Cleavage of 3,6-Dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II) with 2 Equiv of Potassium Ethoxide.—To a solution of 0.168 g (0.002 mol) of potassium ethoxide in 20 ml of absolute ethanol was added 0.538 g (0.002 mol) of 3,6-dibenzoyl-1,8-diphenyl-4,5-dithia-1,8-octanedione (II, mp 137°). The disulfide reacted immediately giving a clear red solution. The mixture was stirred at 27° for 24 hr. The solid was filtered and washed with water to give 0.082 g (16.1%) of 3,5-dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV), mp 182–185°. Recrystallization from ethanol–chloroform raised the melting point to 193–195° (lit.[4] mp 194–196°).

The filtrate from separation of IV was evaporated *in vacuo* leaving a red residue which was triturated in 50 ml of water. Filtration gave 0.153 g (30.8%) of 1,4-diphenyl-1,4-butanedione (VIII), mp 137–141°. Recrystallization from ethanol raised this to 143–145° (lit.[11] mp 144–145°). The sample was found to be identical with an authentic sample by mixture melting point determination and infrared spectra comparison.

The aqueous filtrate from separation of VIII was treated with carbon dioxide until pH 9 was reached. The solution was evaporated *in vacuo* leaving a red solid which was treated with 20 ml of absolute ethanol. The mixture was filtered removing potassium carbonate and the filtrate evaporated *in vacuo* to give 0.247 g (40.3%) of potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII), mp 117–120° (lit.[13] mp 118–121°).

Treatment of 3,5-Dibenzoyl-1,7-diphenyl-3-thia-1,7-heptanedione (IV) with 1 Equiv of Potassium Ethoxide.—To a solution of 0.168 g (0.002 mol) of potassium ethoxide in 20 ml of absolute ethanol was added 1.04 g (0.002 mol) of 3,5-dibenzoyl-1,7-diphenyl-3-thia-1,7-heptanedione (IV). The sulfide reacted immediately giving a red solution containing a small amount of solid. The mixture was stirred at 26° for 24 hr. The solid was filtered and washed with water to give 0.37 g of a mixture of IV and 1,4-diphenyl-1,4-butanedione (VIII). The mixture was triturated in 20 ml of warm ethanol. Filtration gave 0.22 g (20.9%) of recovery IV, mp 186–190° (lit.[4] mp 194–196°). The filtrate was cooled to give 0.11 g (11.5%) of VIII, mp 142–144° (lit.[11] mp 144–145°).

The original filtrate was evaporated *in vacuo* leaving a red gum which was partitioned between 60 ml of water and 60 ml of ether. The ether layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo* to give an additional 0.16 g (17%) of VIII, mp 138–143°. Total yield of VIII was 0.27 g (28.5%). Recrystallization from ethanol raised the melting point to 143–145° (lit.[11] mp 144–145°).

The aqueous layer was treated with carbon dioxide until pH 9 was reached. The solution was evaporated *in vacuo* to give 0.32 g (25.7%) of potassium 1,4-diphenyl-2-butene-1,4-dione-2-mercaptide (VII), mp 116–119° (lit.[2] mp 118–121°).

Addition of 2-Mercapto-1,4-diphenyl-1,4-butanedione (IX) to Potassium 1,4-Diphenyl-2-butene-1,4-dione-2-mercaptide (VII).—Potassium ethoxide (8.4 mg 0.1 mol) in 0.1 ml of ethanol was added to 270 mg (1 mmol) of IX in 5 ml of ethanol. The mixture was cooled and filtered to give 346 mg of a mixture of 3,5-was added to a solution of 306 mg (1 mmol) of VII in 5 ml of ethanol. After 30 min 32.1 mg (0.125 mmol) of sulfur was added and the mixture stirred at 28°. After 24 hr the mixture dibenzoyl-1,7-diphenyl-4-thia-1,7-heptanedione (IV) and sulfur. The mixture was triturated in 20 ml of acetone. Filtration gave 18 mg of sulfur, mp 115–117°. The filtrate was evaporated *in vacuo* to give 341 mg (67.4%) of IV, mp 176–179°. Recrystallization from ethanol–chloroform raised the melting point to 193–195° (lit.[4] mp 194–196°).

Registry No.—II, 4006-76-2; IX, 16704-51-1; 3-benzoyl-1,6-diphenyl-4-thia-1,6-hexanedione, 16704-52-2.

Di-*t*-Butylthioketene

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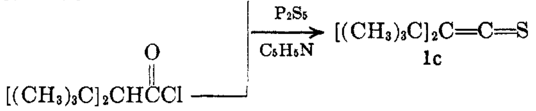
Di-*t*-butylthioketene (**1c**) may be prepared by heating either di-*t*-butylacetyl chloride or di-*t*-butylketene with phosphorus pentasulfide in pyridine. Thioketene **1c**, in contrast to other nonhalogenated thioketenes reported previously, shows no tendency to dimerize or polymerize on storage at room temperature. It may be converted into O esters (**3**) of di-*t*-butylthioacetic acid by reaction with methyl or ethyl alcohol, into di-*t*-butylthioacetanilide (**4**) by reaction with aniline, and into the S-oxide by oxidation with hydrogen peroxide or monoperphthalic acid. Spectral evidence indicates that there is a substantial barrier to rotation about the C_1–C_2 bond axis of the esters (**3**) and the anilide (**4**).

Although there have been several attempts to prepare thioketenes since the discovery of ketene and its homologs, these have usually given only polymers or dimers.[1–4] Apparently, only two attempts to prepare the monomers have been successful. Howard prepared thioketene (**1a**) by pyrolysis of *t*-butyl ethynyl sulfide and found it to be unstable at temperatures above −80°.[5] More recently, Raasch prepared bis(trifluoromethyl)thioketene (**1b**) by pyrolysis of its dimer, 2,4-bis[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene]-1,3-dithietan, and found that the monomer is stable for many months when kept in glass bottles at room temperature.[6] Raasch attributed the stability of this thioketene to the strongly electron-withdrawing trifluoromethyl groups.

Newman, *et al.*, described the preparation of di-*t*-butylketene and commented upon its extreme unreactivity, which is apparently due to steric hindrance.[7]

In the hope that a similarly substituted thioketene would also be more stable than its less sterically hindered homologs, we undertook the preparation of di-*t*-butylthioketene (**1c**). We prepared the compound successfully by the reactions summarized in Scheme I.

SCHEME I



$$[(CH_3)_3]_2C{=}C{=}O,\ [(CH_3)_3C]_2CHC(=O)Cl \xrightarrow[C_5H_5N]{P_2S_5} [(CH_3)_3C]_2C{=}C{=}S\ \ \mathbf{1c}$$

When a solution of di-*t*-butylketene in pyridine was refluxed with phosphorus pentasulfide for 15 hr, it was

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[1] H. Staudinger, G. Rathsam, and F. Kjelsberg, *Helv. Chim. Acta*, **3**, 853 (1920).

[2] A. Schönberg, E. Frese, and K.-H. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).

[3] A. Schönberg, L. V. Vargha, and H. Kaltschmidt, *Ber.*, **64**, 2582 (1931).

[4] E. U. Elam and H. E. Davis, *J. Org. Chem.*, **32**, 1562 (1967).

[5] E. G. Howard, Jr. (to E. I. du Pont de Nemours and Co.), U. S. Patent 3,035,030 (1962).

[6] M. S. Raasch, *Chem. Commun.*, 577 (1966); M. S. Raasch (to E. I. du Pont de Nemours and Co.), U. S. Patent 3,275,609 (1963).

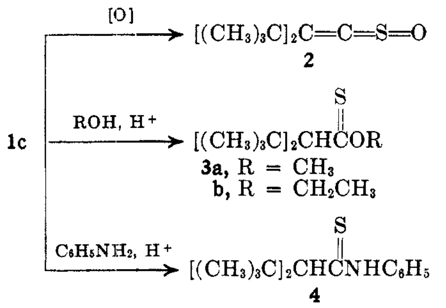
[7] M. S. Newman, A. Arkell, and T. Fununaga, *J. Amer. Chem. Soc.*, **82**, 2498 (1960).

converted smoothly into **1c**, which was isolated in 41% yield by distillation of the reaction mixture.[8] Thioketene **1c** is a deep purple oil, bp 59–60° (6 mm), which showed no tendency to dimerize or polymerize after standing at room temperature for many months, after exposure (in a cyclohexene solution) to sunlight for 20 days, or after irradiation by a medium-pressure mercury lamp for 24 hr. The identity of the compound was established by elemental analysis and by the presence of a strong peak in the mass spectrum at *m/e* 170.1119, corresponding to the molecular ion. The infrared spectrum contained a band at 1745 cm^{-1}, in good agreement with the position previously reported for the thioketene band in **1a** (1750 cm^{-1})[5] and **1b** (1783 cm^{-1}).[6] The nmr spectrum ($CDCl_3$) consisted of a singlet at 1.27 ppm.

A more convenient synthesis of the thioketene, which avoids isolation of di-*t*-butylketene, consists of refluxing the ketene precursor, di-*t*-butylacetyl chloride, with phosphorus pentasulfide in pyridine solution. Under these conditions, **1c** was obtained in 64% yield from the acid chloride.

Although, as already noted, **1c** is a relatively unreactive compound, a number of reactions were carried out successfully (Scheme II). Oxidation with monoperphthalic acid in ether or with hydrogen peroxide in methanol afforded di-*t*-butylthioketene S-oxide (**2**) in good yield. The structure **2** for this compound was supported by the usual elemental analysis and spectral data. The infrared spectrum contained absorptions at 1074 and 1036 cm^{-1}, which are consistent with the absorptions previously reported for sulfines (S-oxides of thioaldehydes or thio ketones);[9–11] the nmr spectrum ($CDCl_3$) consisted of a singlet at 1.35 ppm.

SCHEME II



$$\mathbf{1c} \xrightarrow{[O]} [(CH_3)_3C]_2C{=}C{=}S{=}O \quad \mathbf{2}$$

$$\mathbf{1c} \xrightarrow{ROH,\ H^+} [(CH_3)_3C]_2CH\overset{\overset{S}{\|}}{C}OR \quad \mathbf{3a},\ R = CH_3;\ \mathbf{b},\ R = CH_2CH_3$$

$$\mathbf{1c} \xrightarrow{C_6H_5NH_2,\ H^+} [(CH_3)_3C]_2CH\overset{\overset{S}{\|}}{C}NHC_6H_5 \quad \mathbf{4}$$

Compound **2**, the first reported thioketene S-oxide, or allenic sulfine is also comparatively stable. As far as we are aware, the only sulfine that has been reported which contained only alkyl substituents is thioacetone S-oxide; this oxide was too unstable for isolation.[9] The stability of **2** is comparable with that of aromatic thio ketone S-oxides.[10] Compound **2** was apparently unaffected by methanol or by aqueous sodium bicarbonate solution used to extract by-product phthalic acid. Exactly 1 equiv of per acid was required to oxidize **1c** to **2**, and excess oxidizing agent (perphthalic acid or hydrogen peroxide) did not appear to oxidize or degrade **2**. Attempts to purify **2** by distillation on a Nester–Faust spinning-band column at 0.8 mm led to decomposition, however, and a sample deteriorated after standing at room temperature for a few weeks. The decomposition products were not identified.

There was no evidence of reaction when methyl or ethyl alcohol solutions of **1c** were allowed to stand at room temperature in the absence of catalyst, but there was a slow reaction to give the corresponding O-alkyl thio esters when a trace of hydrochloric acid was added. The esters **3a** and **3b** were characterized by elemental analyses and by high-resolution mass spectra. The mass spectrum of each ester showed prominent peaks corresponding to the expected parent molecular ion. The infrared spectra showed no absorption in the 1675-cm^{-1} region, which would have been expected had any appreciable amount of the isomeric S-alkyl thio ester been present.

Although these esters gave only one peak on two glpc columns (Carbowax 20M and Silicone QF-1) and gave the correct elemental analyses, the resonance in the nmr spectra ($CDCl_3$) due to the methynyl hydrogen unexpectedly appeared as two peaks at δ 3.05 ppm (0.76 H, **3a**; 0.73 H, **3b**) and 2.59 ppm (0.23 H, **3a**) or 2.61 ppm (0.24 H, **3b**). In addition, the resonance due to the methoxyl protons of **3a** was split into two peaks at δ 3.99 ppm (2.37 H) and 3.85 ppm (0.73 H). The assignment of two peaks to the methynyl hydrogen of **3a** was confirmed by the greatly reduced intensity of the peaks at 3.05 and 2.59 ppm in the spectrum of the corresponding methanol-*d* adduct. When a tetrachloroethane solution of the ethanol adduct **3b** was heated to 100°, the peaks at 3.05 and 2.61 coalesced into a broad singlet at 2.98 ppm.

The evidence suggests that this splitting is due to the existence of a substantial barrier to rotation between carbon atoms 1 and 2. The possibility that this splitting is caused by the presence of the isomeric S-alkyl thio ester was rejected because there was no absorption in the carbonyl stretching region of the infrared spectrum, as noted previously. The possibility that the doublet is due to the presence in the sample of enethiol tautomer **5** was rejected because there was no exchange with D_2O and no observable reaction or exchange with trifluoroacetic acid-*d*. Saturation of the absorption at 3.05 ppm in **3b** with a strong radio-frequency field greatly decreased the intensity of the peak at 2.61 ppm, indicating a transfer of spin saturation from the irradiated peak to the peak at 2.61 and providing further evidence that the species are in rapid equilibrium and eliminating an impurity as the source of the additional peak.[12] Finally, the possibility that the splitting is caused by a rapid, reversible equilibrium between monomeric thio ester and a dimer or trimer was also considered and rejected because there was no change in the relative amounts of the components of the doublet with change in concentration.

In an appreciable barrier to rotation about the C_1–C_2 bond of the esters does exist, it is reasonable to expect that the band in the infrared spectrum due to the C–H stretching vibration of the tertiary hydrogen would

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[8] An unsuccessful attempt to prepare diphenylthioketene by a similar method has been reported; *cf.* H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p 128.

[9] W. A. Sheppard and J. Diekman, *J. Amer. Chem. Soc.*, **86**, 1891 (1964).

[10] J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav. Chim.*, **83**, 631 (1964); *Tetrahedron Lett.*, 65 (1966); *Rec. Trav. Chim.*, **86**, 641 (1967); B. Swanenburg, L. Thijs, and J. Strating, *ibid.*, **86**, 577 (1967).

[11] See also a recent review on sulfines and sulfenes: G. Opitz, *Angew. Chem. Intern. Ed. Engl.*, **6**, 107 (1967).

[12] B. M. Fung, *J. Chem. Phys.*, **47**, 1409 (1967).

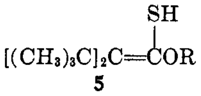
actually be a doublet. To observe this, the 2-deuterio ester was prepared by the reaction of **1c** with methanol-*d*. The C–D stretching frequency of the product appeared at 2160 cm^{-1}. A shoulder which appeared on this band at 2150 cm^{-1} was considered to be further indication of the presence of rotational isomers. The relative intensities of the main absorption band at 2160 cm^{-1} and the shoulder were of the same order as the intensities of the resonances due to the methynyl proton in the nmr spectrum.

When **1c** was refluxed with aniline in the presence of a trace of sulfuric acid, di-*t*-butylthioacetanilide (**4**) was obtained in 57% yield. This compound, which has not been reported previously, was characterized by elemental analysis and spectral data. Thioanilide **4** was obtained, after repeated recrystallization, as a pale yellow, crystalline solid, mp 130–131.5°. The nmr spectrum of a freshly prepared solution in *o*-dichlorobenzene showed sharp singlets at 1.22 and 2.25 ppm. After this solution had been allowed to stand overnight at room temperature, two resonances were observed in each of these regions, at 1.22, 1.13, and 2.25 and 3.11 ppm. When the freshly prepared solution was heated to 80°, the methyl and methynyl resonances were observed as doublets; at 160° the components of these doublets broadened but did not coalesce. When the solution which had been heated was allowed to cool to room temperature, the methyl and methynyl resonances remained as doublets. Saturation of the methynyl resonance at 3.11 ppm with a strong radiofrequency field at a temperature of 80° caused a large decrease in the intensity of the resonance at 2.25 ppm. As with the esters, this was interpreted as an indication that, at this temperature, the species responsible for the doublet are in rapid equilibrium. When this experiment was repeated after the solution had cooled to room temperature, the intensity of the peak at 2.05 ppm was not affected by saturation of the 3.11-ppm absorption.

Our interpretation of these observations is that the barrier to rotation about the C_1–C_2 bond in the thioanilide **4** is even higher than that in the esters **3a** and **3b**. Apparently, the single conformer obtained by recrystallization is stable for long periods (at least several weeks) in the crystalline state at room temperature, but it is able to isomerize slowly in solution at room temperature or rapidly at 80°.

$R_2C{=}C{=}S$

1a, R = H
b, R = CF_3
c, R = $C(CH_3)_3$



$$[(CH_3)_3C]_2C{=}C(SH)OR$$

5

Experimental Section[13]

Preparation of Di-*t*-butylthioketene (1c) from Di-*t*-butylketene.—A mixture of 4.0 g (26 mmol) of di-*t*-butylketene[7] and 4.0 g (18 mmol) of phosphorus pentasulfide in 50 ml of pyridine was refluxed 15 hr. Glpc indicated almost complete conversion of ketene into product. The mixture was cooled and the liquid was decanted. The residue was extracted with two portions of warm pyridine. The combined pyridine solutions were distilled rapidly, without fractionation, at pressures between 60 and 35 mm to remove inorganic material. The purple distillate was concentrated at reduced pressure and distilled on a short Nester–Faust spinning-band column to afford 1.8 g (40.6%) of di-*t*-butylthioketene (**1c**), as a deep purple oil: bp 59–60° (6.0 mm); nmr spectrum ($CDCl_3$), singlet at 1.27 ppm; uv max (cyclohexane) 239 mμ (log ε 3.62), 211 (4.51). There was also a weak visible absorption (cyclohexane) at 570 mμ (ε 7.8). The infrared absorption at 1745 cm^{-1} is consistent with the absorptions attributed to the thioketene group of bis(trifluoromethyl)thioketene (1783 cm^{-1})[6] and thioketene (1750 cm^{-1}).[5] Major peaks in the mass spectrum (70 eV) were at *m/e* (relative intensity) 57 (100), 99 (31), 41 (18), 170.1119 (18, calcd for parent 170.1129), 29 (9).

Anal. Calcd for $C_{10}H_{18}S$: C, 70.52; H, 10.65; S, 18.83. Found: C, 70.53; H, 10.50; S, 19.00.

Preparation of Di-*t*-butylthioketene (1c) from Di-*t*-butylacetyl Chloride.—A mixture of 14.6 g (77 mmol) of di-*t*-butylacetyl chloride,[7] 14.6 g (66 mmol) of phosphorus pentasulfide, and 200 ml of pyridine was stirred at reflux under nitrogen for 21.5 hr. At the end of this period, glpc indicated that the only volatile materials present were pyridine and thioketene **1c**. The pyridine solution was decanted and distilled without fractionation initially at 42 mm; in the latter stages of the distillation, the pressure was reduced to 5 mm. Pyridine was removed by redistillation at 30 mm through a 2 × 25 cm column packed with Penn State metal packing. The purple residue was distilled through a small Vigreux column to afford 8.3 g (63.6%) of thioketene **1c**, bp 60–63° (6 mm). The product was pure, according to glpc, and the glpc retention time and infrared spectrum were identical with those of the product obtained from di-*t*-butylketene.

Oxidation of 1c to Di-*t*-butylthioketene S-Oxide (2). A. With Monoperphthalic Acid.—A 1.0-g (±2%) sample of thioketene **1c** was diluted with 10 ml of anhydrous ether and an 11.2% solution of monoperphthalic acid in ether[14] was added dropwise until the purple color disappeared. This oxidation required 9.47 ml of solution (0.99 equiv of monoperphthalic acid). A duplicate run required 1.06 equiv. Glpc indicated only one significant product and no starting material. The ethereal solution was filtered and then washed with sodium bicarbonate solution to remove by-product phthalic acid. The solution was dried over $MgSO_4$, and the solvent was removed. Analysis of the residue by glpc indicated that the product was approximately 98% one component. Pure **2**, mp 34–35°, was obtained by low-temperature recrystallization from pentane or by preparative glpc: uv max (cyclohexane) 330 mμ (log ε 2.80), 315 (2.88), 251 (4.13), 210 (4.72); mass spectrum (70 eV) *m/e* (rel intensity) 57 (100), 130 (27), 41 (24), 115 (15), 29 (14), 113 (12), 186 (1, parent).

Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74; S, 17.21. Found: C, 64.62; H, 9.59; S, 17.37.

B. With Hydrogen Peroxide.—A mixture of about 0.1 ml of di-*t*-butylthioketene (**1c**), 0.1 ml of 30% hydrogen peroxide, and 0.6 ml of methanol was allowed to stand at room temperature with occasional shaking. The purple color disappeared after 6 days. Glpc indicated substantially complete conversion into one product having the same retention time as **2**. The compound was isolated by glpc, and its identity was confirmed by comparison of the infrared and mass spectra with those of the product obtained by oxidation of **1c** with monoperphthalic acid. Analysis of the reaction mixture by glpc indicated that it had not changed after standing 1 month.

Addition of Methanol to Thioketene (1c).—Di-*t*-butylthioketene (**1c**) (about 0.3 g or 1.7 mmol) was mixed with two volumes of methanol and allowed to stand 1 day at room temperature. Glpc indicated that no reaction had occurred. A trace of 12 *M* hydrochloric acid was added. After 1 week, the purple color had disappeared and glpc indicated substantially complete conversion to one product. The mixture was diluted with ether and dried over $MgSO_4$, and the solvent was removed under reduced pressure without heating. Th product, O-methyl di-*t*-butylthioacetate (**3a**), was purified by preparative glpc. The proposed structure was supported by infrared absorptions at 2950, 1395, 1366, 1242, 1185, and 1121 cm^{-1} and mass spectrum (70 eV) *m/e* (rel intensity) 131 (100), 57 (75), 146 (42), 41 (19), 202.1401

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[13] Melting points were taken on a Thomas–Hoover melting point apparatus in open capillary tubes and are corrected. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 505 instrument. Infrared spectra were determined with Perkin-Elmer 421 and 137 spectrophotometers with potassium bromide pellets of solids and with neat samples of liquids on sodium chloride plates. Mass spectra were recorded on a Consolidated Engineering Type 21-620 instrument. Nmr spectra were obtained using a Varian A-60 spectrometer, except for the spectra of **3a–b** and **4**, for which a Varian HA-100 instrument was used.

[14] G. B. Payne, *Org. Syn.*, **42**, 77 (1962).

(16, calcd for parent 202.1391), 99 (13). The nmr spectrum is described in the discussion section.

When the experiment was repeated with methanol-*d*, the infrared spectrum of the product contained a closely spaced doublet at 2160 cm^{-1} which was attributed to the C–D stretching vibration of deuterium attached to carbon atom 2 of the ester.

Anal. Calcd for $C_{11}H_{22}OS$: C, 65.29; H, 10.96; S, 15.85. Found: C, 65.33; H, 10.72; S, 15.63.

Addition of Ethyl Alcohol to Thioketene 1c.—A mixture of 1 g (5.9 mmol) of di-*t*-butylthioketene (**1c**), 5 ml of absolute ethyl alcohol, and 1 drop of 12 *M* hydrochloric acid was refluxed under nitrogen for 1.5 hr. The reaction mixture was cooled and the solvent was removed under vacuum (0.5 mm) without heating. Glpc on two columns indicated that the resulting pale orange-pink oil was at least 95% pure. This product, O-ethyl di-*t*-butylthioacetate (**3b**), was purified by preparative glpc. The structure assignment was supported by infrared absorptions at 2953, 1391, 1357, 1237, 1172, and 1144 cm^{-1} and by mass spectrum (70 eV) *m/e* (relative intensity) 145 (100), 57 (43), 160 (34), 216.1555 (18, calcd for parent 216.1548), 117 (14), 41 (8). The nmr spectrum is described in the discussion section.

Anal. Calcd for $C_{12}H_{24}OS$: C, 66.61; H, 11.18; S, 14.82. Found: C, 66.74; H, 11.19; S, 15.10.

Addition of Aniline to Thioketene 1c.—There was no evidence of reaction after a mixture of 1 g (5.9 mmol) of di-*t*-butylthioketene (**1c**) and 10 g (108 mmol) of aniline had been refluxed for 1 hr under nitrogen. One drop of concentrated sulfuric acid was added and reflux was continued for 3 hr. At the end of this time, glpc indicated that all but traces of **1c** had reacted, giving mainly one product. The mixture was cooled, diluted with ether, and washed thoroughly with dilute hydrochloric acid and finally with water. The ethereal solution was dried over $MgSO_4$ and concentrated. The residue was recrystallized from cyclohexane to afford 0.79 g of pale yellow needles, mp 130–131.5°. A second crop was obtained, giving total yield of 0.88 g (57%) of di-*t*-butylthioacetanilide (**4**), mp 130–131° after further recrystallization from cyclohexane and hexane. The nmr spectrum ($CDCl_3$) consisted of a methyl singlet at 1.26 ppm (18 H), a methynyl singlet at 2.29 ppm (1 H), and an aromatic multiplet at 7.07–7.55 ppm (5 H). The broad N–H peak at ~8.2–8.8 ppm was not integrated. Results of a more detailed study of the nmr spectrum of an *o*-dichlorobenzene solution of this compound are given in the discussion section. The structural assignment was also supported by infrared absorptions at 3165, 1524, 1295, 1135, 755, and 697 cm^{-1}[15] and by mass spectrum (70 eV) *m/e* (relative intensity) 214 (100), 77 (18), 229 (17), 158 (16), 57 (14), 41 (14), 191 (10), 263 (0.4, parent).

Anal. Calcd for $C_{16}H_{25}NS$: C, 72.95; H, 9.57; N, 5.31; S, 12.17. Found: C, 72.91; H, 9.72; N, 5.44; S, 12.17.

Registry No.—**1c**, 16797-75-4; **2**, 16797-76-5; **3a**, 16797-77-6; **3b**, 16797-70-9; **4**, 16797-78-7.

Acknowledgment.—We thank Dr. E. Bright Wilson, Jr., for a helpful discussion of the nmr spectra of **3a**, **3b**, and **4**, and for suggestions that evidence for the existence of rotamers in **3a** might be observed in the infrared spectrum of the reaction product of **1c** with methanol-*d*.

[15] These are consistent with the thioamide absorptions reported by K. A. Jensen and P. H. Nielsen, *Acta Chem. Scand.*, **20**, 597 (1966).

Synthesis and Photoisomerization of the Stereoisomeric 1,4-Dichlorospiropentanes[1]

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Reduction of 1,1,4,4-tetrachlorospiropentane has afforded *syn*- and *anti*-1,1,4-trichlorospiropentanes, which have been distinguished by their dipole moments. Further reduction of the trichlorospiropentanes has yielded the *syn,syn*-, *syn,anti*-, and *anti,anti*-1,4-dichlorospiropentanes, whose configurations have been assigned from the configurations of the trichlorides which yield them. Photolysis in the gas phase of individual dichlorides has produced interconversion of *syn,syn* with *syn,anti* and *anti,anti* with *syn,anti* presumably by a bond-breaking and reformation process. The direct interconversion of *syn,syn* with *anti,anti*, expected if the excited states have planar carbon skeletons, has not been observed, but a competing polymerization process has made it impossible to determine whether any electronically excited states return to ground state prior to chemical reactions.

Spiropentane (1) has long been known to have a structure with a perpendicular arrangement of the two rings,[2] but a recent extended Hückel molecular orbital calculation by Hoffmann[3] has ledt o the prediction that the lowest electronically excited states of spiropentane prefer a geometry with all carbons coplanar. Excitation should thus lead to relative rotation of the two rings, and such rotation might be demonstrable in appropriately substituted spiropentanes because of the stereoisomerization that would result if the excited states return to spiropentanes. We report here one such test.

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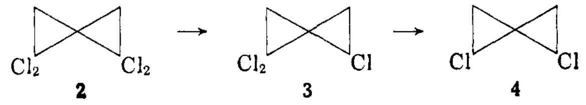
1,1,4,4-Tetrachlorospiropentane (2) was prepared from allene, ethyl trichloroacetate, and sodium methoxide (method of Parham and Bhausar[4]). The infrared and nmr spectra agreed with those reported by Seyferth[5] for 2.

Compound 2 was reduced with tri-*n*-butyltin hydride to a mixture of *syn*- and *anti*-1,1,4-trichlorospiropentanes (**3a** and **3b**, respectively) and *syn,syn*-, *syn,anti*-, and *anti,anti*-1,4-dichlorospiropentanes (**4a**, **4b**, and **4c**, respectively). A very small amount of chlorospiropentane[6] was also formed. Compounds **3a** and **3b** were formed in a ratio of 1:2.9; **4a**, **4b**, and **4c** were formed in a ratio of 0.3:1.6:1. The ratio of trichlorides to dichlorides depended upon the ratio of reagents used, but, within each group, the ratio of isomers was nearly constant over a 100-fold variation of the ratio of tri-*n*-butyltin hydride to 2. The trichlorides and dichlo-



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[1] Abstracted from the Ph.D. Thesis of E. G. Alley, University of Illinois, 1968.

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