yellow, pleasant-smelling oil. Vapor phase chromatography indicated the presence of two products in a ratio of 0.89 to 1. The first product eluted (10.0 cm from the air peak) had a retention time identical with that of the minor component obtained by catalytic reduction of *trans*-1,2-diphenylcyclopropane:[20] ν_{max}^{neat} 693, 730, 755, 1011, 1027, 1066, 1374, 1451, 1494, 1600, 2930, 2965, 3032, 3063, 3093 cm^{-1}. It was tentatively identified as 1,2-diphenylpropane.

The second product eluted (15.3 cm from the air peak) was identified as 1,3-diphenylpropane (X): ν_{max}^{neat} 693, 740, 901, 1028, 1081, 1452, 1495, 1602, 2862, 2940, 3035, 3070, 3092 cm^{-1}. Its retention time and its infrared spectrum were identical with that of an authentic sample of 1,3-diphenylpropane[9] (X) prepared by the hydrogenation of *trans*-diphenylcyclopropane.[15,16] Similar results were obtained on desulfurization of *rac*-bis(*cis*-1,2-diphenylcyclopropyl) disulfide (VII).

Registry No.—I, 24605-73-0; II, 22601-50-9; IV, 30256-27-0; V, 30256-28-1; VI, 30256-29-2; VII, 30256-30-5; VIII, 30256-31-6; IXb, 30256-32-7.

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Notes

Thietanes. V. Products Formed *via* Dimerization of *trans*-2,4-Diphenylthietane

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In our previous publications on 2,4-diphenylthietanes, their monoxides, and dioxides,[1] we have described rearrangements that could be formulated readily as modified Stevens rearrangements. Here, we describe the preparation, isolation, and proof of structure of products whose formation can only be explained by complex and multiple reactions.

Treatment of *trans*-2,4-diphenylthietane (I) with potassium *tert*-butoxide in dimethylformamide yielded a dark brown viscous oil that showed bands in its ir spectrum corresponding to carbonyl (1682 cm^{-1}) and thiol (2535 cm^{-1}) groups. Thin layer chromatography of this material indicated the presence of nine different products. By chromatography on silica gel, four of these products have been separated and identified. An additional three products have been isolated but, because of the very small quantity obtained, have not as yet been identified.

The first product obtained from this reaction was easily identified as 2,3,5-triphenylthiophene (II), mp 141–142°. The structure of the compound was established (1) from its analysis, (2) from the presence in its ir spectrum of bands characteristic of phenylthiophenes (694, 754, 844, 913, 1071, 3070, and 3090 cm^{-1}),[2] and (3) from its mass spectrum which indicated a molecular weight of 312 and a molecular formula of $C_{22}H_{16}S$ However, previous reports on 2,3,5-triphenylthiophene gave melting points of 127[3] and 198°.[4] The synthesis of Smith[3] was repeated. Reaction of 1,2,4-triphenylbutane-1,4-dione with phosphorus pentasulfide yielded, after chromatography and repeated crystallizations, 2,3,5-triphenylthiophene (II), mp 143.5–144°, identical with that obtained above.

Next 1,2,4,5-tetraphenylbenzene (III), mp 267–267.5°, was isolated. Its structure was established by direct comparison (mixture melting point and ir spectra) with a sample of 1,2,4,5-tetraphenylbenzene prepared by the reaction of diphenylacetylene with 3,4-diphenyl-4-hydroxycyclopent-2-enone.[5]

The fourth product eluted was benzylacetophenone (V) (1,3-diphenyl-1-propanone). This was identified by direct comparison with an authentic sample[6] prepared by the hydrogenation of benzalacetophenone.

The third product isolated was most unusual. Its analysis, molecular weight, and mp 143–145° corresponded with that of one of the bis(*cis*-1,2-diphenylcyclopropyl) disulfides previously reported.[1d] However, its ir, uv, and mass spectra differed entirely from that of the bis(*cis*-1,2-diphenylcyclopropyl) disulfide. The ir spectrum of the cyclopropyl disulfides showed no appreciable C–H stretching bands below 3000 cm^{-1}; the new compound showed absorption bands at 2920 and 2985 cm^{-1}. The uv spectrum of the cyclopropyl disulfides showed a maximum at 227.5 nm (ϵ 37,700); the uv spectrum of the new compound showed a maximum at 212 nm (ϵ 32,200). The most definitive comparison came from the mass spectra. The mass spectrum of the new compound showed a relatively intense molecular ion peak, 3.0% of the m/e 91 peak. It also showed strong peaks at m/e 382–386; m/e 386 corresponds to M − S_2. Strong

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[1] (a) R. M. Dodson, E. H. Jancis, and G. Klose, *J. Org. Chem.*, **35**, 2520 (1970); (b) R. M. Dodson, P. D. Hammen, and R. A. Davis, *ibid.*, **36**, 2693 (1971); (c) R. M. Dodson, P. D. Hammen, E. H. Jancis, and G. Klose, *ibid.*, **36**, 2698 (1971); (d) R. M. Dodson, P. D. Hammen, and J. Yu Fan, *ibid.*, **36**, 2703 (1971).

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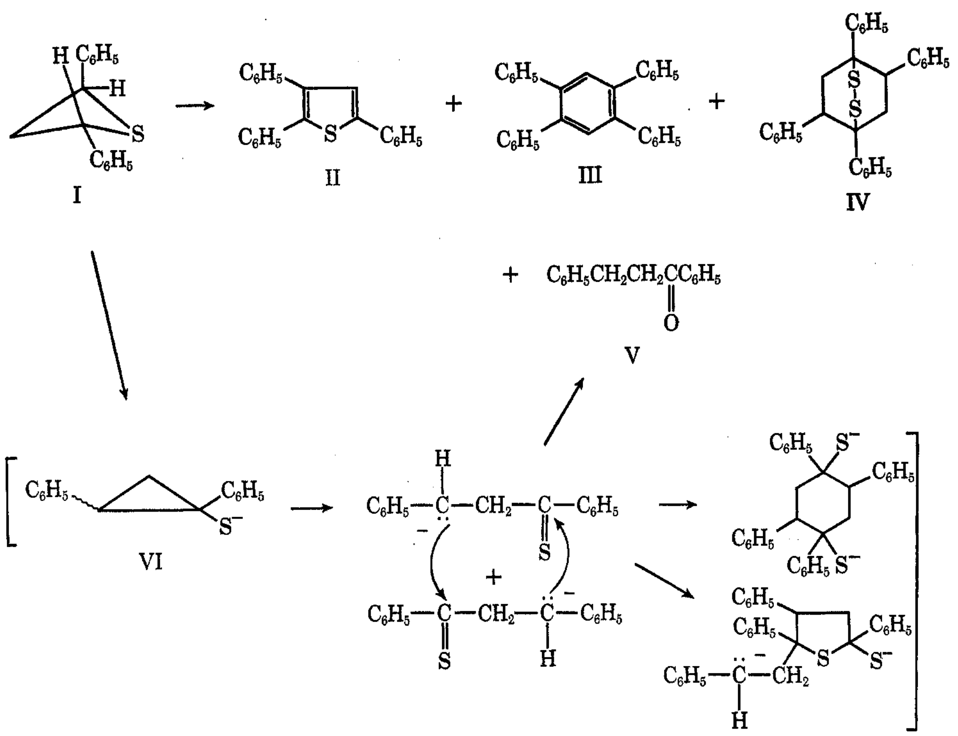
SCHEME I



peaks at m/e 294 and 296 were also found; m/e 296 corresponds to $M - S_2 - C_7H_6$. A strong metastable peak at 331 corresponding to the loss of two atoms of sulfur from the molecular ion was present in one mass spectrum. On the basis of this evidence the structure of IV was tentatively postulated to be 1,4,5,7-tetraphenyl-2,3-dithiabicyclo[2.2.2]octane. Definitive proof of structure must await development of a method for obtaining the compound in larger amounts.

It seems reasonable that the initial product formed on treatment of *trans*-2,4-diphenylthietane (I) with potassium *tert*-butoxide was the potassium salt of the 1,2-diphenylcyclopropanethiol (VI). From this, formation of II, III, IV, and V *via* reactions outlined in Scheme I (plus hydrolysis or air oxidation) can be postulated. However, further discussion of the course of formation of these products must await far more extensive experimental work. It should be realized that IV is a valence bond isomer of *bis*-(1,2-diphenylcyclopropyl) disulfide.

Experimental Section[7]

Reaction of *trans*-2,4-Diphenylthietane (I) with Potassium *tert*-Butoxide.—A solution of *trans*-2,4-diphenylthietane[1a] (I) (11.2 g, 0.05 mol, mp 100–102°) and potassium *tert*-butoxide (15 g, 0.13 mol) in dimethylformamide[8] (200 ml) was stirred under nitrogen at 80° for 24 hr. The mixture was then added to ice–water (600 ml) and extracted with several portions of ether. The combined ether extracts were washed thoroughly with water and dried over magnesium sulfate. Evaporation of the ether solution yielded 10.0 g of a dark brown, highly viscous oil: $\nu_{\max}^{\text{neat}}$ 1682 (s, $C_6H_5C{=}O$), 2535 cm^{-1} (w, SH); thin layer chromatography (silica gel; 85:15 petroleum ether-benzene) of this material indicated the presence of nine different products.

In an attempt to free this material from mercaptan, it was dissolved in ether and thoroughly extracted with 10% aqueous sodium hydroxide solution. After being washed and dried, the ether was evaporated. The 8.12 g of viscous material remaining still showed an ir band for the –SH group. Acidification of the initial and subsequent basic, aqueous extracts yielded 1.00 g of residue which was not furher investigated.

2,3,5-Triphenylthiophene (II).—A 4.0-g portion of the material from the ether extract was chromatographed on 160 g of silica gel (100–200 mesh). The column was successively eluted with petroleum ether and 10% benzene in petroleum ether. Elution with 15% benzene in petroleum ether yielded 50 mg of a white solid, mp 105–110°. Crystallization from petroleum ether yielded pure 2,3,5-triphenylthiophene: mp 141–142°; $\lambda_{\max}^{\text{ethanol}}$ 262 nm (ϵ 20,500), 320 (16,800); $\nu_{\max}^{\text{KBr}}$ 694, 754, 844, 913, 1030, 1071, 1449, 1487, 1600, 3035, 3070, and 3090 cm^{-1}; mass spectrum M$^+$ and base peak 312 [Calcd: (M + 1)/M = 24.8%; (M + 2)/M = 7.1%. Found: M + 1/M = 26%; M + 2/M = 7.6%], 311 (10.6% B) (M − 1H), 310 (8.8% B) (M − 2H), 309 (4.0% B) (M − 3H), 278 (6.0% B) (M − H_2S), 236 (3.7% B) (M − C_6H_4), 235 (2.7% B) (M − C_6H_5), 234 (5.3% B) (M − C_6H_6), 191 (4.2% B) (M − C_6H_5CS), 121 (8.0% B) (C_6H_5CS). This material was identical (melting point, mixture melting point, and uv and ir spectra) with 2,3,5-triphenylthiophene, mp 143.5–144°, prepared by the method of Smith.[3]

Anal. Calcd for $C_{22}H_{16}S$ (312.43): C, 84.58; H, 5.16. Found: C, 84.46; H, 5.15.

1,2,4,5-Tetraphenylbenzene (III).—Further elution of the column with 15% benzene in petroleum ether yielded 56 mg of a light yellow solid, mp 210–250°. Crystallization from benzene-petroleum ether yielded 1,2,4,5-tetraphenylbenzene (III): mp 267–267.5°; $\lambda_{\max}^{\text{ethanol}}$ 248 nm (ϵ 56,800), shoulder at 280 (21,800); $\nu_{\max}^{\text{KBr}}$ 696, 732, 754, 777, 844, 904, 914, 1000, 1014, 1020, 1076, 1162, 1182, 1384, 1450, 1480, 1502, 1580, 1602, 3035, 3075, and 3090 cm^{-1}. The compound was identical (melting point, mixture melting point, ir spectrum) with an authentic sample of 1,2,4,5-tetraphenylbenzene, mp 271–272°, prepared by the reaction of diphenylacetylene with 3,4-diphenyl-4-hydroxycyclopent-2-enone.[5]

1,4,5,7-Tetraphenyl-2,3-dithiabicyclo[2.2.2]octane (IV).—Elution of the column with 20% benzene in petroleum ether yielded no crystalline material. Elution with 25% benzene in petroleum ether gave 43 mg of 1,4,5,7-tetraphenyl-2,3-dithiabicyclo[2.2.2]-

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[7] Melting points were taken on a Fisher-Johns melting point apparatus, calibrated against a set of standard compounds. The mass spectra were determined on a Consolidated 21-103C mass spectrometer equipped with an all-glass inlet or on a Hitachi Perkin-Elmer Model RMU-6D mass spectrometer. Petroleum ether refers to that fraction, bp 60–68°.

[8] Dried over potassium hydroxide pellets and then distilled, bp 153°.

Table I

Mass Spectrum of IV[a]

m/e	Ion$^+$	% of *m/e* 91	Remarks
450	$C_{30}H_{26}S_2$ (M)	3.0	$\frac{M+1}{M} = 34.4\%$ (calcd 34.4%) $\frac{M+2}{M} = 16.4\%$ (calcd 14.0%)
386	$M - S_2$	9.3	
385		18.8	
384		22.0	
383		6.9	
382		18.0	
331*	Metastable		$M^+ \rightarrow (M - S_2)^+$ (calcd 331.1)
296	$M - S_2 - C_7H_6$	36.4	
294	$M - S_2 - C_7H_8$	51.4	
205	$M - S_2 - (C_7H_8 + C_7H_7)$	57.5	
180	$C_6H_5CH{=}CHC_6H_5$	68.6	
128	$C_6H_5C_4H_3$	56.4	
121	C_6H_5CS	57.3	
115	$C_6H_5C_3H_2$	39.1	
91	C_7H_7	100.0 (B)	
78	C_6H_6	24.1	
77	C_6H_5	37.5	
44	CS	232	
34	H_2S	113.6	
33		50.9	
32		55.0	

[a] The strong metastable ion was found on an early spectrum taken on a Consolidated 21-103C mass spectrometer. That spectrum also showed a strong peak at *m/e* 312 (27.3% of *m/e* 91) corresponding to 2,3,5-triphenylthiophene, M + 1/M = 27.7%, M + 2/M = 7.9%.

octane (IV), mp 141–143°. Three crystallizations from petroleum ether yielded 19 mg of analytically pure IV: mp 143–145°; $\lambda_{max}^{ethanol}$ 212 nm (ϵ 32,200); ν_{max}^{KBr} 696, 733, 762, 773, 909, 948, 1031, 1083, 1154, 1183, 1209, 1251, 1267, 1297–1308 (broad), 1449, 1454, 1496, 1586, 1602, 2920, 2985, 3033, and 3070 cm^{-1}.

Anal. Calcd for $C_{30}H_{26}S_2$ (450.67): C, 79.96; H, 5.82. Found: C, 79.72; H, 6.19.

1,4,5,7-Tetraphenyl-2,3-dithiabicyclo[2.2.2]octane (IV), mp 140–145°, was also obtained in low yield from an ether solution of *cis*-1,2-diphenylcyclopropanethiol[1d] that had been allowed to stand at room temperature for 59 days. Isolation was accomplished by chromatography on silica gel and purification by crystallization from petroleum ether (see Table I).

1,3-Diphenyl-1-propanone (V).—Successive elution of the column with 30:70, 35:65, and 40:60 benzene–petroleum ether yielded no crystalline materials. Elution with 75:25 benzene–petroleum ether gave 1.0 g of a viscous yellow oil. Thin layer chromatography showed that this material was a mixture of six components. Further elution with 75:25 benzene–petroleum ether yielded 15 mg of 1,3-diphenyl-1-propanone, mp 60–70°. Crystallization from petroleum ether gave pure V, mp 70–71°. A mixture with an authentic sample, mp 71–72°, of V showed no depression in melting point. The 2,4-dinitrophenylhydrazone had mp and mmp 184–187°.

2,3,5-Triphenylthiophene (II).—The method of Smith[3] was duplicated. The crude product, mp 90–100°, was purified by chromatography on silica gel and elution with petroleum ether. The chromatographed product, mp 127–132°, was further purified by repeated crystallizations from petroleum ether. The purified 2,3,5-triphenylthiophene (II), mp 143.5–144°, was identical in all respects (melting point, mixture melting point, and uv and ir spectra) with that isolated from the reaction of *trans*-2,4-diphenylthietane (I) with potassium *tert*-butoxide. Reported melting points are 127[3] and 198°.[4]

Registry No.—I, 24609-88-9; II, 20851-07-4; III, 3383-32-2; IV, 30158-27-1; V, 1083-30-3.

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Concerning Internal Rotation in Diarylalkynes

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In diarylalkynes the question arises concerning the relative orientation of the two aromatic rings. One possibility is that the p orbitals of both aromatic rings overlap the same set of p orbitals of the alkyne. This leads to the planar geometry illustrated in Figure 1. A second possibility is that the π system of one aromatic ring overlaps one set of p orbitals of the alkyne while that of the second aromatic ring overlaps the other. This results in the perpendicular geometry shown in Figure 2. A third possibility is that no single orientation is preferred and that, due to the cylindrical symmetry of the alkyne, a freely rotating system occurs; see Figure 3.

In the freely rotating case, the system must pass through both the coplanar and the perpendicular geometries, and the internal rotation is truly free only if these two have the same energy. Thus the problem reduces to finding the energies of the coplanar and perpendicular forms of the diarylalkyne. If one form has a lower energy, the molecule exists in that geometry. If the two forms have the same energy, a freely rotating