chloride (1·2).

The Carbonylation Products of 1-*Chloro*-2-*methylprop*-2-*ene* (*Table* 2).—The product from experiment 4 was evaporated at reduced pressure (30 mm.) and the volatile material, which was condensed at −78°, was shown by g.l.c./i.r. comparison to contain t-butyl chloride, 1-chloro-2-methylprop-2-ene, 1-chloro-2-methylprop-1-ene, 1,2-dichloro-2-methylpropane, 3-methylbut-3-enoyl chloride, and 3-methylbut-2-enoyl chloride. The first three compounds were available commerically, 1,2-dichloro-2-methylpropane was prepared according to the method given by Hatch, Russ, and Gordon,[13] 3-*methylbut*-3-*enoyl chloride*, b. p. 33—34°/30 mm. (Found: C, 50·3; H, 5·9. C_5H_8ClO requires C, 50·7; H, 5·95%), was prepared from thionyl chloride and 3-methylbut-3-enoic acid,[14] and 3-methylbut-2-enoyl chloride, b. p. 58°/30 mm., as described by Smith and Engelhardt.[15] The product from experiment 5 contained negligible amounts of 1-chloro-2-methylprop-1-ene and 1,2-dichloro-2-methylpropane and no attempt was made to analyse for these compounds quantitatively. The considerable variation in the retention times of the other four components prevented the use of a single compound as a marker for the complete mixture and consequently the analysis was carried out in two parts. t-Butyl chloride and 1-chloro-2-methylprop-2-ene were analysed on a Shandon FB4 instrument having a 10-ft. column ($\frac{1}{16}$ in. I.D.) of 30% silicone elastomer on Celite operated at 75°. The carrier gas was a mixture of hydrogen (2 lb./sq. in.) and air (20 lb./sq. in.) with a flame ionisation detector operated at 300 v. *p*-Xylene was employed as the marker and the retention times relative to *p*-xylene were t-butyl chloride (0·10) and 1-chloro-2-methylprop-2-ene (0·18). 3-Methylbut-3-enoyl chloride and 3-methylbut-2-enoyl chloride were analysed on a Griffen and George instrument provided with a 6-ft. column ($\frac{3}{16}$ in. I.D.) packed with 30% vaseline on Celite operated at 76°. The carrier gas was nitrogen (2·5 l./hr.) and the bridge current of the katharometer was 165 mA. Benzene was used as the marker and the retention times relative to benzene were 3-methylbut-3-enoyl chloride (1·9) and 3-methylbut-2-enoyl chloride (4·9).

The Carbonylation of Allyl Chloride with Methanol as Solvent.—(a) *Reactions with di-μ-chloridi-π-allyldipalladium as catalyst* (*Table* 3). Allyl chloride (18·0 g.) in methanol (18·0 g.) and the catalyst (1·0 g.) were charged into the autoclave which was pressured with carbon monoxide at 500 atm. The temperature was slowly raised until at 110° an exothermic reaction started and the temperature quickly rose to 160° although the autoclave was immediately cooled. After the vessel had cooled to room temperature the gaseous products were vented through a trap cooled to −186°, and the condensate was subsequently shown by mass spectrography be mainly methyl chloride. The liquid products (25·0 g. from experiment 1, and 22·0 g. from experiment 2; Table 3) were decanted from the autoclave and were examined qualitatively by g.l.c./i.r. comparison with known materials, and the constituents listed in Table 3 were identified. The reference materials were obtained as follows. Methyl but-3-enoate, b. p. 110°, was prepared from but-3-enoyl chloride, methanol, and pyridine (cf. Jeffery

---

[9] Von Auwers, *Annalen*, 1923, 432, 46.
[10] Goldberg and Linstead, *J.*, 1928, 2351.
[11] Lane, Fentress, and Sherwood, *J. Amer. Chem. Soc.*, 1944, **66**, 545.
[12] Lane, Robertson, and Young, *J. Amer. Chem. Soc.*, 1944, **66**, 544.
[13] Hatch, Russ, and Gordon, *J. Amer. Chem. Soc.*, 1947, **69**, 2616.
[14] Wagner, *J. Amer. Chem. Soc.*, 1949, **71**, 3214.
[15] Smith and Engelhardt, *J. Amer. Chem. Soc.*, 1949, **71**, 2671.

and Vogel[16] who record b. p. 108—108·5°/774 mm.). Methyl crotonate, b. p. 120·5°, was prepared from crotonoyl chloride, methanol, and pyridine (cf. Jeffery and Vogel[16] who record b. p. 119°/768 mm.). Methyl isobutyrate, b. p. 90—91°, was prepared as described by Vogel,[17] who gave b. p. 91—92°. Methyl 3-chlorobutyrate, b. p. 155—156°, was obtained from crotonoyl chloride and methanol by allowing the reaction to proceed to completion (cf. Arndt, Schwarz, Martius, and Aron[18] who record b. p. 60°/15 mm.). The structure of our sample was confirmed by the n.m.r. spectrum (multiplicities are given in parentheses): $\tau = 8{\cdot}44$ (2) $CH_3{\cdot}CH-$; $\tau = 7{\cdot}25$ (2) $-CH{\cdot}CH_2{\cdot}C-$; $\tau = 6{\cdot}34$ (1) $-OCH_3$; $\tau = 5{\cdot}59$ (multiplet) $CH_3{\cdot}CH{\cdot}CH_2-$. The resonance of the methyl in the butyrate group is characteristic of chlorine substitution on the adjacent carbon atom,[19] and the compound is thus uniquely determined as methyl 3-chlorobutyrate.

Methyl methacrylate possessed the same retention time as methyl but-3-enoate when the Griffen and George instrument described at the beginning of the Experimental section was employed. The conditions necessary to effect a separation of the two esters were established by using a 200-ft. copper capillary column coated with dinonyl phthalate operated at room temperature with nitrogen as the carrier gas and employing a flame ionisation detector. The esters were then readily resolved; retention times were methyl methacrylate (29 min.) and methyl but-3-enoate (32 min.). Under these conditions the absence of methyl methacrylate from the products of the experiments reported in Table 3 was conclusively demonstrated. The esters identified in that part of the chromatogram studied were methyl isobutyrate (18 min.), methyl but-3-enoate (29 min.), and methyl crotonate (57 min.). The quantitative analysis of the products was carried out on a Shandon FB4 instrument having a 10-ft. column ($\frac{1}{16}$ in. I.D.) of 30% vaseline on Celite operated at 78°. The carrier gas was a mixture of hydrogen (1·5 lb./sq. in.), nitrogen (10 lb./sq. in.), and air (20 lb./sq. in.) passed at 14 l./hr. The flame ionisation detector was operated at 300 v. With toluene as the marker the relative retention times were methanol (0·06), methyl isobutyrate (0·34), methyl but-3-enoate (0·43), methyl crotonate (0·68), and methyl 3-chlorobutyrate (1·6).

(b) *Reactions with nickel carbonyl as catalyst* (*Table* 4). The conditions of the experiments were as described by Fischer and Bürger.[5] Allyl chloride (19·0 g.) and nickel carbonyl (5 ml.) in methanol (13·5 g.) were heated at 100° for 13 hr. in the presence of carbon monoxide (50 atm.). The main gaseous constituent was methyl chloride (mass-spectrographic analysis). The components of the liquid products (12·5 g. from experiment 1 and 11·2 g. from experiment 2) are recorded in Table 4. The necessary reference materials not already described were obtained as follows. Allyl methyl ether, b. p. 41°, was prepared as described by Irvine, Macdonald, and Soutar,[20] who quote b. p. 42·5—43°/757 mm.; hexa-1,5-diene, b. p. 61—63°, was made according to Cortese[21] who gave, b. p. 59—60°. The absence of methyl methacrylate was established by g.l.c. on the 200-ft. capillary column.

The quantitative analysis was carried out as already described and using toluene as the marker; the retention times relative to toluene were methanol (0·06), allyl methyl ether (0·13), allyl chloride (0·14), hexa-1,5-diene (0·22), and methyl but-3-enoate (0·43).

HEAVY ORGANIC CHEMICALS DIVISION,
IMPERIAL CHEMICAL INDUSTRIES LIMITED, BILLINGHAM, CO. DURHAM.
[Present address (R. L.): BOROUGH POLYTECHNIC,
LONDON S.E.1.]

[*Received, September* 23*rd*, 1963.]

---

[16] Jeffery and Vogel, *J.*, 1948, 658.
[17] Vogel, *J.*, 1948, 624.
[18] Arndt, Schwarz, Martius, and Aron, *Rev. Fac. Sci. Istanbul*, 1948, *A*13, 57.
[19] Jackman, " Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, London, 1959, p. 53.
[20] Irvine, Macdonald, and Soutar, *J.*, 1915, **107**, 351.
[21] Cortese, *J. Amer. Chem. Soc.*, 1929, **51**, 2266.