MERCAPTANS AND DISULFIDES AS INHIBITORS OF NON-CHAIN RADIATION INDUCED REACTIONS.[1]

Sir:

The light-induced conversion of benzophenone in 2-propanol to benzopinacol[2] and acetone is a non-chain reaction of quantum yield approximating unity,[3] apparently proceeding *via* an excited triplet state[4] of benzophenone and the radicals I and II:[3]

$$(C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_2C{=}O^* \quad (1)$$

$$(C_6H_5)_2C{=}O^* + (CH_3)_2CHOH \longrightarrow (C_6H_5)_2\dot{C}OH\ I + (CH_3)_2\dot{C}OH\ II \quad (2)$$

$$(C_6H_5)_2C{=}O + II \longrightarrow I + (CH_3)_2C{=}O \quad (3)$$

$$2\ I \longrightarrow (C_6H_5)_2C(OH)\,C(OH)\,(C_6H_5)_2 \quad (4)$$

We have reported[5] that phenyl thiol, 2-mercaptomesitylene and their disulfides lead to marked retardation of this reaction and, at appropriate concentrations, to inhibition. In the retarded reactions, as in the absence of additive, benzopinacol forms from the start of the irradiation, with zero order kinetics to high extents of conversion. In the inhibited reactions there appear to be no definite inhibition periods, the sulfur compounds being effective during prolonged irradiation, each molecule negating the chemical action of many quanta. Spectra of the sulfur compounds in 2-propanol indicate that their absorptions at λ_{max} of benzophenone are too low for the observed effects to be due to absorption of the effective radiation. Also, the efficient mercaptan catalyzed light-initiated decarbonylation of aldehydes[6] indicates that mercaptans may not quench excited states of carbonyl compounds. We have proposed[5] that these sulfur compounds may act repeatedly with the intermediate radicals I and II, regenerating the starting materials and leading to retardation and inhibition.

$$I + ArS{\cdot}(ArSSAr) \longrightarrow (C_6H_5)_2C{=}O + ArSH(ArSH + ArS{\cdot}) \quad (5)$$

$$II + ArSH \longrightarrow (CH_3)_2CHOH + ArS{\cdot} \quad (6)$$

Dependence of the extent of retardation on the concentration of the sulfur compound is summarized in Table I. The percentages of retardation are linear with concentration of additive up to about 80% inhibition, and the thiol and disulfide have equal effectiveness when the values of the disulfide concentration are doubled so that equal concentrations of sulfur moieties may be compared. The initially high effectiveness falls after 80% inhibition and extrapolation indicates full inhibition at about 10^{-2} m./l. of thiyl group.[5]

When solutions of 0.37 m./l. benzophenone and 0.0088 m./l. 2-mercaptomesitylene in 2-propanol were irradiated, rapid partial oxidation to disulfide occurred, levelling off with about 72% of thiyl groups present as mercaptan, the remainder as disulfide (Fig. 1). When solutions of 0.37 m./l. benzophenone and 0.0044 m./l. of mesityl disulfide in 2-propanol were irradiated, reduction of the disulfide occurred rapidly and levelled off at the same concentrations of mercaptan and disulfide. In the inhibited reactions, chemical change occurs and interconversion of mercaptan and disulfide takes place. Benzophenone is needed for this equilibration, since irradiation of disulfide in 2-propanol in the absence of benzophenone leads to only slight reduction to mercaptan (Fig. 1).

TABLE I

RETARDATION OF FORMATION OF BENZOPINACOL: 4 HOURS IRRADIATION 0.5 M./L. BENZOPHENONE IN 2-PROPANOL

Additive Compound	10^3 m./l.	Inhibition, %
None	..	0
Mesityl disulfide	0.25	9
Mesityl disulfide	0.50	17
Mesityl disulfide	1.00	36
Mesityl disulfide	2.00	70
Mesityl disulfide	3.00	89
Mesityl disulfide	4.00	96
2-Mercaptomesitylene	0.52	9
2-Mercaptomesitylene	2.07	35
2-Mercaptomesitylene	3.04	48
2-Mercaptomesitylene	4.00	65
2-Mercaptomesitylene	4.79	80

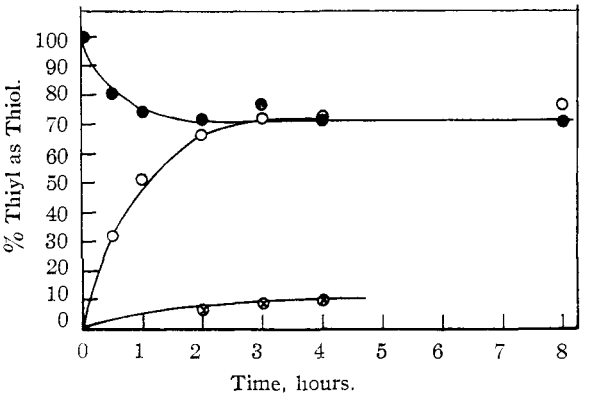

Fig. 1.—Equilibration of 2-mercaptomesitylene and mesityl disulfide, ultraviolet irradiation of 0.375 m./l. benzophenone in 2-propanol: O, 0.0044 m./l. mesityl disulfide; ●, 0.0088 m./l. 2-mercaptomesitylene; ⊗, 0.0044 m./l. mesityl disulfide, no benzophenone.

Irradiation of benzophenone in optically active 2-octanol leads to benzopinacol and to no racemization of the remaining alcohol; irradiation of dimesityl disulfide in 2-octanol leads to no racemization which we can detect. However, irradiation for 29 hours of 0.32 m./l. of benzophenone and 0.033 m./l. of mesityl mercaptan leads to marked retardation of formation of benzopinacol, but to racemization of about 0.44 m./l. of the 2-octanol, α observed falling from 7.97° to 7.40°.

The equilibration of mercaptan and disulfide and the racemization of the alcohol, and the requirement that both benzophenone and sulfur compound be present for these results, indicate that reactions 1, 2, 5 and 6 occur during the inhibited reaction. The benzophenone- and alcohol-derived radicals I and II are formed and the compounds of sulfur in their two valence states reconvert them to benzophenone and 2-propanol. The sul-

(1) We are pleased to acknowledge support of this work by the U. S. Atomic Energy Commission, AT(30-1) 2499.

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fur compounds are converted to their alternate valence states, and are in effect regenerated and may be effective repeatedly, not being consumed. The percentage of inhibition depends on the concentration of inhibitor; the period of inhibition does not, providing a new mechanism of inhibition. In classical inhibition of chain reactions the inhibitor is consumed and the inhibition period is related to the rate of initiation and the quantity of inhibitor.[7]

The ^{60}Co γ-ray irradiation of benzophenone in 2-propanol leads to benzopinacol and acetone in a non-chain process,[8] apparently *via* radicals I and II. We find that under conditions of ^{60}Co radiation which otherwise lead to 0.19 mmole of benzopinacol, the presence of 0.025 mmole of mesityl disulfide or 0.050 mmole of 2-mercaptomesitylene leads to complete inhibition of formation of this product. In both light and high energy radiation induced reactions the mercaptan–disulfide system inhibits non-chain processes, each molecule countering the action of many quanta. The radiation converts compounds into radicals by removal or addition of hydrogen atoms. The sulfur compounds, in rapid hydrogen transfer processes, convert the free radicals to stable molecules, and may do this repeatedly. Such reactions may describe a chemical mechanism by which mercaptans protect biological systems against damage by high energy radiation.[9a,b] In other circumstances the hydrogen transfer reactivity of the mercaptan–thiyl system leads to catalysis.[6,10a,b,c]

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CLEAVAGE OF TRIMETHYLAMINE TRIBORANE[1]

Sir:

We wish to report a unique degradation reaction of a triborane Lewis base adduct. The reaction of trimethylamine triborane with triphenylphosphine resulted in cleavage of the triborane to triphenylphosphine borane and a triphenylphosphine adduct of a new boron hydride, I. The yield of I increased as the ratio of triphenylphosphine to the triborane complex was increased. Based on the reaction

$$3(C_6H_5)_3P + (CH_3)_3NB_3H_7 \xrightarrow[50°]{C_6H_5H} ((C_6H_5)_3PBH_2)_2\downarrow + (C_6H_5)_3PBH_3 + N(CH_3)_3\uparrow$$

I

a 93% yield of the insoluble I was obtained, m.p. 185° (*Anal.* Calcd. for $(C_6H_5)_3PBH_2$: B, 3.94; C, 78.60; H, 6.19; P, 11.27. Found: B, 3.79; C, 78.61; H, 6.27; P, 13.2). Triphenylphosphine borane (m.p. 187–188°) was isolated in 67% yield and a 98% recovery of the trimethylamine liberated was achieved. It was demonstrated that I was different from either triphenylphosphine borane or triphenylphosphine triborane, by mixed melting points and a comparison of their solubilities and infrared spectra. The B^{11} n.m.r. spectrum (at 12.8 megacycles) of a saturated solution of I in methylene chloride showed a single unresolved band at 53.1 p.p.m. relative to methyl borate.[2]

An ebullioscopic molecular determination in methylene chloride indicated that I was dimeric (Calcd. 550. Found: 570, 566, 580). This suggests that I is the bis-triphenylphosphine adduct of the hitherto unknown diborane (4); $((C_6H_5)_3P)_2B_2H_4$. Hydrolysis experiments supported this formulation. Treatment of I with trifluoroacetic acid–ethanol (1:3) at 100° for 24 hours resulted in an active hydrogen to boron ratio of 1.97, while reaction of I with ethanolic potassium hydroxide under the same conditions yielded a H/B ratio of 2.46. The difference in the active hydrogen boron ratios of the two hydrolysis experiments is attributed to cleavage of the boron–boron bond by the basic ethanolic mixture. Apparently, the boron–boron bond was stable in the trifluoroacetic acid solution. The relative stability of the boron–boron bond toward hydrolysis in acid media as opposed to its facile hydrolysis in base was demonstrated by Brotherton, *et al.*, for several alkoxy and dialkylamino diboron derivatives.[3]

The formulation of I as a diboron derivative would make it isoelectronic with the unstable boron hydride ion, $B_2H_6^=$, proposed by Hough and coworkers,[4] and similar to the reported diadducts formed between diboron tetrachloride and phosphines or sulfides.[5] The alternate formulation of I as the salt $(C_6H_5)_3P)_2BH_2^+BH_4^-$ is not completely eliminated although the observed hydrolytic stability is in contrast with that expected from the borohydride group.

Although displacement of trimethylamine from trimethylamine triborane upon treatment with triphenylphosphine occurred, no evidence for the formation of triphenylphosphine triborane was found.

Triphenylphosphine triborane was therefore prepared from triphenylphosphine and the tetrahydrofuran adduct of triborane in a manner analogous to that reported by Parry for the preparation of ammonia triborane.[6] A yield of 54% of $(C_6H_5)_3PB_3H_7$ was obtained, m.p. 161° (*Anal.* Calcd. for $(C_6H_5)_3PB_3H_7$: B, 10.77; C, 71.66; H, 7.30; P, 10.27. Found: B, 10.80; C, 71.42; H, 7.11, P, 9.20). However, if dimethylsulfide triborane was employed instead of the tetrahydrofuranate only a small yield of triphenylphosphine triborane

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(2) The B^{11} n.m.r. spectrum of $(C_6H_5)_3PBH_3$ in methylene chloride was practically identical to that of I. It showed a broad band (centered at 52.8 p.p.m. relative to methyl borate) which was not completely resolved. The spectrum was complicated due to P–B coupling as well as B–H coupling.

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