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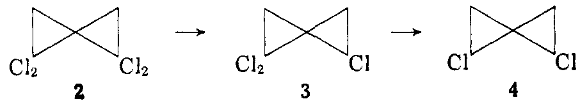
1,1,4,4-Tetrachlorospiropentane (2) was prepared from allene, ethyl trichloroacetate, and sodium methoxide (method of Parham and Bhausar[4]). The infrared and nmr spectra agreed with those reported by Seyferth[5] for 2.

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-



2 3 4

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

[2] J. Donohue, G. L. Humphrey, and V. J. Schomaker, *J. Amer. Chem. Soc.*, **67**, 332 (1945).

[3] R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965).

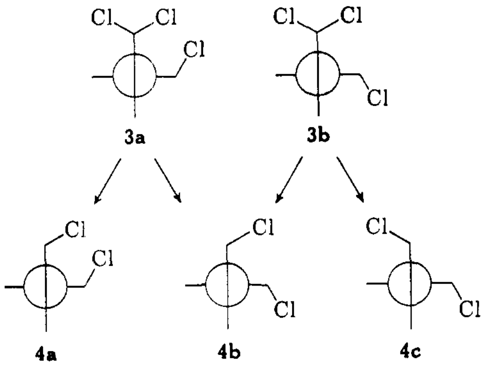
[4] W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, **29**, 1575 (1964).

[5] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

[6] D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *ibid.*, **82**, 2368 (1960).

rides were analyzed and separated preparatively by glpc.

The dipole moments of the two trichlorides were found to be 1.27 and 3.04 D. The calculated moment for the *anti* isomer is 1.04 D, and that for the *syn* isomer is 3.38 D. The isomer with the moment 1.27 D was therefore assigned the *anti* geometry (**3b**). The configurations of the dichlorides were assigned from the facts that one (**4a**) was formed from reduction of **3a** only, one (**4b**) from both **3a** and **3b**, and one (**4c**) from **3b** only. The nmr spectra of the dichlorides all showed multiplets for $-CHCl-$ and $-CH_2-$ at δ 3.4–3.6 and 1.1–1.8, respectively, in the expected 1:2 ratios.



An alternative method of reduction of **2** was treatment with *t*-butyllithium in pentane at −110°, followed by addition of isobutyl alcohol. The same products were obtained, but the **3b**/**3a** ratio was just 1.3, and the dichlorides **4a**, **4b**, and **4c** were in the ratio 1.5:2.2:1. This method was therefore the more favorable one for the preparation of the *syn,syn* isomer (**4a**).

If the lowest lying excited electronic states of the dichlorospiropentanes have a geometry with all carbons coplanar, and if the excited states return to ground states of 1,4-dichlorospiropentanes, then isomers **4a** and **4c** should interconvert upon irradiation while isomer **4b** should show no reaction.[7] An important concern, of course, is that the chlorine substituents may have perturbed the spiropentane system in such a way as to change the lowest excited-state geometry, and another possible difficulty is photochemistry involving C–Cl bond breaking. Hope that the experiments would not be rendered invalid for either of these reasons was found in the fact that chlorine substitution does not significantly affect the ultraviolet spectrum of spiropentane, which consists of end absorption only. At 254 mμ, the liquid phase extinction coefficients of spiropentane, 1,4-dichlorospiropentane (mixed **4b** and **4c**), and tetrachlorospiropentane (**2**) are 0.4, 0.5, and 0.4, respectively.

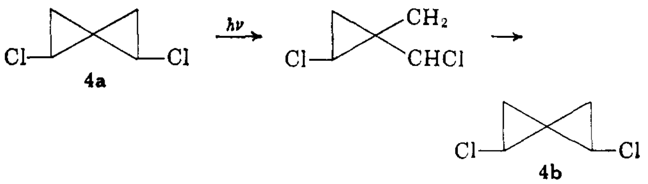
Photochemical studies of the 1,4-dichlorospiropentanes were made by both sensitized and direct methods. Sensitization was attempted by irradiation of benzene solutions of **4a** and **4c** with 2537-Å light. Benzene has been used to sensitize the isomerization of 1,2-dimethylcyclopropanes.[8] No evidence was found for any isomerization, nor did the amounts of dichlorides present diminish by other reactions. No conclusion can be drawn regarding the geometry of the spiropentane triplet, since it was not possible to show that any energy transfer had occurred.

Direct photochemical studies of **4a**, **4b**, and **4c** were carried out in the gas phase, because of the low extinction coefficients and hence serious problems with solvent absorption. A zinc resonance lamp, which has 46% of its output at 2138 Å,[9] was used as the light source to take advantage of the improved extinction coefficients at lower wavelength (ε 8 at 2150 Å for a mixture of **4b** and **4c** in the liquid phase). Ammonia was used as a chemical actinometer to measure quantum yields.[10]

When **4c** was irradiated in the gas phase until 22% of it had disappeared, mainly by formation of a polymer, a 9% conversion into **4b** was observed. No **4a** could be detected. Likewise, **4a** irradiated until 36% had disappeared gave a 1% conversion into **4b**, but no **4c**. Finally, **4b** was photolyzed to give 3% **4c** and 0.2% **4a**. The pattern of isomers formed is thus exactly contrary to the predictions of extended Hückel theory.

The measurement of quantum yields was complicated greatly by the polymer, which in every case quickly coated the walls of the photolysis chamber, restricting the transmission of light. It was possible to show, nevertheless, that both **4a** and **4c** formed polymer with quantum yields considerably above one. The unfortunate consequence is that it cannot be concluded that any electronically excited dichlorospiropentane molecules returned to ground-state dichlorospiropentanes. Hence, the absence of interconversion of **4a** and **4c** does not rule out the planar excited state predicted by Hoffmann.

The isomerization observed could have involved a secondary chain process, such as chlorine atom transfers.[11] Another possible path, perhaps more likely in view of existing precedent,[12,13] is photochemical cleavage of the 1,2 bond, followed by reclosure of the ring.



Experimental Section[14]

1,1,4,4-Tetrachlorospiropentane.—To a stirred mixture of 10.8 g (0.2 mol) of sodium methoxide and 4.0 g (0.1 mol) of allene in 50 ml of dry olefin-free pentane at 0–15° was added 38.2 g (0.2 mol) of ethyl trichloroacetate in 50 ml of pentane over a period of 0.5 hr. The temperature was maintained at about 10° for 1 hr, and then the mixture was stirred at room temperature for 3 hr. After this time 16.4 g (0.3 mol) of sodium methoxide was added and the mixture cooled to 0°. Ethyl trichloroacetate (57.3 g, 0.3 mol) was added over a period of 0.5 hr, and the temperature maintained at 5–15°. The temper-

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[7] A single enantiomer of **4b** would show racemization.

[8] J. A. Bell, *J. Amer. Chem. Soc.*, **87**, 4966 (1965).

[9] T. A. Cutting, "Manual of Spectroscopy," Chemical Publishing Co., New York, N. Y., 1949, p 185.

[10] E. O. Wiig, *J. Amer. Chem. Soc.*, **57**, 1559 (1935).

[11] J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 3939 (1965).

[12] G. R. De Mare, L. G. Walker, O. P. Strausz, and H. E. Gunning, *Can. J. Chem.*, **44**, 457 (1966). These authors interpret the photosensitized rearrangement and decomposition of spiropentane in terms of initial cleavage of the 1,3 bond, but their results seem equally consistent with initial 1,2 cleavage.

[13] J. J. Gajewski, *Chem. Commun.*, 920 (1967).

[14] Microanalyses were done by Mr. Josef Nemeth and associates. Nmr spectra were recorded on a Varian Model A-60 instrument; infrared spectra on Perkin-Elmer Models 137, 237, and 521; and ultraviolet spectra on Bausch and Lomb Model 505 and Cary Model 15 spectrophotometers.

ature was then maintained at 10-15° for 1 hr and then the mixture stirred at room temperature for 3 hr. Water (100 ml) was added and this mixture stirred with 80 g (2.0 mol) of sodium hydroxide in 500 ml of water for 2 hr, at reflux temperature. The pentane layer was removed and dried. Distillation of the dried solution yielded 10.0 g (50%) of a colorless liquid, bp 43-44° (1.8 mm). This material was shown by glpc (10% Apiezon L on Anakrom ABS at 150°) to be 98% 1,1,4,4-tetrachlorospiropentane.

Runs up to twice the size of this one were successful. During the addition of the ethyl trichloroacetate, an exothermic reaction occurred and in the larger runs the temperature was more difficult to control. If the temperature exceeded 20°, the reaction was uncontrollable.

The product from these syntheses was further purified by preparative glpc (20% Apiezon L on Chromosorb P). The flow rate was 75-100 ml/min. The first 20 min of each peak, when 0.5-ml injections were made, was not collected. The refractive index of this purified material was $n^{28}\text{D}$ 1.5014 (lit.[5] $n^{24}\text{D}$ 1.5447).

Reduction of 1,1,4,4-Tetrachlorospiropentane.[15]—A solution of 8.24 g (0.04 mol) of 1,1,4,4-tetrachlorospiropentane and 14.00 g (0.048 mol) of tri-*n*-butyltin hydride was heated at 135-140° for 30 min. Distillation of the reaction mixture yielded 3.4 g, bp up to 45° (2 mm), and 2.3 g, bp 45-60° (2 mm). The two fractions were separated by glpc (20% tricresyl phosphate on Chromosorb P at 125°) into *anti,anti*- and *anti,syn*-1,4-dichlorospiropentanes (**4c** and **4b**), *anti*-1,1,4-trichlorospiropentane (**3b**), *syn,syn*-1,4-dichlorospiropentane (**4a**), and *syn*-1,1,4-trichlorospiropentane (**3a**), in that order of elution. The retention times at a flow rate of 60 ml/min were 19, 21, 26, 43, and 69 min, respectively.

Anal. Calcd for $C_5H_6Cl_2$: C, 43.79; H, 4.38. Found for a mixture of **4b** and **4c**: C, 43.86; H, 4.48. Found for **4a**: C, 44.01; H, 4.53. Calcd for $C_5H_5Cl_3$: C, 34.98; H, 2.92. Found for **3b**: C, 35.28; H, 2.92. Found for **3a**: C, 35.09; H, 2.99.

Infrared and nmr spectra are recorded elsewhere.[1] Infrared bands of particular value for identification (medium or strong bands below 1000 cm^{-1} in CCl_4) are as follows: **4a**, 645, 687, 835, 927, and 978 cm^{-1}; **4b**, 655, 681, 840, 888, 911, 937 and 963 cm^{-1}; **4c**, 654, 861, 882, and 929 cm^{-1}; **3a**, 659, 840, 891, 930, and 948 cm^{-1}; **3b**, 678, 870, and 916 cm^{-1}.

Dipole Moments of the Two 1,1,4-Trichlorospiropentanes.—The measurements were all made at 293°K. The solutions used to obtain the dielectric constant data were in benzene which had been purified by partially freezing it three times and then passing this benzene through a column of molecular sieves immediately before its use. The slope of the line obtained when a plot of mole fraction *vs.* dielectric constant was made for the *anti*-trichloride was 1.4 and for the *syn*-trichloride 12.4. The slope of the line obtained when the density of these solutions was plotted *vs.* mole fraction of trichloride was for the *anti*-trichloride 0.26 and for the *syn*-trichloride 0.25. The refractive index for the *anti*-trichloride was 1.4950 and for the *syn*-trichloride 1.5025. The density of the *anti*-trichloride was 1.333 g/cm^3, and for the *syn*-trichloride 1.366 g/cm^3. From these data and the known values for the dielectric constant,[16] molecular weight, and density of benzene the dipole moments were calculated. These calculated values were for the *anti*-trichloride $\mu = 1.270$ and for the *syn*-trichloride $\mu = 3.040$.

Reduction of ***anti*-1,1,4-Trichlorospiropentane.**—*anti*-1,1,4-Trichlorospiropentane (100 μl) and 220 μl of tri-*n*-butyltin hydride in a tube made by sealing both ends of a 6-in. piece of 5-mm Pyrex tubing were heated in an oil bath at 140° for 1 hr. The glpc retention times of the components of this mixture were compared with the retention times of the three 1,4-dichlorospiropentanes from reduction of **2**. The mixture contained only the first two dichlorides in order of elution, in the ratio 1:0.9. The second was collected and further identified by its infrared spectrum.

Reduction of ***syn*-1,1,4-Trichlorospiropentane.**—The reduction of the *syn*-trichloride was accomplished exactly as with the *anti* isomer. Glpc showed that only the second and third dichlorospiropentanes in order of elution were present, in the ratio 2.8:1. The first of these was collected and further identified by its infrared spectrum.

Reduction of 1,1,4,4-Tetrachlorospiropentane with *t*-Butyllithium.—To a stirred solution of 2.06 g (0.01 mol) of 1,1,4,4-tetrachlorospiropentane in 80 ml of tetrahydrofuran, 20 ml of ether and 20 ml of pentane at −110°, under an argon atmosphere, was added 20 ml (0.032 mol) of a 1.59 *M* solution of *t*-butyllithium in pentane at a rate such that the temperature did not exceed −100°. The solution was stirred 1 hr at −100 to −110° and then 20 ml of isobutyl alcohol was added at −110°. The solution was washed five times with water and the organic layer dried with sodium sulfate. The solution was analyzed by glpc. Retention times were used to identify the various components. The analysis showed that *anti,anti*-, *anti,syn*-, and *syn-syn*-1,4-dichlorospiropentanes and *anti*- and *syn*-1,1,4-trichlorospiropentanes were in the ratio 2.1:4.6:3.4:1.3:1.0 in this mixture.

After the solvents were removed, preparative glpc yielded 199 mg of a mixture of *anti,anti*- and *anti,syn*-1,4-dichlorospiropentanes, 77 mg of *syn,syn*-1,4-dichlorospiropentanes, and 48.5 mg of *anti*-1,1,4-trichlorospiropentane.

Photolysis of 4a and 4c in Benzene.—A solution of 23.3 mg of *syn,syn*-1,4-dichlorospiropentane, 6.6 mg of *n*-decane, and 0.5 ml of benzene was prepared. This mixture was irradiated at 2537 Å for 3 hr in a Srinivasan-Griffin reactor. Potassium ferrioxalate actinometry showed that an average of 2.6 × 10^{16} photons/sec passed through the reactor. The reaction mixture was analyzed by glpc initially and after 3 hr. No peaks were observed in the 3-hr sample that were not present in the 0-hr sample. The glpc analysis showed that 101% of the *syn,syn*-1,4-dichlorospiropentane was still present after 3 hr of irradiation.

In a similar experiment, the photolysis of *anti,anti*-1,4-dichlorospiropentane in benzene, for 8 hr, caused no change in the composition of the mixture as determined by glpc.

Gas Phase Photolysis of 4a, 4b, and 4c.—The photolysis chamber was a cylindrical quartz vessel with an axial hole for insertion of the zinc resonance lamp (Phillips 93196E, 25 W). Surrounding the chamber externally was a concentric cylindrical chamber for the ammonia actinometer.[10] Both chambers were connected to a high-vacuum system, which permitted efficient transfers of materials into and out of the chambers and accurate measurement of the nitrogen and hydrogen produced in the photolysis of ammonia. Details of the apparatus and its use are reported elsewhere.[1]

Each sample was purified before photolysis by treatment of a cyclohexane solution of the compound with 1% alkaline potassium permanganate solution for 15-20 min at 0°, followed by preparative glpc (20% Apiezon L on Chromosorb P at 150°). After introduction into the high-vacuum system, each sample was degassed by three freeze-thaw-pump cycles, with Dry Ice and isopropyl alcohol used as the freezing mixture.

In all cases, accurate measurements of light absorbed by the spiropentanes were made very difficult by the rapid formation of a polymer on the walls of the reaction chamber. As a result, it was necessary to measure the light passing through the empty (pumped down) chamber before, after, and even in the middle of a run to obtain an effective light intensity, from which the light absorbed could be estimated by comparison with actinometric measurements made during photolysis (*i.e.*, with spiropentane in the photolysis chamber).

The best datum obtained on **4c** was a quantum yield of at least 8 for disappearance of **4c** in a run in which 38 ± 7% of the **4c** had disappeared (glpc analysis) to form 7.5 ± 0.7% of **4b** and about 30% of polymer (measured by difference). The implied quantum yield of greater than 1 for formation of **4b** is not to be accepted without reservation, in view of the large errors introduced by the polymer formation. In photolysis of **4a**, a quantum yield of at least 4.1 was observed for disappearance of **4a** in a run in which 36 ± 4% of the **4a** was consumed and about 1% of **4b** was formed.

Registry No.—**3a**, 16717-31-0; **3b**, 16717-32-1; **4b**, 16717-34-3; 1,1,4,4-tetrachlorospiropentane, 3781-45-1.

Acknowledgment.—This work was supported in part by the National Science Foundation and in part by the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund.

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[15] D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

[16] R. Mecke and K. Rosswog, *Z. Electrochem.*, **60**, 47 (1956).