221. *Peroxides of Elements other than Carbon. Part X.*[1] *Organoperoxyaluminium Compounds as Intermediates in Redox Reactions.*

By Alwyn G. Davies and C. D. Hall.

A number of reaction systems have been studied in which organoperoxyaluminium compounds are formed as intermediates or as products. It is shown that: (*a*) aluminium isopropoxide reduces alkyl hydroperoxides, diacyl peroxides, and peroxyesters (but not dialkyl peroxides) in a process which is probably akin to the Meerwein–Ponndorf reaction; (*b*) nucleophilic substitution by a hydroperoxide at an aluminium atom gives in solution a tri(alkylperoxy)aluminium compound which decomposes extensively when the solvent is removed; and (*c*) autoxidation of a trialkylaluminium gives initially an alkylperoxyaluminium compound which is reduced by the reagent to give the aluminium alkoxide as the major product.

ORGANOPEROXYMETALLIC compounds can in general be prepared by the nucleophilic substitution of an alkyl hydroperoxide at a metal atom (M) (equation 1), or by the autoxidation of an organometallic compound (equation 2).[2]

$$\mathrm{RO{\cdot}OH} + \mathrm{MX} \longrightarrow \mathrm{RO{\cdot}OM} + \mathrm{HX} \qquad (1)$$

$$\mathrm{O_2} + \mathrm{RM} \longrightarrow \mathrm{RO{\cdot}OM} \qquad (2)$$

Peroxides of boron have been obtained by both routes. By reaction (1), boron trichloride readily yields tri(alkylperoxy)borons, but alkyl borates are less reactive and require repeated treatment with the hydroperoxide; alkylborons have not been reported to react in this manner (in contrast to the cadmium and zinc alkyls), but instead reduce the hydroperoxide (equation 3).[3]

$$\mathrm{RO{\cdot}OH} + \mathrm{R'M} \longrightarrow \mathrm{ROH} + \mathrm{MOR'} \qquad (3)$$

By reaction (2), most trialkylborons in dilute solution yield the diperoxyboronates $\mathrm{R{\cdot}B(O{\cdot}OR)_2}$,[4,5] but trimethylboron in the gas phase gives the peroxyborinate $\mathrm{Me_2B{\cdot}O{\cdot}OMe}$.[6]

The object of the present work was to explore the behaviour of aluminium compounds in similar reaction systems. The results are relevant to potential industrial methods for preparing oxygen-containing compounds by the reaction of aerobic oxygen with organoaluminium compounds, or with hydrocarbons in the presence of compounds of Group III metals.

Reaction of Alkyl Hydroperoxides with Aluminium Isopropoxide.—A number of organic peroxides were heated at 70—75° in isopropyl alcohol (and in some cases in dioxan) containing aluminium isopropoxide (see Table 1). With t-butyl, 1-phenylethyl, 1-methyl-1-phenylethyl, 1-methyl-1-phenylpropyl, 1,2,3,4-tetrahydro-1-naphthol, and *trans*-decahydro-9-naphthyl hydroperoxide, acetone was evolved, and the corresponding alcohols were isolated in good yield. Benzoyl peroxide was reduced to benzoic acid, and t-butyl peroxybenzoate and peroxyacetate to t-butyl alcohol and the corresponding carboxylic acid, but di-t-butyl peroxide and bis(triphenylmethyl) peroxide gave no acetone and were recovered.

To check that these results were not due simply to thermal decomposition of the peroxides, control experiments were carried out in the absence of aluminium isopropoxide. Decomposition of the peroxides was usually relatively slow and much could be recovered.

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[1] Part IX, Davies, Hare, and Khan, *J.*, 1963, 1125.

[2] Davies, " Organic Peroxides," Butterworths Scientific Publns., London, 1961, Chap. 8.

[3] Davies and Moodie, *J.*, 1958, 2372.

[4] (*a*) Abraham and Davies, *J.*, 1959, 429; (*b*) Davies and Hare, *J.*, 1959, 438; Davies, Hare, and White, *J.*, 1960, 1040; 1961, 341.

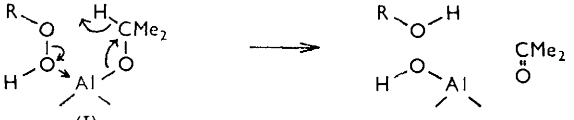
[5] Wilke and Heimbach, *Annalen*, 1962, **652**, 7.

[6] Petry and Verhoek, *J. Amer. Chem. Soc.*, 1956, **78**, 6416.

Only t-butyl hydroperoxide gave acetone, and, although benzoyl peroxide underwent substantial decomposition, the yield of benzoic acid was relatively low.

Optically active 1-phenylethyl hydroperoxide [7] was reduced by aluminium isopropoxide to the alcohol with retention of configuration; acetophenone, which might be a product of thermal decomposition, is therefore not an intermediate.

It appears then that the peroxide is reduced by the aluminium isopropoxide. The first step of the reaction probably involves co-ordination of the peroxide to the aluminium; the reduction may then be brought about by transference of a hydride ion in a cyclic transition state (I) similar to that commonly postulated for the Meerwein–Ponndorf reduction of aldehydes and ketones.



(I)

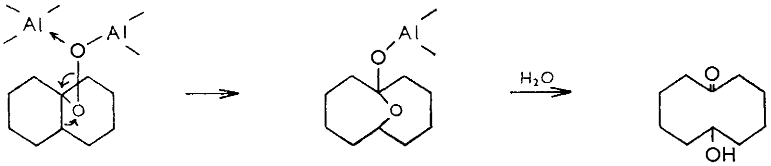
No experiments have been reported where tri-isopropyl borate has been used under these conditions for reducing an organic peroxide, or indeed apparently in the Meerwein–Ponndorf reaction.*

Reaction of Alkyl Hydroperoxides with Aluminium t-Butoxide.—An alkyl hydroperoxide and an aluminium t-alkoxide would give an intermediate which could not transfer hydride but would be expected to be in equilibrium with the corresponding aluminium alkyl peroxide and t-butyl alcohol.

Decahydro-9-naphthyl hydroperoxide was treated with aluminium t-butoxide in ethylbenzene. t-Butyl alcohol was removed completely as its azeotrope with ethylbenzene, with no loss of peroxide; at this stage, therefore, the solution presumably must contain tris(decahydro-9-naphthylperoxy)aluminium. However, when the solvent was removed under reduced pressure, the residue contained only about one-third of the expected peroxide content. When the reaction was carried out in dioxan, about two of the three peroxide groups persisted. The elementary analysis indicated the composition $Al(C_{10}H_{17}O_2)_3$; hydrolysis gave decahydro-9-naphthyl hydroperoxide and an unidentified oil, but not t-butyl alcohol.

Similar experiments with t-butyl hydroperoxide likewise gave a product containing only 10—15% of the expected peroxidic oxygen and probably consisting largely of alumina.

It appears then that aluminium peroxides of the composition $Al(O{\cdot}OR^t)_3$ can be prepared in solution, but that extensive decomposition occurs during attempted isolation. This is in contrast to most of the organoperoxy-compounds $(R^tO{\cdot}O)_nM$ of lithium, sodium, potassium, calcium, strontium, barium, zinc, cadmium, boron, silicon, and germanium, which are isolable and relatively stable.[2] It is reminiscent, however, of the behaviour of tetra-t-butylperoxytin, which underwent violent decomposition at 60—70°,[8] and



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* Recent work in this Department by Mr. P. J. Gaston has shown that benzaldehyde and benzophenone are not reduced by tri-isopropyl borate in isopropyl alcohol, nor is benzaldehyde by (the less sterically congested) triethyl borate in ethanol, under the usual conditions of the Meerwein–Ponndorf reaction. Similarly, when a mixture of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide and isopropyl borate in isopropyl alcohol is kept at 70—75° for 6 hr., no acetone is formed, and the loss of peroxide (10%) is no more than that which occurs in the absence of the borate.

[7] Davies and Feld, *J.*, 1958, 4637.

[8] Alleston and Davies, *J.*, 1962, 2465.

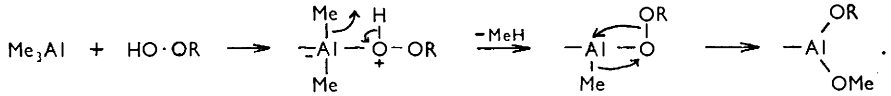
particularly of the 1-methyl-1-phenylethylperoxyboron group which decomposed at 70° giving phenol.[3] The latter reaction was regarded as an example of a redox rearrangement within the alkylperoxy-group, brought about by the electron-accepting properties of the boron atom, and it is possible that a similar mechanism applies to the alkylperoxyaluminium compounds, as illustrated.

Reaction of Alkyl Hydroperoxides with Aluminium Chloride.—Aluminium alkoxides can be prepared by a reaction between alcohols and aluminium chloride in the presence of a base such as ammonia. When alkyl hydroperoxides were treated similarly, part of the aluminium chloride was precipitated as the amine complex, and no trialkylperoxyaluminium compound was isolated. Similar experiments in the absence of base—conditions under which trialkylperoxyborons can be prepared from boron trichloride—led to considerable decomposition of the hydroperoxides. This is reasonable since aluminium chloride and hydrogen chloride would be expected to be powerful catalysts for the type of rearrangement concerned.

Reaction of Alkyl Hydroperoxides with Aluminium Alkyls.—Trimethyl- or triethylaluminium in cyclohexane was treated with t-butyl hydroperoxide or decahydro-9-naphthyl hydroperoxide. The results are summarised in Table 2. Typically, trimethylaluminium with decahydro-9-naphthyl hydroperoxide (3 mol.) at room temperature liberated 1·5 mol. of methane instead of the 3 mol. required by equation (1), and 53% of the hydroperoxide was reduced. Hydrolysis of the product with acetic acid confirmed the view that no methyl–aluminium bonds remained. The overall reaction is therefore represented by equation (4); in contrast to the analogous reaction of the cadmium[9] and zinc[10] alkyls, it appears to be impossible now to avoid quantitative reduction (equation 3) of the peroxide by the aluminium alkyl.

$$\mathrm{RO{\cdot}OH + 2MeAl_{1/3} \longrightarrow ROAl_{1/3} + MeOAl_{1/3} + MeH} \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

When the reactions were carried out in the presence of methyl methacrylate or styrene, no polymerisation occurred; the decomposition of the peroxide is thus probably largely heterolytic. One possible sequence of the probable steps is shown in equation (5); alternatively, reduction might precede substitution, and might involve a second methylaluminium molecule.



. (5)

Reaction of Oxygen with Aluminium Alkyls.—This ready reduction of peroxides by aluminium alkyls prevented our isolating organoperoxylaluminium compounds by autoxidation of aluminium alkyls.

In cyclohexane at room temperature, triethylaluminium absorbed 1·5 mol. of oxygen and the solution contained only 6·3% of the peroxide content calculated for the compound $\mathrm{Al(O{\cdot}OEt)_3}$. Hydrolysis gave ethanol. The principal overall reaction is thus:

$$\mathrm{AlEt_3 + 1{\cdot}5O_2 \longrightarrow Al(OEt)_3}$$

In ether, only 1 mol. of oxygen was taken up and the product contained 10% of the triperoxide. Walling and Buckler[11] found that high yields of organoperoxymagnesium compounds could be obtained if solutions of Grignard reagents were added to ether saturated with oxygen (" inverse oxidation ") at —80°. We found, however, that this technique with triethylaluminium still gave a maximum peroxide yield of 10%. This

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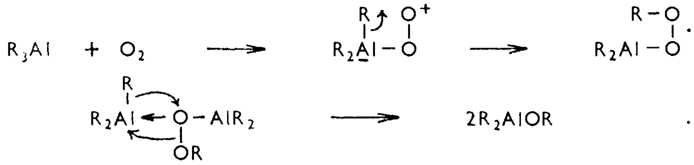
[9] Davies and Packer, *J.*, 1959, 3164.

[10] Abraham, *J.*, 1960, 4130.

[11] Walling and Buckler, *J. Amer. Chem. Soc.*, 1953, **75**, 4372; 1955, **77**, 6032, 6039.

corresponds to Hock and Ernst's report[12] that autoxidation of butylaluminium dichloride at 0° and —50° gave peroxide yields of 9% and 10%, respectively.

Trimethylaluminium absorbed only 1 mol. of oxygen in cyclohexane or (more slowly) in ether; the products contained a negligible amount of peroxide. This can be correlated with the reduced reactivity towards oxygen of trimethylboron[6] and dimethylcadmium,[9] and of the higher trialkylboranes in ethereal solvents.[1]



$$R_3Al + O_2 \longrightarrow \begin{array}{c}R\ \ O^+\\ |\ \ \ \ |\\ R_2\underline{A}l-O\end{array} \longrightarrow \begin{array}{c}R-O\\ \ \ \ \ |\\ R_2Al-O\end{array} \quad \cdot\ \cdot\ \cdot\ \cdot\ (6)$$

$$\begin{array}{c}R\\ |\\ R_2Al\leftarrow O-AlR_2\\ \ \ \ \ \ \ |\\ \ \ \ \ \ \ OR\end{array} \longrightarrow 2R_2AlOR \quad \cdot\ \cdot\ \cdot\ \cdot\ (7)$$

In common with the alkyls of the other metals of Groups II and III that have been studied, aluminium alkyls thus appear to react with oxygen to give alkylperoxymetallic compounds as the initial products (equation 6). In contrast, the intermolecular (equation 7) or intramolecular reduction of the peroxide by an alkylaluminium group is relatively fast and the ultimate product is principally the alkoxide.

EXPERIMENTAL

Analysis.—Peroxide oxygen was determined iodometrically in isopropyl alcohol. Aluminium chlorides were hydrolysed in an excess of standard alkali, and the chloride was estimated by back-titration with standard acid.

Aluminium bonded to oxygen (as in the alkoxides) could usually be determined from the alumina ash left after combustion in the analysis for carbon and hydrogen. Sometimes the results were low and variable and were then associated with low values for carbon. This was probably due to the formation of aluminium carbide. Compounds containing the AlCl bond also gave too little ash, probably because of the volatility of aluminum chloride. In these cases, a weighed sample of the compound was treated with concentrated nitric acid and ignited to alumina.

Precautions. Operations involving peroxides were carried out on a small scale behind a safety screen, and, *e.g.*, during distillations, below 100°. Aluminium alkyls were handled in a gloved box filled with dry nitrogen and fitted for filtration under reduced pressure; alkoxy- and alkylperoxy-aluminium compounds were exposed only to dry atmospheres and reagents.

Reactions of Organic Peroxides with Aluminium Isopropoxide.—Equimolar amounts of the organic peroxide (1—2 g.) and aluminium isopropoxide (redistilled; b. p. 138—140°/10 mm.) in dry redistilled isopropyl alcohol (*ca.* 20 c.c.) (solvent A) or dioxan (20 c.c.)–isopropyl alcohol (3 c.c.) (solvent B) were heated at 70—75° in a Claisen flask. A stream of dry nitrogen was passed through the solution and into a 0·5% (w/v) solution of 2,4-dinitrophenylhydrazine in 2N-hydrochloric acid.

The reaction was continued until no further acetone 2,4-dinitrophenylhydrazone was precipitated; analysis then showed that a negligible amount of peroxide remained. The residue in the flask was diluted with water (30 c.c.), acidified with 2N-sulphuric acid, and extracted with ether (2 × 10 c.c.; 5 c.c.). The extracts were washed and dried, and then examined by standard procedures.

Under these conditions, di-t-butyl peroxide and bis(triphenylmethyl) peroxide were unreactive and were recovered. The results with other peroxides are shown in Table 1.

Parallel experiments were carried out with selected peroxides in solvent A under the same conditions as above but in the absence of aluminium isopropoxide, with the following results (percentages refer to decomposition): t-butyl hydroperoxide, 4 hr., 80%; decahydro-9-naphthyl hydroperoxide, 3 hr., 50%; 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide, 5 hr., 10%; benzoyl peroxide, 3 hr., 80%, giving benzoic acid in 30% yield; t-butyl peroxyacetate, 6 hr., 20%. Acetone was formed only from t-butyl hydroperoxide.

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[12] Hock and Ernst, *Chem. Ber.*, 1959, **92**, 2716.

TABLE 1.

Reduction of organic peroxides by aluminium isopropoxide.

Peroxide	Solvent	Time (hr.)	Product	Yield (%)	Characterised by
$Ph\cdot CMe_2\cdot O\cdot OH$	A	6	$Ph\cdot CMe_2\cdot OH$	74	p-*tolyl sulphone,** m. p. 146—147°.
$C_{10}H_{11}\cdot O\cdot OH$	A	3	$C_{10}H_{11}\cdot OH$	70	*p*-tolyl sulphone, m. p. 130—131°; phenylurethane, m. p. 121°.
$C_{10}H_{17}\cdot O\cdot OH$	A	8	$C_{10}H_{17}\cdot OH$	81	chromate, m. p. 88—90°; p-*nitrobenzoate,*† m. p. 106·5—107°.
$Ph\cdot CMeEt\cdot O\cdot OH$	A	10	$Ph\cdot CMeEt\cdot OH$	54	b. p. 80—85°/10 mm., n_D^{25} 1·5220.‡
$Ph\cdot CHMe\cdot O\cdot OH$	A	6	$Ph\cdot CHMe\cdot OH$	53	b. p. 39—40°/0·1 mm., n_D^{25} 1·5273.§
$Bu^tO\cdot OH$	B	4	Bu^tOH	—	Gas–liquid chromatography.
$(Ph\cdot CO)_2O_2$	A	4	$Ph\cdot CO_2H$	90—100	m. p. 120—121°; equiv., found and calc., 122.
$Me\cdot CO\cdot O\cdot OBu^t$ ...	B	5	Bu^tOH $Me\cdot CO_2H$	—	Gas–liquid chromatography.
$Ph\cdot CO\cdot O\cdot OBu^t$	A, B	6	Bu^tOH $Ph\cdot CO_2H$	—	Gas–liquid chromatography; m. p. 121°

$C_{10}H_{11}$ = 1,2,3,4-tetrahydro-1-naphthyl. $C_{10}H_{17}$ = *trans*-decahydro-9-naphthyl. For solvents see text.

* Found: C, 70·4; H, 6·8; S, 11·5. $C_{16}H_{18}O_2S$ requires C, 70·0; H, 6·6; S, 11·7%. † Found: N, 4·5. $C_{17}H_{21}NO_4$ requires N, 4·6%. The analysis for C was not reproducible, probably because the compound exploded during combustion. ‡ Impure; contains olefin. § 1-Phenylethyl hydroperoxide, α_D^{17} $-1{\cdot}94°$ ($l = 1$), gives 1-phenylethanol, α_D^{20} $-0{\cdot}50°$ ($l = 1$), whence $\alpha(ROH)/\alpha(RO_2H) = +0{\cdot}26$, to be compared with the mean value of $+0{\cdot}30$ obtained with other reducing agents.[7, 13]

Reaction of Alkyl Hydroperoxides with Aluminium t-Butoxide.—Aluminium t-butoxide was sublimed at 175—185°/1 mm.

(i) Aluminium t-butoxide (1·0 g.) and decahydro-9-naphthyl hydroperoxide (2·1 g.) in ethylbenzene (expt. *a*) or dioxan (expts. *b* and *c*) (20 c.c.) were stirred for 1 hr. at room temperature. Part of the solvent was then removed at 45° (bath)/60 mm., and was shown by gas–liquid chromatography to contain t-butyl alcohol. Analysis showed that all the peroxide was still present at this stage. The remaining solvent was removed at 45—50° (bath)/20 mm., leaving a gelatinous solid [expt. *a*, 2·4 g.; expt. *b*, 2·7 g.; expt. *c*, 2·4 g. Calc. for $Al(O_2C_{10}H_{17})_3$, 2·2 g.] [Found, in expt. *b*: C, 63·3; H, 10·0; Al, 4·5; peroxidic O, 11·6 (10·4 after 2 days). In expt. *a* and *c*: peroxidic O, 10·8 and 5·6, respectively. Calc. for $Al(O\cdot OC_{10}H_{17})_3$: C, 67·4; H, 9·6; Al, 5·1; peroxidic O, 18·0%].

(ii) In similar experiments with t-butyl hydroperoxide, t-butyl alcohol was recovered as an azeotrope with ethylbenzene. When the solvent was removed the remaining solid contained 3·1%, 5·0%, and 5·0% of peroxidic oxygen in three experiments [Calc. for $Al(O\cdot OC_4H_9)_3$: periodic O, 32·7%].

Reaction of Alkyl Hydroperoxides with Aluminium Chloride.—Aluminium chloride in dry ether, chloroform, or dioxan was treated with t-butyl hydroperoxide or decahydro-9-naphthyl hydroperoxide (3 mol.) in the absence or presence of ammonia or pyridine. The following experiment is typical.

Aluminium chloride (0·2 g.) in ether (5 c.c.) was added under dry nitrogen and with stirring to decahydro-9-naphthyl hydroperoxide (0·76 g.) in ether (15 c.c.) at 0°. After 0·5 and 1·5 hr. there was negligible loss of peroxide. The solvent was removed quickly under reduced pressure leaving a fawn-coloured solid (0·5 g.) [Found: peroxidic O, 3·4. Calc. for $Al(O\cdot O\cdot C_{10}H_{17})_3$: peroxidic O, 18·0%]. Reversing the order of mixing the reagents gave a slighly better product (up to 8·6% of peroxidic oxygen) but this contained chloride.

Reaction of Alkyl Hydroperoxides with Aluminium Alkyls.—10% (w/v) Solutions of trimethyl- and triethyl-aluminium in cyclohexane were kindly given to us by Imperial Chemical Industries Limited, Billingham Division.

The results are summarised in Table 2. In experiments 1—5, the reagents were mixed in cyclohexane and the peroxide was determined periodically until the reaction appeared to be complete. Experiments 6 and 7 were carried out at the gas-burette, with the encapsulated

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[13] Ref. 2, p. 7.

alkyl[4a] and the solvent saturated with methane so that the gas which was evolved could be measured.

Triethylaluminium and trimethylaluminium in cyclohexane solution (10% w/v; 2 c.c.) were each added to t-butyl hydroperoxide (3 mol.) in the presence of either methyl methacrylate or styrene. In both cases the reaction was vigorous but did not initiate polymerisation.

TABLE 2.

Reaction of alkyl hydroperoxides with aluminium alkyls.

	R_3Al	Peroxide	Mol.	Solvent	Methane evolved (mol.)	Peroxide reduced (mol.)	Time (hr.)
1	Et_3Al	$Bu^tO{\cdot}OH$	3	C_6H_{12}	—	1·46	70
2	Et_3Al	$Bu^tO{\cdot}OH$	3	C_6H_{12}	—	1·32	4
3	Me_3Al	$Bu^tO{\cdot}OH$	3	C_6H_{12}	—	1·65	3
4	Me_3Al	$Bu^tO{\cdot}OH$	3	C_6H_{12}	—	1·05 1·98	0·25 20
5	Me_3Al	$C_{10}H_{17}{\cdot}O{\cdot}OH$	3	Et_2O	—	1·71	4 *
6	Me_2Al	$C_{10}H_{17}{\cdot}O{\cdot}OH$	3	Et_2O	1·5	1·59	0·41 †
7	Me_3Al	$C_{10}H_{17}{\cdot}O{\cdot}OH$	1	Et_2O	1·0	0·90	0·33 ‡

C_6H_{12} = cyclohexane. Experiments were at room temperature except expt. 2 at 50°, and expt. 5 at the b. p. of the solution.

* 44% of the hydroperoxide was recovered on hydrolysis. † Addition of acetic acid gave very little methane, therefore no Al–Me bonds remained. ‡ Addition of acetic acid gave *ca.* 0·7 mol. of methane in a violent reaction.

Reaction of Oxygen with Aluminium Alkyls.—(i) *At the gas-burette.* The reactions at the gas-burette were carried out by a technique we described previously.[4,9] The results are summarised in Table 3.

TABLE 3.

Autoxidation of aluminium alkyls.

Solvent	AlR_3	Wt. (g.)	Oxygen absorbed (mol.)	Peroxide formed (mol.)	Time (min.)
C_6H_{12}	$AlMe_3$	0·11	0·94	0·00	60
C_6H_{12}	$AlMe_3$	0·14	1·0	0·00	180
Et_2O	$AlMe_3$	0·12	0·7	0·00	35
Et_2O	$AlMe_3$	0·14	1·0	0·00	62
C_6H_{12}	$AlEt_3$	0·15	1·5	0·19 *	47
C_6H_{12}	$AlEt_3$	0·12	1·6	— *	45
C_6H_{12}	$AlEt_3$	0·19	1·6	— *	40
Et_2O	$AlEt_3$	0·16	0·9	0·30	40
Et_2O	$AlEt_3$	0·15	1·1	—	30

* These three products were combined and the cyclohexane was removed under reduced pressure, leaving a cream-coloured solid which was hydrolysed to give ethanol, identified by gas–liquid chromatography.

(ii) *By "inverse oxidation."* Triethylaluminium (2 c.c. of a 10% solution in cyclohexane, diluted with 5 c.c. of ether) was added dropwise during 15 min. to ether at −75° through which oxygen was bubbled. Aliquot parts were analysed at intervals of 30 min. After 3 hr. at room temperature, 0·30 mol. of peroxide was present; after a further 6 hr. at 0°, this had fallen to 0·15 mol.

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