

SOME REACTIONS OF ORGANOTIN COMPOUNDS WITH METAL-METAL BONDS

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Abstract—On irradiation by ultraviolet light as well as by the action of AlCl_3 , Et_4Sn and Et_3Sn , form dark-red polymeric organotin compounds. These compounds are decomposed at 200° , evolving gases, tetraethyltin and tin, are very easily oxidized by air and react with benzoyl peroxide and with CCl_4 in the presence of traces of air at normal temperatures, i.e. take part in reactions characteristic of alkyl derivatives having Sn-Sn bonds.

The study of the products of the interaction between the compounds thus obtained and benzoyl peroxide proves their branched structure.

It has been shown¹ that organometallic compounds will undergo cleavage of the carbon-metal bond on photolysis or thermal decomposition, the reaction producing metal as well as free radicals. In the liquid phase or in solutions this process is complicated by the subsequent reactions. If the metals are bonded with a number of substituents then the decomposition may take place with the successive abstraction of certain radicals and further formation of metal-containing intermediates, for example²⁻⁴:



Because of the lability of the lead-containing intermediates and the difficulty of isolating these in a pure state, we have studied this type of reaction using the ethyl derivatives of tin, which are considerably more stable. The gradual elimination of radicals from the molecules being decomposed served to bring about the formation of polymeric organotin compounds.

Thus, on photolysis of tetraethyltin, ethane, ethylene and butane are formed. On irradiation, the colour of the starting material changed gradually from yellow to red, and finally to an intense cherry-red. It was only after this stage that the liberation of metallic tin took place. The residue after vacuum distillation of the unreacted tetraethyltin is a viscous dark-red substance.

The same sequence of colour change and liberation of metal is observed during the irradiation of hexaethylditin, when evolution of gaseous hydrocarbons also takes place.

The above evidence lends support to the idea that the intensely coloured viscous photolysis products are complex polymeric compounds with tin-tin bonds. Substances of this type are rather stable if there is no access to air, but they decompose at 200° , forming gaseous hydrocarbons, tin and tetraethyltin. They are extremely

¹ E. W. R. Steacie, *Atomic and Free Radical Reactions* (2nd edition) Vol. 1., pp. 244-249, 392-395. Reinhold, New York (1954).

² G. A. Razuvaev, N. S. Vyazankin and N. N. Vyshynskii, *Zh. Obshch. Khim.* **29**, 3662 (1959).

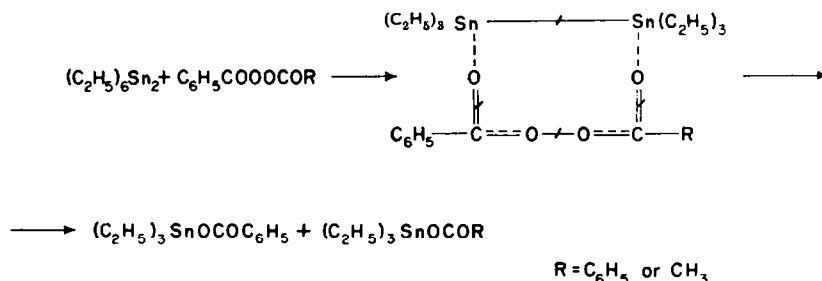
³ G. A. Razuvaev, N. S. Vyazankin and N. N. Vyshynskii, *Zh. Obshch. Khim.* **30**, 967 (1960).

⁴ G. A. Razuvaev, N. S. Vyazankin and N. N. Vyshynskii, *Zh. Obshch. Khim.* **30**, 4099 (1960).

sensitive to oxygen, rapid oxidation being followed by the disappearance of colour. Absence of unshared electrons in the coloured compounds is proved by EPR studies.

Similar complex intensely coloured organotin compounds can also be obtained by the disproportionation of hexaethylditin under mild conditions of temperature in the presence of catalytic quantities of anhydrous aluminum chloride.^{5,6}

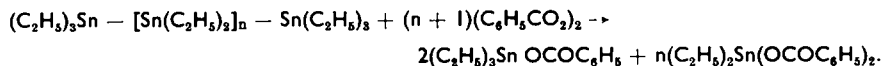
In order to investigate the structure of the coloured organotin compounds under discussion, we studied their interaction with benzoyl peroxide. Our earlier studies have revealed⁷ that hexaethylditin reacts with benzoyl peroxide and acetyl benzoyl peroxide in benzene at normal temperature with the cleavage of the metal-metal bond. The fact that quantitative yields of products are obtained and no carbon dioxide is evolved suggests that these reactions involve an intermediate cyclic complex.



Other cyclic schemes including 4 or 6 atoms in a cycle are also quite possible.

The coloured compounds which are obtained are found to react readily with benzoyl peroxide in benzene solution at room temperature, with loss of colour. As observed with hexaethylditin, these reactions are not accompanied by formation of gaseous hydrocarbons, ethyl benzoate, or evolution of CO_2 . This suggests that in the course of the reactions under discussion only the Sn—Sn bonds in the polymer and the O—O bonds in the peroxide are cleaved. The polymer obtained by heating hexaethylditin with AlCl_3 forms the following products on reaction with benzoyl peroxide: (1) triethyltin benzoate, (2) diethyltin dibenzoate, (3) ethyltin tribenzoate and (4) metallic tin.

If the polymer had been of linear type only the formation of triethyltin benzoate and diethyltin dibenzoate would have been expected as long as the disproportionation of diethyltin dibenzoate into triethyltin benzoate and ethyltin tribenzoate does not occur:



The formation of ethyltin tribenzoate provides evidence for the presence of branched chains with Sn atoms in the polymer. However, one may assume the presence of divalent atoms of tin in the reaction mixture, which can give di- or tri-benzoates when combined with benzoyl peroxide.

⁵ G. A. Razuvaev, N. S. Vyazankin, Yu. I. Dergunov and O. S. D'yachkovskaya, *Dokl. Akad. Nauk S.S.S.R.* **132**, 364 (1960).

⁶ G. A. Razuvaev, N. S. Vyazankin, Yu. I. Dergunov and N. N. Vyshynskii, *Zh. Obshch. Khim.* **31**, 1712 (1961).

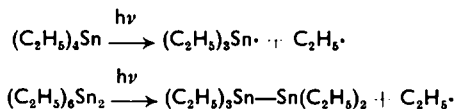
⁷ G. A. Razuvaev, N. S. Vyazankin and O. A. Shchepetkova, *Zh. Obshch. Khim.* **30**, 2498 (1960).

At any rate, the results obtained suggest that the coloured substance under investigation consists of complex molecules with branched Sn—Sn bonds. This structure conforms to our previously developed ideas on the course of disproportionation of hexaethyldilead⁸ and hexaethylditin.⁵ The formation of triethyltin benzoate and diethyltin dibenzoate was stated by us as occurring in the interaction between benzoyl peroxide with polymer, the latter having been obtained by photolysis of tetraethyltin and hexaethylditin.

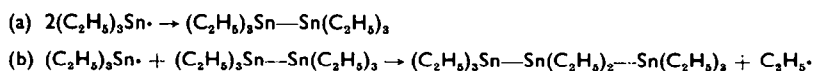
In the second case, 21.6 per cent of tin atoms in the reaction mixture became diethyltin dibenzoate. There was no indication of the presence of ethyltin tribenzoate in the products of the reaction under discussion, which indicates the absence or low degree of branching of metal atom chains in polymers obtained by photolysis.

It is worth emphasizing that the unirradiated tetraethyltin does not react with benzoyl peroxide at normal temperature.

The formation of polymeric organotin compounds upon ultraviolet irradiation of tetraethyltin or hexaethylditin can be explained by a number of subsequently occurring processes of rupture of the Sn—C bond and formation of a more stable Sn—Sn bond:

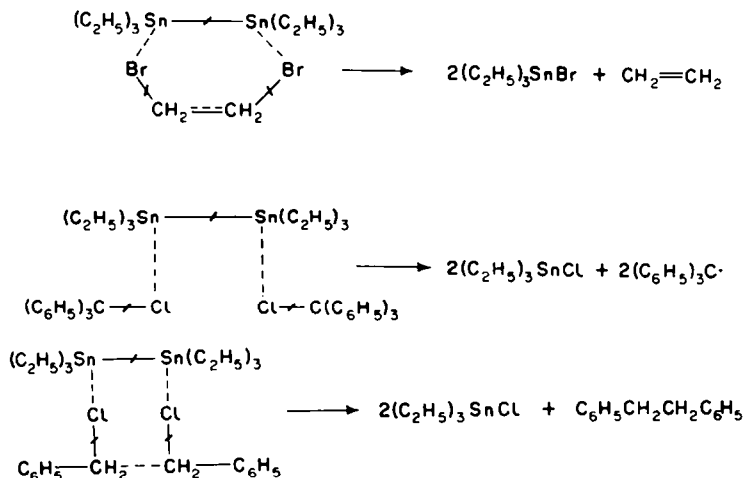


Reactions may then follow involving (a) the combination of organotin radicals or (b) the displacement ethyl radicals by them, as shown:



It is by this process that branched structures may be produced.

Hexaethylditin is known to react with dibromoethane, triphenylchloromethane and benzyl chloride:⁹



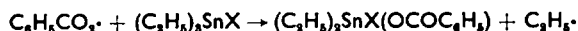
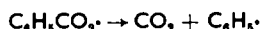
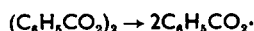
⁸ G. A. Razuvaev, N. S. Vyazankin and Yu. I. Dergunov, *Zh. Obsh. Khim.* **30**, 1310 (1960).

⁹ G. A. Razuvaev, N. S. Vyazankin, Yu. I. Dergunov and M. N. Pinchuk, *Zh. Vsesoyuz. Khim. Obshchestva im. D. I. Mendeleeva*, **5**, 707 (1960).

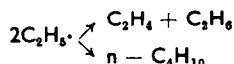
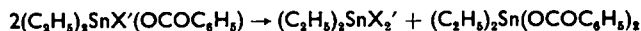
All these processes proceed at rather high temperatures (the second reaction at 100° and the first and third at 180–190°), but not at all sufficient for decomposition of hexaethylditin. It is of definite interest to compare the above reactions with the interaction between Et_6Sn_2 and CCl_4 taking place in the presence of benzoyl peroxide or oxygen, but at room temperature. Thus, a noticeable amount of triethyltin chloride is formed on air oxidation of hexaethylditin in CCl_4 solution at ordinary temperature. A polymeric compound obtained by heating of hexaethylditin with addition of AlCl_3 proved to possess greater reactivity. There is no indication of its interacting with CCl_4 in the absence of oxygen, but if a very small amount of air is let into the reaction flask a reaction begins with formation of triethyltin chloride and dichlorodiethyltin.

From the above data it follows that the reactivity of the Sn—Sn bond in polymeric compounds is higher than the one in hexaethylditin.

So far as Et_4Sn and Et_3SnX compounds which interact with acyl peroxides according to a free-radical mechanism are concerned, changing of the ethyl group for X does not affect the course of the process. The products formed in the decomposition of benzoyl peroxide in Et_4Sn and Et_3SnX (Table 1) may be accounted for by the following series of reactions:



$(\text{C}_2\text{H}_5)_2\text{SnX}'(\text{OCOC}_6\text{H}_5)$ when $\text{X}' = \text{Cl}$ or Br was not obtained in a pure form. The products of its disproportionation were isolated from the reaction mixture:



EXPERIMENTAL

Photochemical decomposition of tetraethyltin. Tetraethyltin 23.5 g (0.1 mole) was placed in a quartz tube (A) which was connected by means of vacuum-rubber with (B) (Fig. 1). The apparatus was evacuated, the tube being cooled in an ice bath, and then sealed in (C).

Upon U.V. irradiation (the lamp used was PRK-7, the distance to the source was equal to 7–10 cm, exposure about 30–35 hr), tetraethyltin acquired a cherry-red colour. After this, the reaction mixture was poured into compartment (D) shielded from U.V. rays, and the unreacted tetraethyltin was distilled from the polymeric product into tube (A), cooled by liquid nitrogen.

The operations described above—photolysis of tetraethyltin, pouring of the reaction mixture into compartment (D) and recondensation of tetraethyltin from compartment (D) into tube (A)—were repeated 8 times. Then the distilled tetraethyltin was frozen by using liquid nitrogen in tube (A) and compartment (D) was sealed at its narrowest place (E). Formation of a gaseous mixture containing 86.3% of ethane, 11.9% of ethylene and 1.8% of butane was shown by chromatographic analysis.

For quantitative calculation of the accumulated polymeric product, the latter was transferred from compartment (D) into ampoule (F), which was sealed at (G) after additional evacuation. Ampoule (F) was thermostated at 220° (16 hr) until its contents became colourless. Then 0.32 g of metallic tin and 27 ml of gaseous mixture—the composition of the latter has not been investigated—were obtained.

TABLE 1. REACTION OF BENZOYL PEROXIDE (Bz_2O_2) WITH Et_4Sn AND Et_3SnX^* IN THE ABSENCE OF ATMOSPHERIC OXYGEN

Reagents taken in moles	Temp.	Time hr	Reaction products (in moles per mole peroxide)					
			CO_2	C_2H_6	C_3H_8	C_4H_{10}	Other products	
0.010 Bz_2O_2 ; 0.20 Et_4Sn	95–97°	16	0.20	0.26	0.55	0.02	0.66 $\text{Et}_3\text{SnOCOPh}$; 0.37 $\text{Et}_3\text{Sn(OCOPh)}_2$	
0.015 Bz_2O_2 ; 0.15 Et_3SnCl	95–97°	16	0.14	0.45	0.37	0.01	0.76 $\text{Et}_3\text{Sn(OCOPh)}_2$; 0.63 Et_3SnCl_2	
0.015 Bz_2O_2 ; 0.16 Et_3SnBr	95–97°	16	0.15	0.44	0.24	0.01	0.71 $\text{Et}_3\text{Sn(OCOPh)}_2$; 0.50 Et_3SnBr_2	
0.010 Bz_2O_2 ; 0.044 $\text{Et}_3\text{SnOCOPh}$	95–97°	16	0.06	0.29	0.16	—	0.50 $\text{Et}_3\text{Sn(OCOPh)}_2$; 0.29 PhCOOEt	

* X = Cl, Br or PhCO_2

Hence, on a single photolysis of tetraethyltin till it became dark cherry-red there formed a polymer, upon thermodecomposition of which 0.34% of tin (initially Et_4Sn) was formed.

When unirradiated tetraethyltin was kept at 220° for many days there was no indication of metal formation.

It was also established that the polymer thus obtained does not initiate the decomposition of pure tetraethyltin at 220° .

Photolysis of hexaethylditin. Hexaethylditin 16.5 g (0.04 mole) of free of oxidation products was distilled in a stream of purified hydrogen at $160\text{--}161^\circ$ and 23 mm from a Claisen flask into a quartz tube (A) fitted with (B) (Fig. 2). On finishing the distillation, the vacuum was increased to 1–1.5 mm, the left part of the apparatus being sealed in (C) and (D).

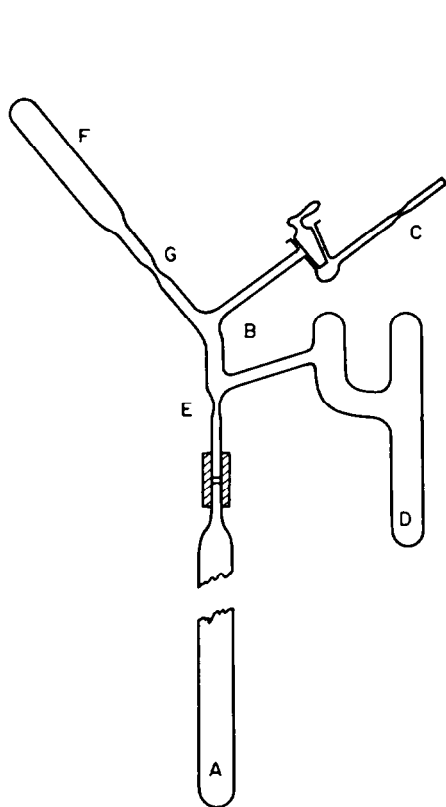


FIG. 1.

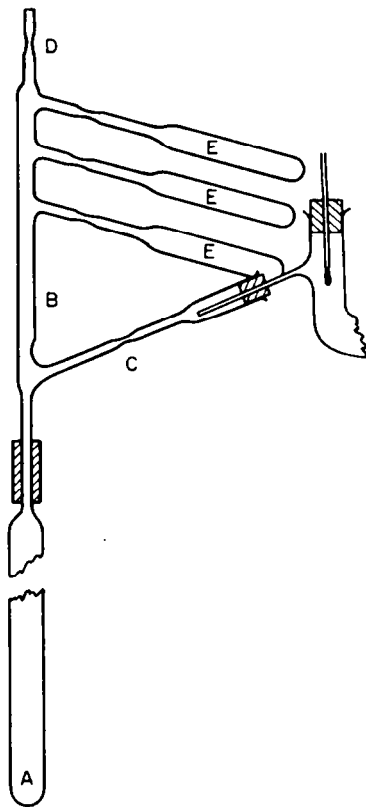


FIG. 2.

After 80 hr of irradiation, the cherry-red reaction mixture was poured into ampoules (E) which were sealed at the narrowest places, tube (A) being cooled by liquid nitrogen. From tube (A; after refrigerating) 260 ml of gaseous mixture was obtained, containing 54.7% of ethane, 36.8% of ethylene and 8.5% of butane. By EPR methods the absence of single electrons in the polymeric product was shown.

When the ampoules (E) were heated to $220\text{--}230^\circ$ (for 16 hr) the polymer was decomposed completely. Based on the amount of the metal formed, at least 23.2% of the total tin (previously in hexaethylditin) was present in the polymeric product after irradiation, this fact conforming to the yield of gaseous products of photolysis. The unirradiated hexaethylditin is known to begin decomposing at 260° .

Interaction of benzoyl peroxide with the polymer formed by disproportionation of hexaethylditin. Into section (A) of the apparatus (Fig. 3) was placed 6.87 g of hexaethylditin and 0.14 g (2.0% by

weight) of anhydrous AlCl_3 ; into section (B) was introduced the solution of 4.04 g of benzoyl peroxide in 20 ml of dry benzene. In the usual way the apparatus was evacuated and sealed at (C). The contents of section (A) were thermostated at 70° until traces of metallic tin appeared in the resulting polymeric mass.

The mixture was cooled, the valve (D) was opened, and the solution of peroxide was poured into section (A). The polymer gradually dissolved with decoloration of the solution and precipitation of the colourless crystalline substance. In the course of the described process, metallic tin separated from the polymer.

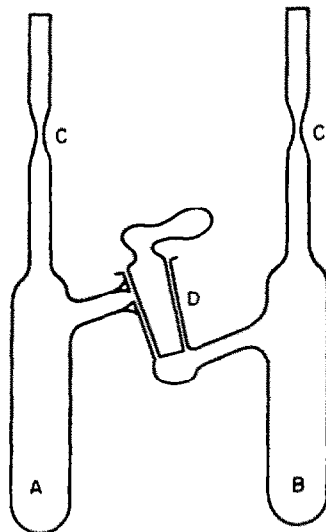


FIG. 3.

After 24 hr the crystalline precipitate was separated from the metallic tin (taking advantage of differences in rates of precipitation) and filtered. The crystals were washed with 3 portions of dry hot benzene. 1.69 g of ethyltin tribenzoate was obtained. The m.p. varied from 185 – 188° . (Found: C, 54.34; H, 3.94; Sn, 21.66. Calc. for $\text{C}_{23}\text{H}_{20}\text{SnO}_6$: C, 54.05; H, 3.95; Sn, 21.82%).

The substance was slightly soluble in hot benzene, toluene and methylethylketone. During attempts to recrystallize it from solvents containing water, it was hydrolyzed with formation of benzoic acid.

The metallic tin, purified by treatment with hot benzene and acetone washing, weighed 0.4 g. The mother liquor was combined with benzoic extracts, and the benzene and 2.43 g of tetraethyltin contaminated with triethyltin chloride were distilled under red press, b.p. 175 – 190° (755 mm); n_D^{20} 1.4790.

The remaining crystalline mass was transferred into a flask fitted with a sabre-formed outlet tube, and the mixture of triethyltin benzoate and diethyltin dibenzoate was isolated by distillation, b.p. 130 – 168° at 1 mm. After distillation of the mixture, tarry products (0.8 g) were obtained. By fractional crystallization of the mixture from *n*-hexane 0.99 g of diethyltin dibenzoate, m.p. 120 – 123° , was obtained. (Found: C, 51.89; H, 4.94; Sn, 27.92. Calc. for $\text{C}_{18}\text{H}_{20}\text{SnO}_4$: C, 51.59; H, 4.81; Sn, 28.32%).

In order to determine the yield of poorly-crystallized triethyltin benzoate (m.p. of the substance and mixed sample 79 – 80°), it was converted into triethyltin acetate. For this purpose the mother liquors were processed with a 10% solution of caustic soda. The organic layer was separated, and the aqueous layer extracted with ether. The extract was combined with the organic layer and 0.5 ml of glacial acetic acid was added. During slow evaporation 0.90 g of triethyltin acetate was crystallized, m.p. 131 – 133° . No depression of the m.p. was caused by mixing with the pure substance.

No ethane, ethylene, carbon dioxide or ethylbenzoate were found in the products of reaction.

Action of benzoyl peroxide on the polymer obtained by photolysis of hexaethyliditin. In an evacuated assembly representing a combination of the apparatus shown in Fig. 2 and Fig. 3, 5.59 g hexaethyliditin

was irradiated during 100 hr. A solution of 5.50 g benzoyl peroxide free from atmospheric oxygen in 20 ml benzene was added to the dark cherry-red reaction mixture. After 24 hr the colourless reaction mixture was filtered from the insoluble precipitate (0.1 g) and analysed by the method used in the previous experiment, 4.12 g of diethyltin dibenzoate was obtained, yield 21.6%, m.p. 122–123° (from hexane). No depression of the m.p. was caused by mixing with the pure substance. In order to determine the yield of triethyltin benzoate, it was converted into triethyltin acetate, m.p. and mixed m.p. was 132°, yield, 7.64 g. Hence, about 61.8% of triethyltin benzoate was obtained. No ethyltin tribenzoate was observed in the reaction mixture.

Air-initiated reaction between the organotin polymer and CCl_4 . In the evacuated assembly (Fig. 3) a polymer was obtained by heating 4.73 g hexaethylditin in the presence of 2 wt % of AlCl_3 (4 hr at 70°). To the polymer from section (B) was added 9.20 g dry CCl_4 (free from atmospheric oxygen), and the mixture was allowed to stand at room temp. for 3 days. No changes occurred in the polymeric mass.

Valve (D) was closed, section (B) was opened and a moderate vacuum (200 mm) was created, after which it was sealed again. Valve (D) was opened, and under the influence of the entering air the polymeric mass dissolved in CCl_4 completely in 24 hr with a diminution of the colour intensity of the solution. After the air was introduced repeatedly, the solution became pale pink. Section (A) was opened and the reaction mixture allowed to come in contact with the air for another period of 24 hr. In this way, 4.13 g triethyltin chloride was isolated by fractional distillation, yield 74.4%, b.p. 202–207°; n_D^{20} 1.5057 (lit.¹⁰ b.p. 206° at 760 mm; n_D^{20} 1.5055). In addition, 0.14 g diethyltin dichloride was obtained, m.p. 82–83°. No depression of the m.p. was caused by mixing of the sample with the pure substance.

Reaction between hexaethylditin and CCl_4 in the presence of air. In a 10 ml ampoule 7.52 g hexaethylditin was dissolved in 5 ml CCl_4 . After 2 hr the ampoule was sealed without evacuation and allowed to stand for 24 hr. Then the ampoule was opened again for 2 hr, again sealed and allowed to stand for 24 hr, after which period it was opened and maintained overnight. By fractional distillation in vacuum 4.34 g of the unreacted hexaethylditin was obtained, b.p. 157–161° at 23 mm; n_D^{20} 1.5413 (lit.¹¹ b.p. 161–163° at 23 mm). In addition 0.70 g triethyltin chloride was obtained, b.p. 100–108° at 16 mm; n_D^{20} 1.5063 and identified as triethyltin acetate, m.p. 132–133° (from heptane) without causing depression of m.p. of the mixed sample. The yield of Et_3SnCl based on reacted hexaethylditin was 18.6%.

Interaction of benzoyl peroxide with Et_3Sn and Et_3SnX when $\text{X} = \text{Cl}$, Br or $\text{C}_6\text{H}_5\text{COO}$. Reactions of this type were carried out in a round-bottomed flask sealed to a reflux condenser. The flask had a side entrance for admitting reagents and nitrogen. The other end of the condenser was subsequently connected with carbon dioxide absorbers filled with 30% solution of KOH and a gas burette.

After the initial substances were introduced the assembly was flushed with purified nitrogen, and the side entrance was sealed. Then the reaction mixture was heated to 60–70° on a water bath and periodically shaken until the peroxide dissolved completely. After this the temp. of the bath was increased till the reaction began (80–100°). The amount of CO_2 separated was determined by weighing the absorbers. Gaseous hydrocarbons were collected in the burette and analysed by the chromatographic method. Identification of the other products is described below.

Reaction of benzoyl peroxide with triethyltin chloride. A solution of benzoyl peroxide (0.015 mole) in triethyltin chloride (0.15 mole) was heated for 16 hr at 95–97°. The liquid portion of the reaction mixture was fractionated *in vacuo* and the mixture of Et_3SnCl and Et_2SnCl_2 , b.p. 98–108° at 15 mm, separated. To determine the yield of diethyltin dichloride (m.p. of the purified product and mixed sample 82–83°), the fraction was treated with an alcoholic solution of ammonia. In this way, 0.63 mole of infusible and insoluble diethyltin oxide (per 1 mole of decomposed peroxide) was obtained. After distillation of chlorides the crystalline residue was placed in a flask with a sabre-formed outlet tube and distilled at 1 mm, at 150–250° (temp. of bath) 0.76 mole of diethyltin dibenzoate was distilled m.p. 122–124° (from hexane). (Found: C, 51.80; H, 5.18; Sn, 27.87. Calc. for $\text{C}_{18}\text{H}_{18}\text{SnO}_4$: C, 51.59; H, 4.81; Sn, 28.32%).

The other reactions of this type were carried out in a similar way. The results of the experiments are shown in Table 1.

¹⁰ C. R. Dillard, E. H. McNeill, D. E. Simmons and J. B. Yeldell, *J. Amer. Chem. Soc.*, **80**, 3607 (1958).

¹¹ A. N. Nesmeyanov, K. A. Kocheshkov and V. P. Puzyreva, *Zh. Obsh. Khim.* **7**, 118 (1937).