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REACTION OF BENZOYL PEROXIDE WITH ALLYLTRIMETHYLTIN (1)

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Decomposition of benzoyl peroxide in allyltrimethyltin affords allyl benzoate and trimethyltin benzoate. Kinetic investigation shows that the reaction mainly proceeds through the cyclic transition state. This is the first example of molecular reaction between peroxide and allyltin compound.

Decomposition of benzoyl peroxide (BPO) in allyltrimethyltin at 80°C affords allyl benzoate (60% mole/mole of BPO) and trimethyltin benzoate (100%). This fact might be explained in terms of radical chain mechanisms involving S_H2 or S_H' type, since a number of examples of such reactions has been known.[2,3]

a) S_H2 Mechanism.

$$PhCOOCOPh \longrightarrow 2\ PhCOO\cdot$$

$$PhCOO\cdot + CH_2{=}CHCH_2SnMe_3 \longrightarrow PhCOOSnMe_3 + CH_2{=}CH\dot{C}H_2$$

$$CH_2{=}CHCH_2 + PhCOOOCOPh \longrightarrow CH_2{=}CHCH_2OCOPh + PhCOO\cdot$$

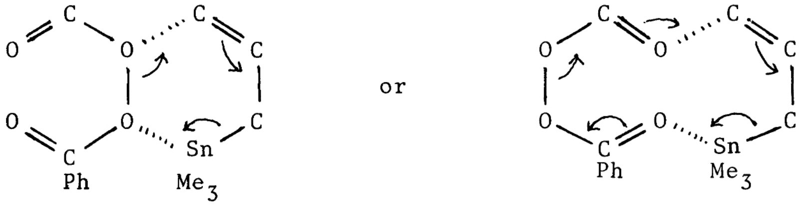
b) S_H' Type Mechanism.

$$PhCOO\cdot + CH_2{=}CHCH_2SnMe_3 \longrightarrow PhCOOCH_2CH{=}CH_2 + Me_3Sn\cdot$$

$$Me_3Sn\cdot + PhCOOOCOPh \longrightarrow Me_3SnOCOPh + PhCOO\cdot$$

However, there are several preliminary observations against these chain mechanisms: 1) Formation of these products were not completely inhibited by the presence of galvinoxyl. 2) No allylbenzene was formed at all even when the reaction was carried out in the system diluted with benzene, which would favor the decomposition of PhCOO· into Ph· and CO_2. 3) With crotyltrimethyltin, only α-methylallyl benzoate was obtained, but not crotyl benzoate. 4) The reaction seemed particularly sluggish, compared the reaction of BPO with hydrostannanes, which had been known to involve the induced decomposition of BPO by stannyl radical.[4]

Another possible mechanism may be the one step reaction involving a cyclic transition state,



though no example of such molecular reaction between peroxide and allyltin compound has been known. Kinetic investigation strongly supported that at least a major part of the reaction proceeds through such a mechanism.

Rate of disappearance of BPO was followed by recording IR spectrum of the reaction mixture, since characteristic absorption at 1789 cm^{-1} of the carbonyl groups of BPO was found not to overlap with the absorptions of any other components. The observed pseudo-first order rate constants shown in Table are represented by the following equation,

$$k_{obs} = k_2[CH_2{=}CHCH_2SnMe_3] + k_1$$

where k_1 was 0.21×10^{-5} (at 60°C) and 2.0×10^{-5} (at 70°C), being in reasonable agreement with the rate constant of the spontaneous decomposition of BPO (0.26×10^{-5} at 60°C, and 1.0×10^{-5} at 70°C).5) From the temperature dependence of k_2, activation enthalpy and entropy of the bimolecular reaction were found to be 17 kcal/mole and -34 e.u., respectively. The large negative value of the activation entropy, being comparable with that of Diels-Alder reaction (-36 e.u.),6) is compatible with the multicenter reaction such as proposed above.

TABLE. Rate Constants for the Reaction of BPO with Allyltrimethyltin in Benzene

Temperature (°C)	BPO (M)	$CH_2{=}CHCH_2SnMe_3$ (M)	$k_{obs} \times 10^5$ (sec^{-1})	$k_2 \times 10^5$ ($M^{-1}sec^{-1}$)
60	0.040	0.502	0.520	
		1.01	1.05	0.74
		2.01	1.67	
70	0.040	0.509	2.76	
		0.999	3.49	1.54
		1.50	4.29	

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