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FORMATION AND CHEMICAL FATE OF TRISPHENYLTHIOMETHYL RADICAL1)

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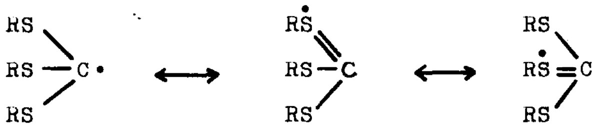
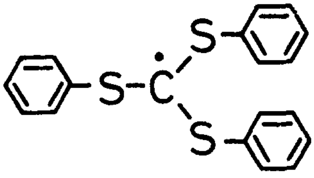
Earlier, we have suggested that the facile hydrogen abstraction from phenylorthothioformate is mainly due to the stabilization of the resulting radical by the following electron-sharing conjugation shown below.2)



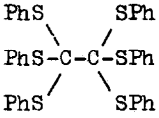
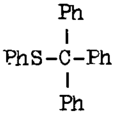
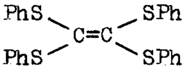
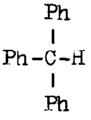
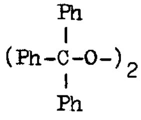
As an extention we have attempted preparation and possible isolation of the radical (I) and also studied its chemical fate. Radical (I) was prepared by the following two ways ; one is addition of phenyl radical to thiocarbonyl group of phenyltrithiocarbonate (II) and another is hydrogen abstraction from phenylorthothioformate (III) by phenyl radical.

(I)



The reaction of phenyltrithiocarbonate (II) with phenylazotriphenylmethane was carried out by heating a benzene solution of a mixture of an equimolar amount of phenylazotriphenylmethane and two equimolar amount of trithiocarbonate (II) at 60°C for 4 hours under nitrogen atmosphere. The products isolated through silicagel column-chromatography are listed in Table I.

TABLE I. Products Formed from Reaction of Phenyltrithiocarbonate with Phenylazotriphenylmethane in Benzene at 60°C 1) 2)

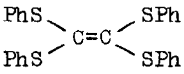
	PhS-SPh	 $PhS-\overset{Ph}{\underset{Ph}{C}}-Ph$		 $Ph-\overset{Ph}{\underset{Ph}{C}}-H$	 $(Ph-\overset{Ph}{\underset{Ph}{C}}-O-)_2$
80	80	13	trace	26	6

1) Yield to phenylazotriphenylmethane (%)

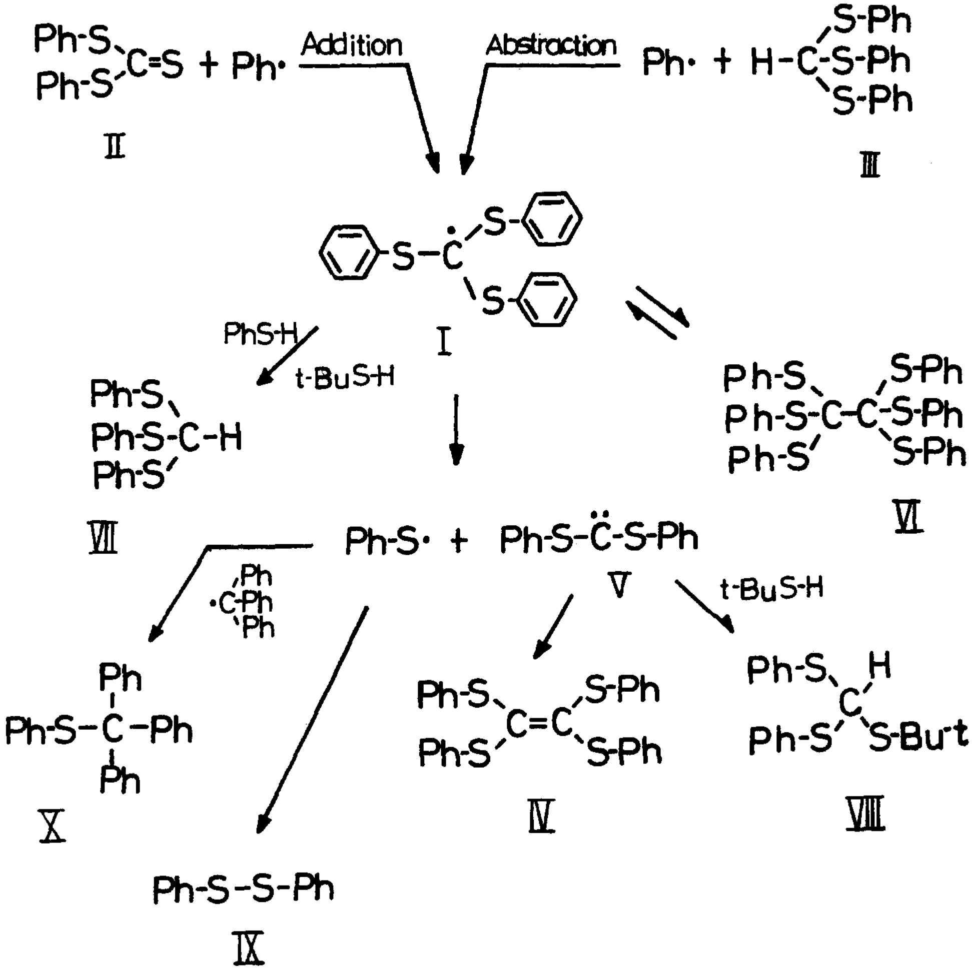
2) There are two unidentified products

Hexakisphenylthioethane (VI) m.p. 176 - 179°C was identified and characterized by n.m.r. (single peak at 7.22 ppm in CCl_4), mass spectroscopy (at 80 eV m/e values for major peaks 109 $[PhS^+]$, 218 $[PhS-SPh]^+$ and 242 $[(PhS)_2C=C]^+$) and elemental analysis (Found, 67.69 % (C) and 4.39 % (H) ; calcd. for $C_{38}H_{30}S_6$ 67.21 % (C) and 4.45 % (H). Other products were characterized by comparing the physical properties of these and the corresponding authentic samples. From the hydrogen abstraction reaction of phenylorthothioformate with a less amount of PAT under the same condition gave the crystals (VI) in 13 % yield. The compound (VI) was found to undergo thermal decomposition slowly at 130°C in chlorobenzene and tetrakisphenylthioethylene (IV) was obtained quantitatively while phenyldisulfide was also obtained as shown in Table (II).

TABLE II. Products of Thermal Decompostion of Hexakisphenylthioethane in Chlorobenzene at 130°C

	PhS-SPh
100 %	88 %

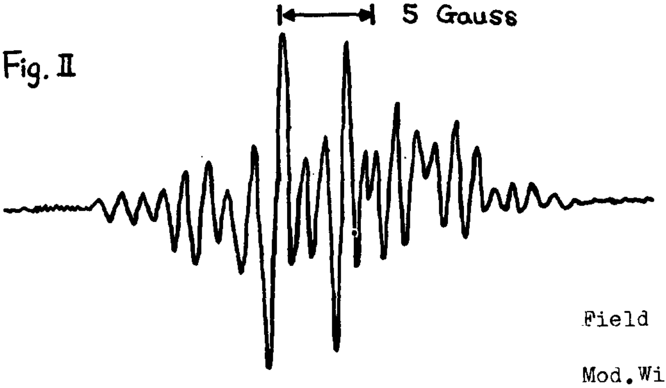
The formation of hexakisphenylthioethane from the two reactions indicates clearly that triphenylthiomethyl radical is formed at the initial steps of both reactions. The main reaction of the radical (I) is the dimerization to give the compound (VI), at a low temperature 60°C, while the formation of trace amounts of tetrakisphenylthioethylene (IV) may be rationalized by assuming that a minor portion of the radical (I) underwent homolysis to form bisphenylthio carbene (V) and benzenethiyl radical which gave eventually two dimerized products, (IV) and (IX). In fact, when hexakisphenylthioethane was heated at 130°C in chlorobenzene for 40 mins., the radical formed by the dissociation of (VI) undergoes fission of benzenethiyl radical to result in the formation of bisphenylthiocarbene which eventually dimerized to give (IV).



However, this carbene could also be trapped by the presence of a mercaptan like other carbenes.[3] Thus when the dissociation of (VI) was carried out at 130°C in the presence of t-butylmercaptan, t-butyl diphenyltrithioorthoformate (VIII) was isolated in 10 % yield as was expected. The trithio orthoformate (VIII) was characterized by comparing in with an authentic sample prepared by the reaction of t-butylformiminothioester H-C(SBu-t)=NH•HCl with two equimolar amount of thiophenol. The radical (I) abstracted hydrogen from both thiophenol and t-butylmercaptan to give phenylorthothioformate (VII). Thus, the chemical fate of the radical (I) may be schematically illustrated as shown in Fig.1.

In order to make a direct proof of the radical (I), hexakisphenylthioethane (VI) was dissolved in xylene and the solution was subjected to ESR measurements at 130°C. Though the exact assignment of the hyperfine structure and the degree of dissociation of the compound (VI) have to await further detailed investigation, the spectra consisted of 23 hfs with line width of 1.2 and 1.0 gauss shown in Fig.II is probably the radical (I).

Fig. II



Field 3235 ± 25G

Mod.Width 0.2 G

Reference

1) 3d-Orbital Resonance in Divalent Sulfides. (XVII)

2) K. Uneyama, H. Namba and S. Oae. Bull. Chem. Soc. Japan, 41, 1928 (1968)

3) A. Ohno and Y. Onishi. Tetrahedron Letters, in press.