808. *Organometallic Compounds. Part I. The Autoxidation of Dialkylzincs.**

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The rapid autoxidation of diethyl- and di-n-butyl-zinc is shown to give dialkylperoxyzincs, $Zn(O{\cdot}OEt)_2$ and $Zn(O{\cdot}OBu^n)_2$. Reduction of the dialkylperoxyzincs by excess of dialkylzinc leads to zinc dialkoxides, which are the products of slow autoxidation of the above dialkylzincs. It is suggested that autoxidation of an alkylzinc compound gives an alkylperoxyzinc as the initial product.

Co-ordination of oxygen to the zinc atom, and migration of an alkyl group from zinc to oxygen, are considered to be the probable mechanism of autoxidation.

This paper is the first of a series which will describe the autoxidation and other reactions of alkylmetals.

Autoxidation of Dialkylzincs.—Although Lissenko[1] claimed that autoxidation of diethylzinc gave $EtZn{\cdot}OEt$, most of the early investigators considered the autoxidation of dialkylzincs, in solution or as neat liquids, to give zinc dialkoxides (R = Et,[2] Pr^i,[3] C_5H_{11} [4]):

$$R_2Zn + O_2 \longrightarrow Zn(OR)_2 \quad (I)$$

Frankland and Duppa also showed that autoxidation of diethylzinc in ether gave first a soluble monoalkoxide, $EtZn{\cdot}OEt$, and then the dialkoxide which was precipitated as a white solid.[2] Although this was formulated as $Zn(OEt)_2$, its analysis did not agree with this composition and it was suggested that zinc acetate and zinc hydroxide were also formed. In addition, Frankland[5] noted that the solid exploded when heated.

Meyer and Demuth[6] also found that diethylzinc, on autoxidation in ligroin, gave an insoluble solid to which, however, they assigned the structure $EtZn{\cdot}O{\cdot}OEt$. The solid liberated iodine from potassium iodide and on hydrolysis gave ethyl alcohol and no ethane.

A solid, Et_2ZnO_2, considered to be of a peroxidic nature has been obtained[7] by vapour-phase autoxidation of diethylzinc; more recent work[8] suggests that the main reactions are:

$$Et_2Zn\ (g) + \tfrac{1}{2}O_2 \longrightarrow Et_2ZnO\ (s)$$
$$Et_2Zn\ (g) + O_2 \longrightarrow Et_2ZnO_2\ (s)$$

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* Cf. *Chem. and Ind.*, 1959, 750.

[1] Lissenko, *Jahresber.*, 1864, 470.

[2] Frankland and Duppa, *Annalen*, 1865, **135**, 29.

[3] Ragosin, *Ber.*, 1893, **26**, Ref. 380.

[4] Frankland and Duppa, *J.*, 1864, **17**, 29.

[5] Frankland, *Phil. Trans.*, 1859, **145**, 259; *Annalen*, 1855, **95**, 46.

[6] Meyer and Demuth, *Ber.*, 1890, **23**, 394.

[7] Thompson and Kelland, *J.*, 1933, 756.

[8] Bamford and Newitt, *J.*, 1946, 688.

The mono- and di-oxide were formed in presence of excess of dialkyl and of oxygen respectively.

Quite recently, Walling and Buckler[9] have shown that addition of di-n-butylzinc to oxygen-saturated ether at −80° gives 0·96 mol. of peroxide and, since the preliminary account of the present work appeared, Hock and Ernst,[10] by a similar procedure at 0°, have obtained 0·94 and 1·88 mol. of peroxide from n-butylzinc chloride and di-n-butylzinc respectively. These peroxides were estimated iodometrically.

Autoxidation of Organometallic Compounds.—It has been shown that solutions of the alkyls of magnesium,[9] boron,[11] and cadmium[12] on autoxidation give initially a peroxide of type M·O·OR. Alkyls of lithium[9] and aluminium[10] also give peroxidic products on autoxidation and it seems well established that the initial product of reaction of many metal and similar alkyls is a peroxide of this type.[13] It has also been demonstrated that peroxides containing the group MO·OR ($M = \frac{1}{2}Mg, \frac{1}{3}B$) are reduced to alkoxides, MOR, by an excess of alkyl-element compound.[9,11]

It is thus possible that oxidations and reductions of the above type also occur in the autoxidation of dialkylzincs; the present work seeks to investigate such reactions.

Rapid Autoxidation of Dialkylzincs.—The highest yields of peroxides were obtained by crushing ampoules of diethyl- or di-n-butyl-zinc under dry ether continuously saturated with oxygen at room temperature. After a few minutes diamagnetic white solids, insoluble in aprotic solvents, were deposited, with analyses corresponding to $Zn(O{\cdot}OEt)_2$ and $Zn(O{\cdot}OBu^n)_2$. These were hydrolysed rapidly in moist air.

Diethylzinc, autoxidised and then hydrolysed, gave 1·93 mol. of peroxide (iodometrically); similarly, di-n-butylzinc gave 1·96 mol. of peroxide which was estimated (2·00 mol.) and identified by gas–liquid chromatography[14] as n-butyl hydroperoxide. In a gas burette, a solution of diethylzinc in anisole absorbed 1·98 mol. of oxygen to give a product containing 1·92 mol. of peroxide, and the rapid autoxidation can thus be represented as follows ($R = Et, Bu^n$):

$$R_2Zn \xrightarrow{O_2} RZn{\cdot}O{\cdot}OR \xrightarrow{O_2} Zn(O{\cdot}OR)_2 \quad (II)$$

Although the final products of autoxidation do not evolve alkane on hydrolysis, the autoxidised solution, just before precipitation of the solid, is hydrolysed to give both peroxide and alkane and no doubt contains the soluble intermediate, RZn·O·OR ($R = Et, Bu^n$).

Slow Autoxidation of Dialkylzincs.—Solutions of diethyl-, di-n-butyl-, and di-t-butylzinc were allowed to absorb oxygen slowly for several weeks. The products of autoxidation were again insoluble solids, but on hydrolysis they liberated the corresponding alcohol (1·74, 1·55, — mol.) together with small amounts of peroxide (0·20, 0·37, 0·38 mol.); no alkane was evolved. Slow autoxidation thus gives mainly the zinc dialkoxide (I; $R = Et, Bu^n, Bu^t$). The small quantity of peroxide will probably be derived from compounds of type Zn(OR)·O·OR; analysis of the solid product from di-t-butylzinc corresponded to a mixture of $0{\cdot}40Zn(OBu^t)O{\cdot}OBu^t$ and $0{\cdot}60Zn(OBu^t)_2$.

It thus appears that the initial autoxidation product is the peroxide RZn·O·OR, which can react with an excess of oxygen to give $Zn(O{\cdot}OR_2)$ or can be reduced by an excess of dialkyl to give RZn·OR. Further similar reactions will lead to $Zn(OR)_2$ or RO·Zn·O·OR or both.

That alkylperoxyzinc compounds are reduced by dialkylzincs was shown by reaction

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[9] Walling and Buckler, *J. Amer. Chem. Soc.*, 1955, **77**, 6032.

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

[11] Abraham and Davies, *J.*, 1959, 429.

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

[13] Hock, Kropf, and Ernst, *Angew. Chem.*, 1959, **71**, 541.

[14] Abraham, Davies, Llewellyn, and Thain, *Analyt. Chim. Acta*, 1957, **17**, 499.

of diethylzinc with $Zn(O{\cdot}OEt)_2$. The product was not peroxidic, but on hydrolysis gave ethyl alcohol in 94% yield based on the reaction

$$Zn(O{\cdot}OEt)_2 + Et_2Zn \longrightarrow 2Zn(OEt)_2$$

From a similar experiment, using di-n-butylzinc and $Zn(O{\cdot}OBu^n)_2$, were obtained 0·2 mol. of peroxide and 2·44 mol. of the alcohol. The reduction process is thus adequately confirmed.

Hydrolysis of the Autoxidation Products.—Alcohols obtained by hydrolysis of the dialkoxides (I; R = Et, Bu^n) were identified both chromatographically and as the 3,5-dinitrobenzoates, but n-butyl hydroperoxide from dibutylperoxyzinc only by its physical constants. (Attempts to prepare diperterephthalates from ethyl and n-butyl hydroperoxides were not successful.) However, autoxidation of di-t-butylzinc on a large scale gave a mixture of $0{\cdot}18Zn(OBu^t)_2$ and $0{\cdot}82Bu^tO{\cdot}Zn{\cdot}O{\cdot}OBu^t$; on hydrolysis, this mixture gave t-butyl hydroperoxide, identified as the triphenylmethyl derivative (0·66 mol.) and as t-butyl 3,5-dinitroperbenzoate. The presence of a peroxide bond in the peroxidic autoxidation product is thus confirmed.

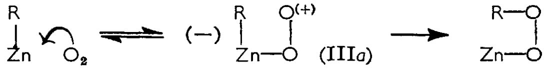
Reaction of Diethylzinc with Alcohols and with Hydroperoxides.—The dialkyl, when hydrolysed with n-butyl alcohol or ethyl alcohol, evolved ethane (2·0 mol.) to give products resembling those from the slow autoxidations. Hydrolysis with t-butyl hydroperoxide (see ref. 12) resulted in reduction of some peroxide (0·29 mol.) and evolution of ethane (1·7 mol.). The peroxidic product closely resembled the products of rapid autoxidation in being a white non-volatile solid, insoluble in aprotic solvents. Additional evidence for the structure of the products of autoxidation is thus provided.

Comparison with Previous Work.—Our results suggest that, in the conditions used by Frankland and Duppa [2,5] and by Meyer and Demuth,[6] the autoxidation of diethylzinc would give a mixture of $Zn(OEt)_2$ and $Zn(OEt){\cdot}O{\cdot}OEt$, and the results obtained by these workers are in agreement with formation of such compounds. (We cannot explain Lissenko's observation that $EtZn{\cdot}OEt$ is the final product.) The peroxidic products obtained by Hock and Ernst (see above) no doubt contain mainly the species $ClZn{\cdot}O{\cdot}OBu^n$ and $Zn(O{\cdot}OBu^n)_2$ respectively.

The nature of the solid products of vapour-phase autoxidation of diethylzinc [8] is not clear, but their probable structures are $EtZn{\cdot}OEt$ and $EtZn{\cdot}O{\cdot}OEt$, the autoxidation now going only to the first stage.

Mechanism of Autoxidation.—Bamford and Newitt [8] suggested that vapour-phase autoxidation of diethylzinc was a chain process. We consider an energy chain unlikely to occur in solution, and a free-radical chain appears improbable in view of the lack of inhibition of the autoxidation by free-radical inhibitors (see Table).

The mechanism of autoxidation of alkylmagnesiums and alkylborons has already been pictured as a co-ordination of oxygen to the metal atom,[9] synchronous with, or followed by, a 1,3-shift of an alkyl group from metal to oxygen.[11] The latter case would lead to the sequence:



We regard a mechanism of this type to be probable for autoxidation of alkylzinc compounds and also of many other organometallic compounds (see refs. 9, 13, 15).

Coates,[16] however, suggests that, as zinc dihalides, which are not autoxidised, form stronger complexes with amines and ethers than do the easily-autoxidised dialkylzincs, co-ordination of oxygen to the metal cannot be a factor in the autoxidation. We suggest that, although oxygen can co-ordinate both to zinc dihalides and to dialkylzincs, a halogen

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[15] Abraham, Ph.D. Thesis, London, 1957.

[16] Coates, "Organo-metallic Compounds," Methuen, London, 1956, p. 39.

atom, unlike an alkyl group, will not migrate readily to the (electrophilic) oxygen; thus (III*b*), although possibly formed more easily than (III*a*), can only revert to its progenitors:

(III*b*)

Both the course and the nature of the autoxidation of dialkylzincs therefore resemble those of other organometallic compounds.

EXPERIMENTAL

Diethylzinc.—This was prepared by Noller's method [17] and redistilled, under nitrogen, at 118°.

Di-n-butylzinc.—The product from n-butylmagnesium chloride and zinc chloride in ether was distilled from an oil-bath (up to 150°) at 1 mm., and the distillate redistilled to give the dialkyl, b. p. 82°/9 mm., in 57% yield (Found: Zn, 36·7. Calc. for $C_8H_{18}Zn$: Zn, 36·4%).

Di-t-butylzinc.—The product from t-butylmagnesium chloride and zinc chloride in ether was filtered under nitrogen, and the filtrate distilled to give di-t-butylzinc, b. p. 34—35°/9 mm., m. p. *ca.* 25°. Much of the dialkyl volatilised with the ether and was collected as an ethereal solution in a cold trap. Neither this solution nor the dialkyl contained magnesium or chloride ion.

Preparation of Ampoules.—The dialkyls were distilled into a receiver fitted with numerous small side-arms, manipulated into these side-arms, and sealed under nitrogen. Some diethylzinc was also stored under nitrogen as a solution in anisole and in xylene.

Autoxidations.—Solutions of the dialkyls were introduced into a gas-burette by use of a hypodermic syringe and a self-sealing cap. Small ampoules were crushed by a method previously described; [11] larger ones were broken under ether.

Analyses.—Methods already described [14] were used to analyse samples by gas–liquid chromatography; peroxides were also estimated iodometrically. Zinc and magnesium were determined as follows: the sample was added to 3N-sulphuric acid, and the mixture boiled to remove organic material and then made up to a standard volume with distilled water. Aliquot parts were added to M/100-EDTA and back-titrated against M/100-zinc sulphate at pH 10, Eriochrome Black T being used as indicator. This procedure [18] estimates the combined zinc and magnesium content. If the above titration is carried out at pH 4·5 in a solvent of " 50% aqueous ethanol " and with dithizone indicator, only zinc is determined, and thus both zinc and magnesium could be estimated in the same solution.[19]

Solutions of Grignard reagents were standardised very conveniently by the first procedure (at pH 10).

Autoxidation of Diethylzinc.—(i) *Slow autoxidation.* The dialkyl, in dry anisole, was allowed to absorb oxygen for six weeks. The mixture was hydrolysed with a few drops of 3N-sulphuric acid, and examination of the anisole by gas–liquid chromatography showed it to contain 1·74 mol. of ethyl alcohol; 0·2 mol. of peroxide was also found.

(ii) *Rapid autoxidation.* An ampoule of the dialkyl (0·1335 g.) was crushed under dry ether (40 ml.) through which oxygen was passed for 5 hr. A white precipitate of *diethylperoxyzinc* began to appear after about 5 min. and was filtered off, washed with dry ether, and dried [Found: Zn, 35·0; peroxidic O, 33·1. $Zn(O{\cdot}O{\cdot}C_2H_5)_2$ requires Zn, 34·8; peroxidic O, 34·1%].

In similar experiments, both with ether and with benzene as a solvent, the final mixture, on hydrolysis, gave 1·93 mol. of peroxide (iodometrically).

(iii) *Reduction of diethylperoxyzinc by diethylzinc.* Diethylzinc was autoxidised as in (ii), the system flushed with dry nitrogen, and an excess of the dialkyl added. The mixture was stirred for 20 hr. and hydrolysed as in (i). Chromatography showed the ether to contain 3·76 mol. of ethyl alcohol, which was also identified as the 3,5-dinitrobenzoate, m. p. and mixed m. p. 84°.

(iv) *Autoxidation in xylene.* Solutions of diethylzinc (0·025 g.) in dry xylene (2·65 ml.) were

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[17] Noller, *Org. Synth.*, Coll. Vol. II, 1950, p. 184.

[18] Schwartzenbach, " Complexometric Titrations," Methuen, London, 1957, pp. 62, 83.

[19] Personal Communication from Mr. J. A. R. Genge and Dr. J. P. Redfern.

added to xylene (50 ml.) stirred in a gas burette under dry oxygen. The Table shows the absorption of oxygen and the peroxidic content of the final product when the autoxidation was carried out in presence of various inhibitors.

Autoxidation of diethylzinc.

Mol. of oxygen absorbed in:			Mol. of peroxide	Inhibitor
10 min.	90 min.	1200 min.		
1·52	1·65	1·72	1·47	—
1·53	1·64	1·72	1·48	0·2 g. Methyl methacrylate
1·41	1·61	1·73	1·58	0·02 g. *m*-Dinitrobenzene
1·44	1·62	1·76	1·53	0·2 g. Pyridine
1·80	—	1·98	1·92	[a]

[a] The solution was squirted into the gas-burette containing only oxygen and stirred rapidly. The blank correction was obtained by using dry boiled-out xylene (2·65 ml.) in the same way.

Autoxidation of Di-n-butylzinc.—(i) *Slow autoxidation.* The dialkyl in dry ether was allowed to absorb oxygen slowly for two weeks, by which time a large white precipitate had collected. The mixture was shaken with 3N-sulphuric acid, and the ethereal layer then shown chromatographically to contain 0·37 mol. of n-butyl hydroperoxide and 1·55 mol. of n-butyl alcohol. The latter was also identified as n-butyl 3,5-dinitrobenzoate, m. p. and mixed m. p. 62—63°.

(ii) *Rapid autoxidation.* An ampoule of the dialkyl (0·2336 g.) was crushed under dry ether (40 ml.) through which oxygen was passed for 8 hr. The white precipitate of *di-n-butylperoxyzinc* was filtered off, washed with dry ether, and dried [Found: Zn, 26·9; peroxidic O, 25·5. $Zn(O{\cdot}O{\cdot}C_4H_9)_2$ requires Zn, 26·8; peroxidic O, 26·3%].

In another similar experiment on a larger scale, the autoxidised mixture was shaken with 3N-sulphuric acid, and the ethereal layer found to contain 1·96 mol. of peroxide (iodometrically). After evaporation of the ether, chromatography of the residue showed only n-butyl hydroperoxide (2·00 mol.) and a trace of ether to be present.

(iii) *Large-scale autoxidation.* Di-n-butylzinc (2·37 g.) was autoxidised in ether, the mixture hydrolysed as in (ii), and the ethereal layer shown to contain 1·65 mol. of n-butyl hydroperoxide and 0·30 mol. of the alcohol (chromatographically). Distillation afforded the hydroperoxide (1·57 g., 1·32 mol.), b. p. 39—40°/8 mm., n_D^{20} 1·4063, n_D^{25} 1·4042 (Found: C, 54·7; H, 11·4; peroxidic O, 31·2. Calc. for $C_4H_{10}O_2$: C, 53·3; H, 11·2; peroxidic O, 35·5%).

(iv) *Reduction of di-n-butylperoxyzinc by di-n-butylzinc.* The dialkyl was autoxidised as in (ii), the system flushed with nitrogen, and an excess of fresh dialkyl added. The mixture was stirred overnight, then hydrolysed with 3N-sulphuric acid, and the ethereal layer shown to contain 0·20 mol. of peroxide (iodometrically) and 2·44 mol. of n-butyl alcohol (3,5-dinitrobenzoate, m. p. and mixed m. p. 61—62°).

Autoxidation of Di-t-butylzinc.—(i) *Isolation of t-butyl hydroperoxide.* The dialkyl (16·3 g.) in dry ether (500 ml.) was added quickly to ether continuously saturated with oxygen. After 12 hr. the white solid which had been formed was filtered off, washed with dry ether, and dried in a vacuum (Found: wt., 20·4 g.; Zn, 29·25; peroxidic O, 10·8. Calc. for following reaction: wt., 20·4 g.; Zn, 29·1; peroxidic O, 11·6%):

$$Bu^t_2Zn + 1{\cdot}41O_2 \longrightarrow 0{\cdot}82Zn(OBu^t){\cdot}O{\cdot}OBu^t + 0{\cdot}18Zn(OBu^t)_2$$

On hydrolysis, the white solid gave t-butyl hydroperoxide (0·67 mol. iodometrically), identified and estimated (0·66 mol.) as the triphenylmethyl derivative (m. p. and mixed m. p. 71—71·5°) and also identified as the 3,5-dinitroperbenzoate (m. p. and mixed m. p. 92—92·5°).

(ii) *Slow autoxidation.* The dialkyl (2·29 g.) in dry ether was allowed to absorb oxygen slowly for 4 weeks, by which time an off-white precipitate had been formed; this was filtered off and dried (Found: wt., 2·71 g.; Zn, 30·1; peroxidic O, 5·7. Calc. on the following reaction: wt., 2·78; Zn, 30·0; peroxidic O, 5·9%).

$$Bu^t_2Zn + 1{\cdot}20O_2 \longrightarrow 0{\cdot}40Zn(OBu^t){\cdot}O{\cdot}OBu^t + 0{\cdot}60Zn(OBu^t)_2$$

Hydrolysis of the solid afforded t-butyl hydroperoxide (0·38 mol., chromatographically).

Reactions of Diethylzinc.—(i) *With ethyl alcohol.* An ampoule of the dialkyl (0·2713 g.), crushed under a mixture of anisole (7 ml.) and ethyl alcohol 0·35 ml.), evolved 2·0 mol. of gas to give an off-white precipitate. The blank correction was obtained by a similar hydrolysis by using anisole (7 ml.) and a few drops of 3N-sulphuric acid. A similar result was obtained on using n-butyl alcohol instead of the ethyl alcohol.

(ii) *With t-butyl hydroperoxide.* A similar experiment was performed with the hydroperoxide (0·51 g.) instead of the alcohol. Evolution of gas was only 1·7 mol., and 0·29 mol. of the peroxide was reduced (estimated iodometrically). The product was again an off-white precipitate.

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