# Synthesis, Chemistry, and Spectroscopic Properties of Spiro[3.3]hepta-1,5-diene

L. A. Hulshof and Hans Wynberg*

Contribution from the Department of Organic Chemistry, The University, Zernikelaan, Groningen, The Netherlands. Received August 28, 1973

Abstract: Three syntheses of spiro[3.3]hepta-1,5-diene (1) are described: (a) pyrolysis of spiro[3.3]heptane-2,6-bis(trimethylammonium) hydroxide in a Hofmann elimination, (b) heating the amine oxide 14 of spiro[3.3]heptane-2,6-bis(dimethylamine) (8), and (c) a Norrish type II photochemical reaction of spiro[3.3]heptane-2,6-bis(aceto-phenone) (15). Optically active Fecht acid (6) has been used for the preparation of racemic spirocycle 1 *via* the Hofmann elimination process. An attempt was made to prepare optically active spiro olefin 1 from enantiomeric spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic acid (16). Spiro acid (6) was converted into the unsaturated analog of Fecht acid (16) which was resolved. The spectroscopic data (pmr, uv, and mass spectra) of spiro[3.3]hepta-1,5-diene (1) are discussed. Theoretical calculations (LAME, CNDO/2, simple Hückel) have been performed in order to elucidate the conformation of 1 and to explain the considerable spiroconjugative interaction in 1.

In recent years several examples of unsaturated dissymmetric spiranes have been described.[1-6] Spirocyclic molecules consist of two perpendicular rings joined by a common atom of tetrahedral geometry. Interest has been concentrated chiefly on those systems in which unsaturated units are in homoconjugation through the spiro atom. This unique situation has provoked detailed theoretical studies of π-electron delocalization (spiroconjugation,[7] spiroaromaticity[8]). Unsaturated spiranes have the ideal property of holding π systems locked in a well-defined orientation. The interaction of the π systems in the specific orientations for spiro[3.3]hepta-1,5-diene (1) prompted us to investigate its spiroconjugative characteristics, its chiroptical properties, and its absolute configuration.[8d] Other representatives of the class of compounds consisting of a dissymmetric, homoconjugated, rigid, spiro-linked 1,4-diene system have been prepared, *i.e.*, compounds 2,[1-3] 3,[5] 4,[9] 5,[6] of which 2 and 5b were recently obtained
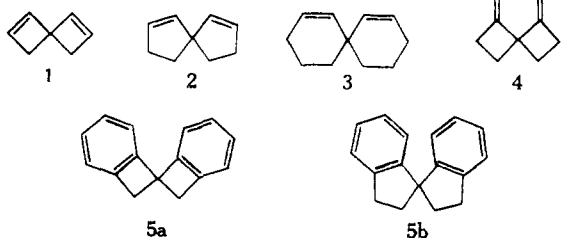
in their enantiomeric forms and to which an absolute configuration could be assigned.[1,2,6b] All of these

chiral compounds possess chromophores with C_2 symmetry. In the present work[10] we report three different syntheses of 1. In addition, the thermal isomerization as well as the spectroscopic properties of this spirene are discussed.
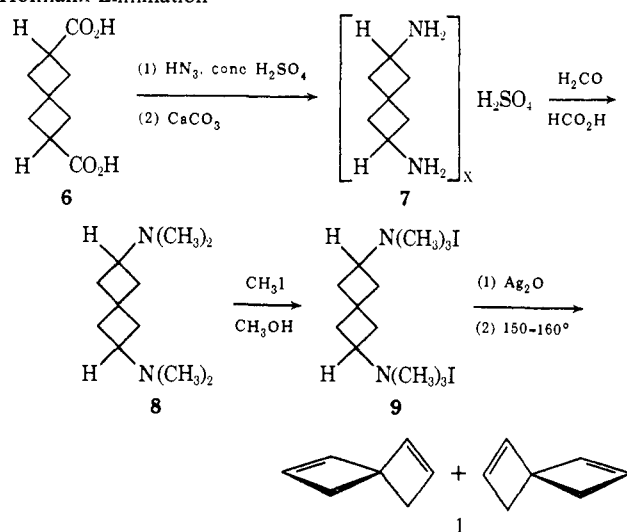
Synthesis

In our preliminary communication[11] we reported the preparation of spiro[3.3]hepta-1,5-diene by a Hofmann exhaustive methylation process[12] as outlined in Scheme I. This reaction sequence was essentially the same as that used by Cram and van Duuren[3] in the preparation of spiro[4.4]nona-1,6-diene and by Roberts and Sauer[13] in the synthesis of cyclobutene. Starting with the preparation and resolution of *dl*-spiro[3.3]heptane-2,6-dicarboxylic acid 6 (Fecht acid), according to Backer and Schurink's method,[14,15] we obtained the racemic and *d* isomer of the sulfate (7) of spiro[3.3]heptane-2,6-diamine from racemic and *l*-Fecht acid in a slightly modified procedure of Janson and Pope.[16] The Leuckart reaction (Eschweiler-Clark procedure)[17] applied to this racemic and *d*-7 furnished *dl*- and *l*-spiro[3.3]heptane-2,6-bis(dimethylamine) (8). Quaternization of this tertiary amine (8) by methiodation afforded racemic and *d*-spiro[3.3]heptane-2,6-bis(dimethylamine) dimethiodide (9) almost quantitatively. Treatment of the racemic and *d* salt with an aqueous suspension of silver oxide, followed by pyrolysis of the product at 150–160° (50 mm), gave optically inactive spiro[3.3]hepta-1,5-diene

(1) H. Gerlach and W. Müller, *Helv. Chim. Acta*, **55**, 2277 (1972).

(2) G. D. Christiansen, Thesis, UCLA, 1971.

(3) D. J. Cram and B. L. van Duuren, *J. Amer. Chem. Soc.*, **77**, 3576 (1955).

(4) W. Baker and J. C. McGowan, *J. Chem. Soc.*, 347 (1938).

(5) H. Gerlach, T. Thi-Huong, and W. Müller, *J. Chem., Soc., Chem. Commun.*, 1215 (1972).

(6) (a) M. P. Cava and J. A. Kuczkowski, *J. Amer. Chem. Soc.*, **92**, 5800 (1970); (b) J. H. Brewster and R. T. Prudence, *ibid.*, **95**, 1217 (1973); R. K. Hill and D. A. Cullison, *ibid.*, **95**, 1229 (1973).

(7) (a) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); (b) R. Boschi, A. S. Dreiding, and E. Heilbronner, *ibid.*, **92**, 123 (1970).

(8) (a) R. Hoffmann, A. Imamura, and G. D. Zeiss, *J. Amer. Chem. Soc.*, **89**, 5219 (1967); (b) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971); (c) A. Tajiri and T. Nakajima, *Tetrahedron*, **26**, 6089 (1971).

(8d) Note Added in Proof. The spirodiene 1 has now been resolved (L. A. Hulshof and H. Wynberg, submitted for publication).

(9) B. Weinstein and A. H. Fenselau, *J. Chem. Soc. C*, 368 (1967).

(10) Since some spiranes are classified as aviation fuels it would be of interest to test the combustion properties of our diene: (a) T. B. McCulloch, *Chem. Abstr.*, **41**, P 1091d (1947); (b) E. R. Buchman, J. C. Conly, D. H. Deutsch, W. G. Finnegan, G. J. Fujimoto, H. L. Herzog, D. R. Howton, M. Madoff, and H. M. Walborsky, "The Preparation of Spirane Hydrocarbons Containing the Cyclobutane Ring," N 60 nr-244 (XI), Technical Report, Gates and Crellin Laboratories of Chemistry, California Institute of Technology.

(11) J. P. M. Houbiers, L. A. Hulshof, and H. Wynberg, *Chem. Commun.*, 91 (1969).

(12) A. C. Cope and E. R. Trumbull, *Org. React.*, **11**, 317 (1960).

(13) J. D. Roberts and C. W. Sauer, *J. Amer. Chem. Soc.*, **71**, 3925 (1949).

(14) H. J. Backer and H. B. J. Schurink, *Proc. Kon. Ned. Akad. Wetensch.*, **37**, 384 (1928); *Recl. Trav. Chim. Pays-Bas*, **50**, 921 (1931).

(15) H. Wynberg and J. P. M. Houbiers, *J. Org. Chem.*, **36**, 834 (1971).

(16) S. E. Janson and W. J. Pope, *Proc. Roy. Soc., Ser. A*, **154**, 53 (1936).
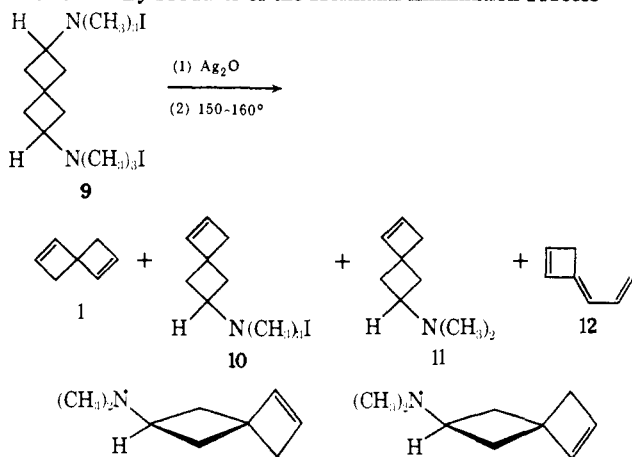
(17) M. L. Moore, *Org. React.*, **5**, 301 (1949).

(1) in yields varying between 39 and 58%. Preparative gas chromatography allowed purification of dl-1.

Scheme I. Synthesis of dl-Spiro[3.3]hepta-1,5-diene via Hofmann Elimination

H CO₂H
(1) HN₃, conc H₂SO₄
(2) CaCO₃
H CO₂H
6

[H NH₂ / H NH₂]ₓ
7

H₂SO₄
H₂CO
HCO₂H

H N(CH₃)₂
CH₃I
CH₃OH
H N(CH₃)₂
8

H N(CH₃)₃I
(1) Ag₂O
(2) 150-160°
H N(CH₃)₃I
9

+
1

After considerable effort we were able to isolate small amounts of the following unsaturated by-products which comprised approximately 10% of the product mixture: 6-trimethylammoniumspiro[3.3]hept-1-ene iodide (**10**), presumably cis and trans, 6-dimethylaminospiro[3.3]hept-1-ene (**11**), probably cis and trans, and allylidenecyclobutene (**12**), as shown in Scheme II.

Scheme II. By-Products of the Hofmann Elimination Process

H N(CH₃)₃I
(1) Ag₂O
(2) 150-160°
H N(CH₃)₃I
9

+
1

+
H N(CH₃)₃I
10

+
H N(CH₃)₂
11

+
12

(CH₃)₂N
H

(CH₃)₂N
H

The structural assignments of **10** and **11** were based on their spectroscopic properties, principally their pmr and mass spectra, respectively. The formation of **10**, the salt of which appeared on the bottom of the pyrolysis flask, might be caused by incomplete conversion of **9** with an aqueous suspension of silver oxide. The formation of **11** can be rationalized by assuming incomplete reaction of **8** with methyl iodide. Attempts to convert the partly reacted product **10** into the spiro olefin **1** by repeated treatment with silver oxide and subsequent pyrolysis were unsuccessful. The only product which condensed in the liquid nitrogen trap was an unstable compound, which could not be identified because it polymerized rapidly to a yellow colored film. The structure of allylidenecyclobutene was assigned to compound **12** mainly on the basis of its spectral data. The pmr spectrum showed a doublet for the allylic protons at δ 3.00 (2 H, J = 3.0 Hz) and a broad multiplet for

the vinylic protons at δ 4.9-6.6 (6 H). In the infrared spectrum there appeared absorptions at 1640 (m) and 890 (m) cm⁻¹, due to an exocyclic double bond and 1590 (m) cm⁻¹, consistent with a conjugated olefinic bond. The ultraviolet spectrum of **12** (λ_{max} 254 nm in methanol[18]) could be explained by making assumptions[19] that require red shifts of the various separate moieties. The mass spectral data (parent peak at m/e 92 and base peak at m/e 91) are in agreement with a C_7H_8 isomer.[22] Compound **12** might have arisen from **9** (eq 1)[24] or from **1** (eq 2) by a thermal isomeriza-

(CH₃)₃N
OH
H H
N(CH₃)₃
OH
150-160°
(1)

155°
+ polymer (2)
?
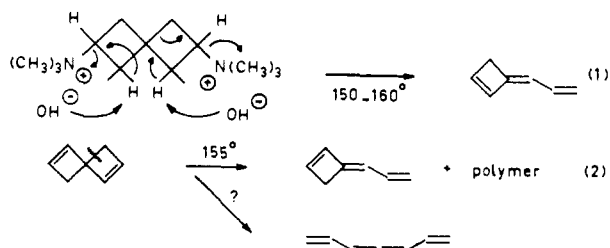
tion in a unique symmetry allowed concerted pathway via electrocyclic opening of the cyclobutene ring.[25,27] Direct evidence was available to support the latter possibility, because **1** also rearranged thermally to **12** under approximately the same conditions (eq 2).[28] Evidence for a further isomerized product (divinylallene)[29] could not be obtained in the latter case, although this isomerization of **1** is an allowed process.[25] However, a polymer could be detected that was different in color from polymerized material arising from **12**.

An attempt to prepare optically active spirene (**1**)

(18) The extinction coefficient could not be determined exactly as consequence of rapid polymerization of the substrate.

(19) 3-Methylenecyclobutene should have an absorption maximum at 218.5 nm, since a maximum at 223.5 nm is reported for 1-methyl-3-methylenecyclobutene.[20] Considering the red shift of 1,3-butadiene with regard to ethylene (32 nm in solution)[21] or the red shift of 1,3,5-hexatriene with regard to 1,3-butadiene (40 nm in solution)[21] and comparing to our case of **12** with respect to 3-methylene cyclobutene, we calculate 250.5 and 258.5 nm, respectively.

(20) F. F. Caserio, S. H. Parker, R. Piccolini, and J. D. Roberts, J. Amer. Chem. Soc., 80, 5507 (1958).

(21) "Organic Electronic Spectral Data," Vol. I, Interscience, New York, N. Y., 1946-1952, pp 27 and 98; Vol. III, 1956-1957, p 3.

(22) Except for the parent peak-base peak ratio (see Table IV), the spectrum was almost identical with the mass spectrum of toluene,[23] which would suggest a rearrangement under electron impact to the tropylium ion (see Experimental Section).

(23) P. N. Rylander, S. Meyerson, and H. M. Grubb, J. Amer. Chem. Soc., 79, 842 (1957).

(24) Analogous to a ring opening in the Chugaev reaction of o-cyclobutyl-S-methylxanthate.[13]

(25) In a personal communication, Professor P. v. R. Schleyer pointed out that the heat of formation of spiro[3.3]hepta-1,5-diene (A), allylidenecyclobutene (B), and divinylallene (C) can be calculated considering the group increments of the different moieties, the strain factor of each molecule, and the resonance contribution. Making use of his values[26] and some estimates, the calculated heats of formation could be obtained and are given below with the three above mentioned contributions in parentheses: A, +89.3 (24.3, 65, 0); B, +73.0 (46.0, 32, −5), and C, +77.0 (83.0, 0, −6) kcal/mol. Knowing these data conclusive evidence is obtained that conversion of spiroheptadiene (A) into allylidenecyclobutene (B) and into divinylallene (C) is thermodynamically feasible, whereas on the contrary divinylallene cannot arise from B. The thermal isomerization experiment seems to support this idea in that sense that the polymer might be the product of the hypothetical intermediate C.

(26) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, J. Amer. Chem. Soc., 92, 2377 (1970).

(27) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969, p 43.

(28) For thermal isomerizations of several substituted cyclobutenes, see D. Dickens, H. M. Frey, and R. F. Skinner, Trans. Faraday Soc., 65, 453 (1969), and earlier papers.

(29) R. Hoffmann, personal communication.

from the *d* isomer of **9** was unsuccessful with only optically inactive **1** being recovered. Optically inactive diene **1** is to be expected if the pyrolysis proceeds *via* 6-trimethylammoniumspiro[3.3]hept-1-ene hydroxide (**13**), which has a plane of symmetry (eq 3).[30]
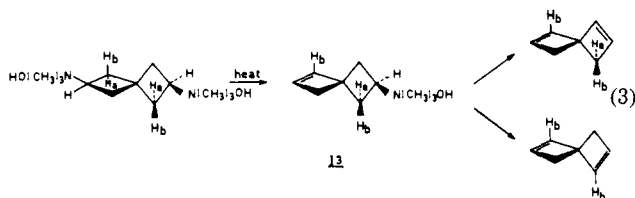
The spirene hydrocarbon (**1**) could be prepared *via* an alternative route according to Scheme III. This

Scheme III. Synthesis of *dl* Diene *via* Cope Elimination
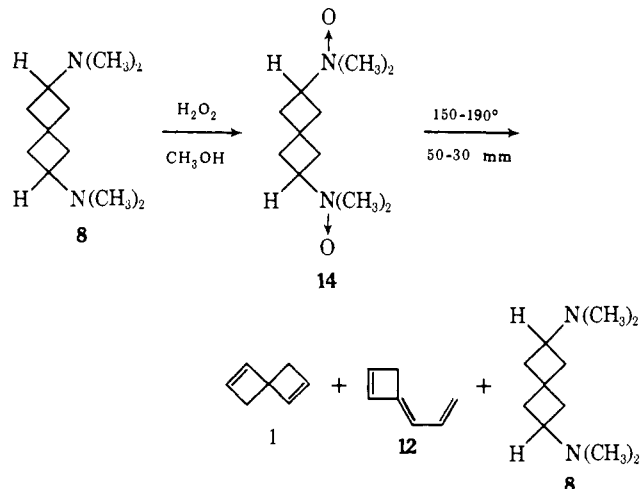
intramolecular cis-elimination process, known as the Cope elimination of amine oxides,[12] afforded a mixture of a ring-opened product (**12**) and predominantly spirene **1** in 4 and 13% yield, respectively. Racemic and *l*-spiro[3.3]heptane-2,6-bis(dimethylamine) (**8**) could be converted into *dl*- and *d*-spiro[3.3]heptane-2,6-bis-(dimethylamine *N*-oxide) (**14**) by a simple quantitative oxidation reaction. By-products **12** and **8** were obtained in better detectable quantities when **1** was prepared by pyrolysis of the amine oxide **14**. Conditions for the latter decomposition had to be more drastic then those during the Hofmann elimination reaction. In this case, both **8** and **12** were identified by their glc retention times. The recovery of the former product was to be expected.[12,13] The latter product was a rather unstable liquid. No Diels–Alder adduct with maleic anhydride[31] could be obtained.

The last route examined to the olefin **1** was achieved *via* a very clean and smooth Norrish type II[33] photolysis of racemic spiro[3.3]heptane-2,6-bis(acetophenone) (**15**) in 28% yield as outlined in Scheme IV. The easy cleavage of the acetophenone moieties is similar to the mode of fragmentation of **15** under electron

(30) If cleavage of the amine fragments would occur in a concerted process by abstraction of the less sterically hindered proton (proton H_a in eq 3), then optically active spirodiene would have been obtained.

(31) Compare the similar experiences of Backer and Strating[32] with the formation of a Diels–Alder adduct of propenylidenecyclohexane and maleic anhydride.

(32) H. J. Backer and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **60**, 391 (1941).

(33) (a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 154; (b) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 382.

Scheme IV. Preparation of *dl*-Spiro Diene *via* Norrish Type II Reaction
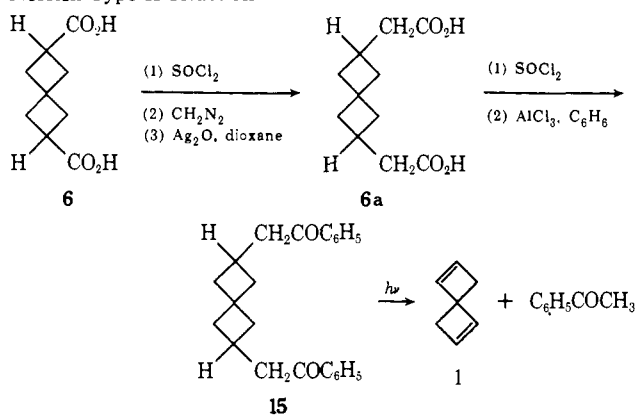
impact in the mass spectrometer (see Experimental Section). The splitting of this appropriately substituted diketone **15** into olefinic and enolic fragments was achieved by a method designed by Neckers, Kellogg, Prins, and Schoustra.[34] The synthesis of the spirocycle **1** by this route makes it clear that the Norrish type II reaction may lend itself to the preparation of some strained systems.[35] The bad overall yield (4% with respect to Fecht acid **6**) of this final route to spirodiene **1** was mainly caused by the low conversion (20–29%) of **6** into spiro[3.3]heptane-2,6-diacetic acid (**6a**) *via* an Arndt–Eistert synthesis.[36] Rice and Grogan[37] obtained the same acid (**6a**) in poor yield by this procedure.

In order to clarify the absolute configuration of spiroheptadiene by correlation with compounds of known absolute configuration,[38] an attempt was made to prepare optically active spirodiene **1** from enantiomeric spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic acid (**16**). Retention of optical activity in the decarboxylation reaction would imply no change in absolute configuration of **1** with regard to **16**, whereas migration of only one double bond would be rather doubtful (eq 4).
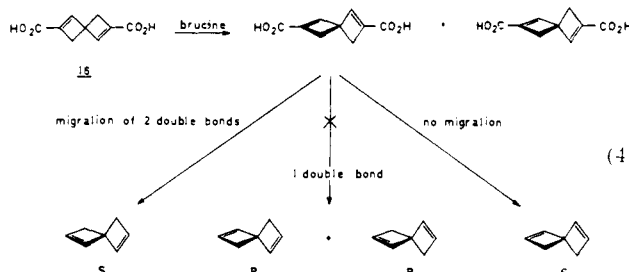
The unsaturated acid **16** is easier to handle than the volatile, relatively stable liquid **1** (bp 71.6° (762 mm)). Therefore, an assignment of the absolute configuration to **16** and **1** would be less complicated, for instance, by conventional X-ray diffraction methods using a heavy atom salt of **16**[39] than by chemical determination of the absolute configuration. The *dl* mixture of **16** could be

(34) D. C. Neckers, R. M. Kellogg, W. L. Prins, and B. Schoustra, *J. Org. Chem.*, **36**, 1838 (1971).

(35) See ref 4 cited in ref 34.

(36) W. E. Bachmann and W. S. Struve, *Org. React.*, **1**, 38 (1942).

(37) L. M. Rice and C. H. Grogan, *J. Org. Chem.*, **26**, 54 (1961).

(38) Destruction of both four-membered rings in spiroheptadiene (**1**) would achieve a transformation of a dissymmetric molecule into a symmetrical one, because of the fact that **1** owes its optical activity only to the nature and the relative position of the two identical cyclobutene rings constituting this spirane system.

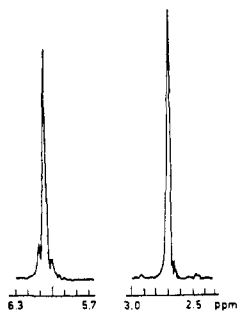(39) An illustrative example in this category is Fecht acid and its barium salt. Manuscript in preparation.
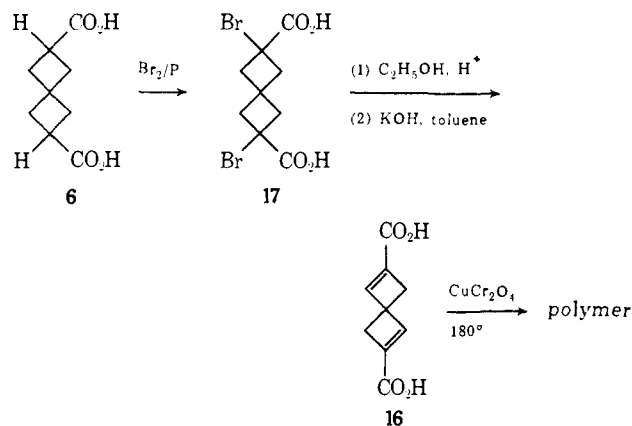
Figure 1. Magnetic resonance spectrum of the diene 1 in carbon tetrachloride at 60 MHz: δ 6.06 (t, $J = 3.1$ Hz, 4 H) and 2.70 (AB quartet, $J = 13, 5$ Hz, $\Delta\nu$ unknown, 4 H).

prepared from Fecht acid in the following manner as outlined in Scheme V. Successively performed bromina-

Scheme V. Synthesis of dl-Spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic Acid

tion and esterification of dl-Fecht acid (6) according to the method of Backer and Kemper[40] furnished racemic diethyl 2,6-dibromospiro[3.3]heptane-2,6-dicarboxylate (18) in 56% overall yield. Kemper[40] failed in his attempt to prepare 16 by dehydrobromination of the acid 17. Using the method of Domnin and Yakovlev[41] (also used by Campbell and Rydon)[42] we succeeded in preparing 16 in 82% yield. The resolution of the dl-acid 16 was accomplished through the formation of a diastereomeric pair of its brucine salts according to a method that Backer, Schurink, and Kemper used for the resolution of the saturated acids 6[14] and 17,[40] respectively. After two fractional recrystallizations of the brucine salt, rotations $[\alpha]_{578}$ $-25.3°$ and $[\alpha]_{578}$ $-23.0°$, respectively, the free acid was obtained from the salt by treatment with ammonia, furnishing resolved dextrorotatory acid 16: $[\Phi]_{578}$ $+15.3°$, $[\Phi]_{546}$ $+17.9°$, and $[\Phi]_{436}$ $+25.4°$ (c 0.7, methanol). The ORD and CD spectra of the d isomer of 16 could be obtained, together with an absorption maximum in the ultraviolet spectrum[43] (223 nm, ϵ 15,600; shoulder at 205

Figure 2. Numbering convention of 1 and cyclobutene.

nm, ϵ 12,100, 96% ethanol). The ORD spectrum showed a plain curve with a strong increase starting at 328 nm to shorter wavelengths and was measurable up to 263 nm. The CD spectrum, however, displayed a positive Cotton effect at 232 nm, $[\theta]$ $+3700$. Further support for the structural assignment of 16 was available from the infrared spectrum, elemental analysis, and comparison of the chemical shifts at 60 MHz. In particular, the difference in these shifts for the vinylic and allylic protons in 16 (δ 6.78, 2.88, CD$_3$OD, respectively) and for the corresponding protons in 1 (δ 6.06, 2.70, CCl$_4$, respectively) is consistent with deshielding due to the presence of the carboxyl group in 16.

However, all efforts[45] to achieve an oxidative decarboxylation of the unsaturated dicarboxylic acid 16 in order to prepare 1 were thwarted by instability of 16 at elevated temperature. A gently heated (to 180°), intimate, and evacuated mixture of copper chromite and 16, on the contrary, was converted into a yellow colored polymer. This polymer could be identified by pmr techniques (deuterated DMSO) as being the same by-product as illustrated in eq 2, suggesting that an intermediate might be the decarboxylated compound 1 which is very unstable under these vigorous reaction conditions.

Nuclear Magnetic Resonance Spectra and Conformation of Spirodiene 1

The initial pmr spectrum of spirene 1 at 60 MHz consisted of two signals, a triplet at δ 6.06 and an apparent singlet at δ 2.70. Spectra taken at higher concentration and gain revealed additional tiny satellites at δ 2.70. The full splitting pattern of both signals is shown in Figure 1. The data in Figure 1 are consistent with the work by Roberts[47] on long-range coupling effects in substituted cyclobutenes and with a more recent study[48] of the pmr spectra of cyclobutenes (Figure 2). Spectra run at 100 MHz confirmed that the triplet at δ 6.06 was a collapsed AB quartet containing fine structure due to the allylic protons as was demonstrated by a decoupling experiment, whereas the "singlet" at δ 2.70 represented a collapsed AB quartet. The experimentally obtained spectrum and the calculated splitting pattern at 100 MHz for the diene 1 are shown in Figure 3 and Table I. Analysis of the

(40) (a) H. J. Backer and H. G. Kemper, Recl. Trav. Chim. Pays-Bas, 57, 761 (1938); (b) H. G. Kemper, Thesis, Groningen, 1937.

(41) N. A. Domnin and J. P. Yakovlev, J. Gen. Chem. USSR, 17, 1899 (1947).

(42) A. Campbell and H. N. Rydon, J. Chem. Soc., 3002 (1953).

(43) A correlation[44] between angle strain (and ring size) and the ultraviolet absorption maximum for endocyclic ring compounds indicated that ring strain shifts the absorption maximum bathochromically.

(44) (a) A. T. Nielson, J. Org. Chem., 22, 1539 (1957); e.g., from the value (216 $\pm$ 5 nm) observed with the unstrained 1-cyclohexene-1-carboxylic acid to approximately 222 nm for the five- and seven-membered endocyclic analogs; (b) E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, J. Chem. Soc., 4073 (1956).
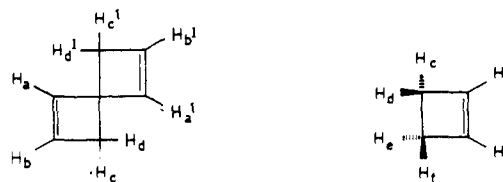
(45) Reagents or reactions failing to give desired product were (a) copper chromite, cupric oxide, copper powder, or lead tetraacetate in a boiling solution of quinoline, (b) soda lime heated to 360°, (c) powdered quartz, (d) intimate mixture of cupric oxide and/or copper with 16, (e) hydrohalogenation of 16 with dried hydrogen bromide and hydrogen iodide and subsequent heating of the sodium salt in order to accomplish an elimination process.[46]

(46) H. J. Lucas and A. N. Prater, J. Amer. Chem. Soc., 59, 1684 (1937).

(47) E. A. Hill and J. D. Roberts, J. Amer. Chem. Soc., 89, 2047 1967), and earlier papers.

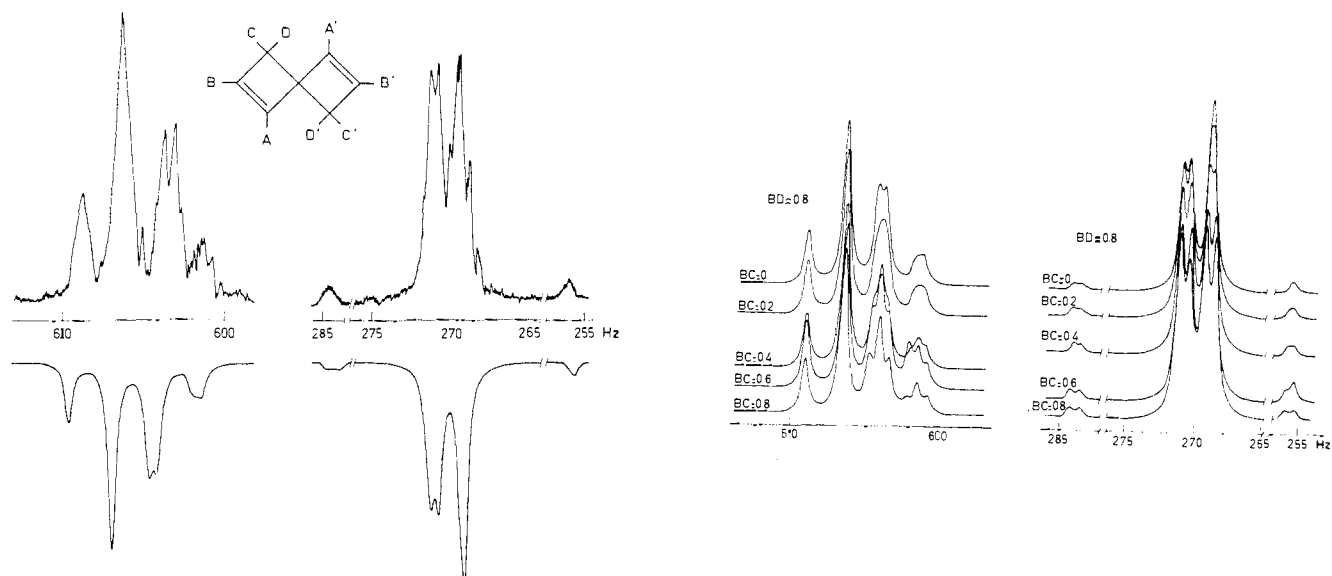(48) S. Farid, W. Kothe, and G. Pfundt, Tetrahedron Lett., 4151 (1968).

Figure 3. 100-MHz spectra of spiro[3.3]hepta-1,5-diene in carbon tetrachloride.

Table I. Pmr Parameters of Spiroheptadiene (Hz)^a and Cyclobutene (Hz)^{a,b}

H_a proton	δ 6.077 ppm	H_a, H_b protons	δ 6.03 ppm
H_b proton	δ 6.032 ppm	H_c, H_d, H_e, H_f protons	δ 2.57 ppm
H_c proton	δ 2.734 ppm	J_{ab} = 2.85	
H_d proton	δ 2.662 ppm	J_{cd} = J_{ef} = -12.00	
J_{ab} = $+2.7$	J_{bc} = J_{ac} =	J_{ac} = J_{ad} = J_{be} =	
	$J_{ad} \sim 0$	J_{bf} = $+1.00$	
J_{cd} = -13.3	J_{bd} = 0.8	J_{ae} = J_{af} = J_{bc} =	
		J_{bd} = -0.35	

^{a} For the numbering convention, see Figure 2. ^{b} Reference 47.

Figure 4. Conformation A, B, and C of 1.

ABCD pattern of the 100-MHz spectrum was carried out by means of a combination of LAOCOON with magnetic equivalence and SIMEQ computer program techniques. The multiplet at lower field could be easily ascribed to protons H_a and H_b. A decoupling experiment, viz., irradiating the AB quartet of the allylic protons at δ 2.70, collapsed the multiplet at δ 6.06 to an AB quartet from which J_{ab} could be inferred. The nature of the splitting at δ 6.06 indicated that proton H_a should be shifted more downfield than proton H_b. From the splitting pattern at δ 2.70 the geminal coupling constant of protons H_c and H_d could be deduced. The individual chemical shift of these protons could only be assigned from geometric considerations. The coupling constants J_{bc} and J_{bd} proved to be unequal. Simulation of the spectrum with J_{bd} = J_{bc} = 0.8 Hz resulted in a triplet for the H_b proton (see Figure 3). This triplet was converted to a doublet agreeing with that observed experimentally when J_{bc} was reduced to zero. Similarly, the H_d proton showed up as a doublet when J_{bc} = J_{bd} = 0.8 Hz was taken. This doublet was reduced to a singlet again agreeing with that observed experimentally for J_{bc} = 0 Hz (see Figure 3). The difference in magnitude between the coupling constants J_{bc} and J_{bd} presumably implies a small puckering of the four-membered ring. This suggestion leads to a conformation of the molecule in which the dihedral angle between H_b and H_d is smaller than that between H_b and H_c or the reversed case, situation A and B in Figure 4, respectively. In addition, a model of the molecule suggested that the
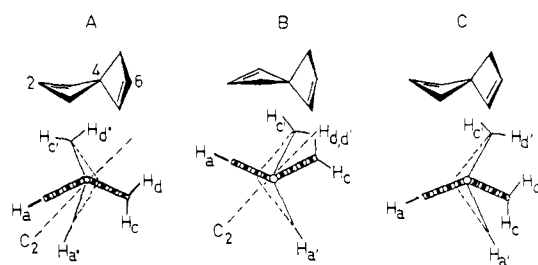
latter situation, wherein the neopentyl protons H_d and $H_{d'}$ can be moved away from each other, might be more favorable because of steric reasons.[49] Therefore, it seems reasonable to assume that the computed chemical shift of δ 2.73 can be assigned to proton H_c.

To establish that ring puckering caused the difference in magnitude between the coupling constants J_{bd} and J_{bc} of the vicinal protons, recourse was taken in CNDO/2 calculations.[50] Several models of spiroheptadiene **1** were constructed having twofold symmetry, the geometry of cyclobutene,[51] and increasing values of the dihedral angle (α) of both rings.[52] A standard CNDO/2 program was modified for this work by Dr. D. Kracht of the laboratory of theoretical chemistry of this university. The results of these calculations showed, however, that no other value of α, but that for the planar form, for which the total energy was minimal, could be found (see Table II). The contribution of the electronic energy dominated that of the sometimes favorable nuclear repulsion energy for the investigated cases.

(49) Figure 4 is somewhat misleading because the angle between the H_c-C-H_d plane and the ring appeared to be dependent on the variation in the puckering of the four-membered ring.

(50) J. A. Pople and G. A. Segal, J. Chem. Phys., 44, 3289 (1966).

(51) B. Bak, J. J. Led, C. Nygaard, J. Rastrup-Andersen, and G. O. Sörensen, J. Mol. Struct., 3, 369 (1969).

(52) The two cyclobutene rings were held in perpendicular planes. Variations of the angle between the planar rings did not show any energy minimum in the CNDO/2 calculations as had to be considered because of a recent study on spirenes and spirarenes.[8c] A combination of both calculations indicated that variations in the angles between the rings seem to increase the energy of the puckered rings of the spiro system.
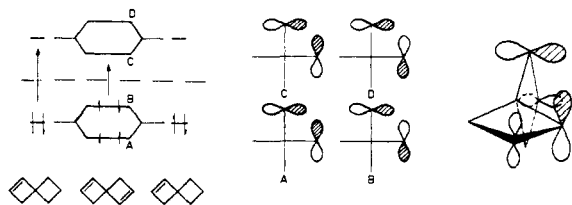
Figure 5. Interaction diagram for two ethylene units with C_2 symmetry in spiro geometry.

Table II. Results of the CNDO/2 Calculations

Models used	Dihedral angle, α, deg	E, eV		
		Total	Electronic Energy	Nuclear repulsion
1^a	7.5	0.185	0.015	0.171
2^a	5.0	0.087	0.064	0.024
3^a	2.5	0.027	0.125	−0.098
4^a	1.0	0.009	0.194	−0.185
5^b	0	0	0	0
6^c	−1.0	0.005	0.271	−0.267
7^c	−2.5	0.016	0.318	−0.302
8^d	1.0, −1.0	0.007	0.232	−0.226
9^d	2.5, −2.5	0.021	0.221	−0.200

[a] Situation A in Figure 4. [b] Planar form. [c] Situation B in Figure 4. [d] Situation C in Figure 4; a combination of a and c, without C_2 symmetry.

Figure 6. Uv spectrum of **1**: (a) gas phase, higher vapor pressure; (b) gas phase, lower vapor pressure.
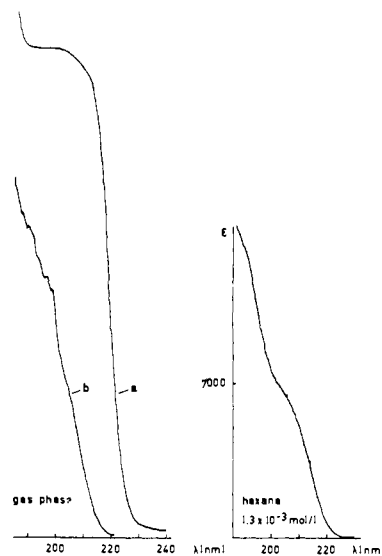

19   **20**   **21**   **22**

Spiroconjugation of Spirene 1

A special case of homoconjugation exists for diene **1** where the two π systems are held in perpendicular planes by a common tetrahedral atom and is designated as spiroconjugation.[7,8] This particular geometry might also give rise to a contribution to a discussion concerning experimentally accessible examples of planar tetracoordinate carbon.[53] A repeated demonstration of agreement between theoretical and experimental spiroconjugative features was recently provided by Semmelhack.[54] Convincing evidence for spiroconjugation was found, viz., a red shift (22 nm) in the uv spectrum of spiro[4.4]nonatetraene (**19**) with regard to the absorption maximum of spiro[4.4]nona-1,3-diene (**20**). Applying the theory of Simmons and Fukunaga[7] we expect a splitting of the ground and excited state energy levels of the diene **1** resulting in a red shift of the long-wavelength absorptions in the electronic spectrum (see the appearence of both levels of the diene **1** after interaction and the orbital diagram in Figure 5). The size of the red shift is directly correlated with the magnitude of splitting of the energy levels of the diene after spiroconjugative interaction. This magnitude is dependent on the efficiency of sideways overlap of the p orbitals, on the number of such interactions between the tetrahedrally arranged p orbitals, and on the degree of energy splittings in LUMO and HOMO. A simple Hückel calculation indicated that the degeneracy of a two-orbital case is removed with a smaller splitting of $2\beta'$ (the $1,1'$ case)[55] comparing to the $4\beta'$ of 19^{7a} or [3.3]spirarene[8a] (**22**) (the $1,\omega$, $1',\omega'$ cases). Spirocycle **1**, however, belonging to the former case, exhibits this energy splitting both in its LUMO and HOMO levels,

whereas the above mentioned compounds of the latter case only split their HOMO levels. On the contrary, **1** shows only one sideways interaction of p orbitals, but the others contain four such interactions. We anticipate, therefore, as a rough estimation that the spiro interaction of **1** is about half that of **19** and **22**. The efficiency of overlap in all three compounds considered being the same in the spiroconjugative interaction (geometry is not much different by approximation), we estimate a red shift of 1570 cm^{-1}[56] for the diene **1** with respect to **21**. Knowing the shift of **20** with regard to cyclopentadiene,[7a] we calculate roughly the absorption maximum of **21** to have a value of 184 nm,[57] resulting in an absorption maximum of the diene **1** at 190 nm.[59] The measurement seems to reveal a spectrum with a slightly larger red shift[60] (see Figure 6 and Experimental Section). This might be due to the fact that a better overlap of the p orbitals in the diene has to be taken into account. In addition, the estimated red shift of spirene **1** in the ultraviolet spectrum caused by spiroconjugation is in excellent agreement with a recent study of Dewar, et al.[61] These authors determined the ionization potential of the diene **1** from its photoelectron
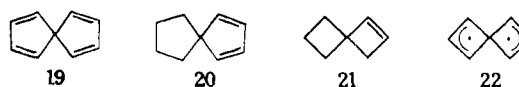
(53) R. Hoffmann, R. W. Alder, and C. F. Wilcox, J. Amer. Chem. Soc., **92**, 4992 (1970).

(54) M. F. Semmelhack, J. S. Foos, and S. Katz, J. Amer. Chem. Soc., **94**, 8637 (1972); see also H. Dürr, B. Ruge, and T. Ehrhardt, Justus Liebigs Ann. Chem., 214 (1973).

(55) Reference 2 cited in ref 7a.

(56) (a) This value is half of the red shift of 19 with respect to 20;[54] (b) extended Hückel calculations on 22 by Hoffmann[8a] indicated a splitting of 0.75–1.0 eV. Making the same assumptions as in the text we calculate an absorption maximum at 194–198 nm for the spirene 1. SCF and SCF–CI calculations on 22[8a] taking now the electronic repulsion integrals into account, turned out to shift this calculated maximum to a considerable higher wavelength.

(57) The literature data are somewhat confusing.[58]

(58) (a) B. B. Loeffler, E. Eberlin, and L. W. Pickett, J. Chem. Phys., **28**, 345 (1958); (b) "Organic Electronic Spectral Data," Vol. IV, Interscience, New York, N. Y., 1958–1959, p 17.

(59) Compare the spectrum of spiro[4.4]nona-1,6-diene (2).[1] Calculation in the same way revealed a smaller red shift for this compound.

(60) Simple Hückel calculations on spirocycle 1 and the spirenes of class II[8a] regarding now the π systems and their spirosymmetry[8a] indicated that the red shift of 1 might be expected to come to more than half of that of 19 (0.190 and 0.274 β units, using $\beta' = 0.2\beta$, respectively). CNDO/2 calculations[5c] appear to confirm this indication.

(61) N. Bodor, M. J. S. Dewar, and S. D. Worley, J. Amer. Chem. Soc., **92**, 19 (1970).

Table III. Ionization Potentials of Spirene 1

PES result,[a] 9.02, 10.30, 11.26, 12.41, 14.18, (14.50), 16.23 (19.26) eV
MINDO/2,[a] 9.03, 9.64, 9.95, 10.28, 10.69, 11.71, 11.91, 12.50, 12.92, 15.04 eV
CNDO/2,[b] 12.11, 12.61, 12.73, 14.43, 15.14, 18.09, 18.24, 18.62, 24.06 eV

[a] Reference 61. [b] Cyclobutene geometry and C_2 symmetry (planar form) were used in the model. The first ionization potential was calculated to be 11.39 eV by application of the equation $I_1 = -[E(\text{mol}) - E(\text{mol}^+)]$.

spectrum (see Table III). We may conclude[62] that there is a considerable spiroconjugative red shift of 0.82 eV or 23.3 nm of 1 with respect to cyclobutene.

Mass Spectrum of the Diene 1

The ms of 1 showed a parent peak at m/e 92 and a base peak at m/e 91. The spectrum was almost identical with that of toluene[23] and cycloheptatriene[64] (see Experimental Section). This would suggest a rearrangement of the C_7H_8 isomer 1 under electron impact to the tropylium ion. A different mode of fragmentation for the diradical of 1 (22) has been visualized by Hoffmann.[8a] The mass spectra of the C_7H_8 isomers, including allylidenecyclobutene[22] (12), vary only essentially with the parent peak–base peak ratio. These differences are compiled in Table IV.

Table IV. Mass Spectra of C_7H_8 Isomers

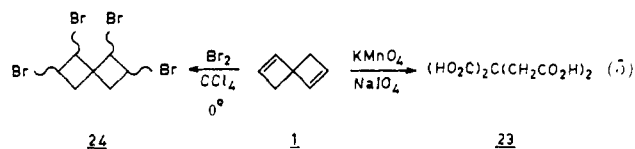|	Spirene 1[a]	Cyclo- butene 12[a]	Toluene[b]	Cyclo- hepta- triene[c]
Ratio: (parent peak/ base peak)100%	31.0	40.4	80	47.5

[a] This work. [b] Reference 23. [c] Reference 64.

Reactions with the Spirene 1

Investigations have been confined only to a preliminary survey. Attempts to establish the structure of the diene 1 by chemical methods were undertaken. Reduction of 1 to the known spiro[3.3]heptane by several methods was not successful. Reaction with hydrogen using catalytic amounts' of platinum in pentane or platinum dioxide in acetic acid and pentane both in a Parr apparatus did not furnish detectable quantities of spiro[3.3]heptane. In addition, employment of a general hydrogenation procedure for reduction of olefins to saturated hydrocarbons utilizing the hydroboration method of Brown with diborane and acetic acid gave unidentifiable products. On the other hand, oxidation with potassium permanganate and sodium periodate converted the olefin 1 to propane-1,2,2,3-tetracarboxylic acid (23) as outlined in eq 5, and bromination of olefin 1 in carbon tetrachloride at 0° gave complete conversion to the tetrabrominated

product 24. The thermal instability of the diene 1 was not only demonstrated by the rearrangement as mentioned in eq 2 but was also confirmed by a gas chromatographic analysis (6 ft $\times$ $^1/_8$ in. stainless steel column with 10% silicon rubber SE-30 on a Chromosorb WAW 80–100 mesh in a F&M research gas chromatograph model 810 with Flame Ionization Detecting). When the temperature of the injection port was gradually increased to 200°, three new products were formed. The oven was maintained at ambient temperature. The structure of these products was not determined. Evidence was obtained that the formation of the C_7H_8 isomer toluene had to be excluded under these reaction conditions. The behavior of spirocycle 1 toward irradiation in a solution of pentane using a quartz-jacketed medium pressure Hanau TQ-81 lamp was as expected for a cyclobutene derivative. The product of this irradiation, causing a white turbidity in the solution, appeared to be polymeric material that was not soluble in any organic solvent and had an undetermined mp above 350°.

Experimental Section

Boiling points are uncorrected. Melting points were determined on a Mettler FP_2 apparatus with microscope attachment at a warmup rate of 0.2°/min. Infrared spectra were recorded on a Unicam SP 200 infrared spectrophotometer or on a Perkin-Elmer grating spectrophotometer (Model 125). Ultraviolet spectra were obtained on a Zeiss PMQ II apparatus or on a Cary 15 spectrophotometer. Pmr spectra were recorded on a Varian A-60 instrument unless otherwise stated using tetramethylsilane as internal standard. Mass spectra were run on an AEI MS 902 mass spectrometer by Mr. A. Kiewiet. Microanalyses were performed in the analytical section of our department under supervision of Mr. W. M. Hazenberg. Optical activity was measured on a Zeiss photoelectric precision polarimeter 005 or on a Perkin-Elmer Model 141 polarimeter using 1-dm or 5-cm cells.

dl-Spiro[3.3]heptane-2,6-dicarboxylic acid (6) was prepared according to a method of Backer and Schurink[14] starting with 273 g (0.7 mol) of 1,3-dibromo-2,2-bis(bromomethyl)propane.[65] In contrast to the procedure of these authors a slight modification described by Wynberg and Houbiers[15] was applied giving dl-spiro[3.3]heptane-2,6-dicarboxylic acid (6) in yields varying from 47 to 54% (lit.[14,15,37] 65 to 80%). dl-Fecht acid (6) was also prepared via an alternative route, which was based on the isolation of tetraethyl spiro[3.3]heptane-2,2,6,6-tetracarboxylate according to a method of Buchta and Merk.[66] Starting from 209 g (0.3 mol) of pentaerythrityl benzenesulfonate,[65] 56 g (0.15 mol or 50%) of the tetraester was obtained (lit.[66] 63%).

l-Spiro[3.3]heptane-2,6-dicarboxylic Acid (l-6). The resolution of dl-acid 6 was accomplished according to the method of Backer and Schurink[14] using 171 g (0.43 mol) of brucine, 40 g (0.22 mol) of dl-Fecht acid (6), and 3 l. of distilled water. The boiling solution was filtered. After cooling to room temperature over a period of 1 day the supernatant liquid was decanted. The mother liquor obtained after the first crystallization of the brucine salt of dl-acid 6 was boiled in a beaker until the volume (originally 3 l.) was reduced to 2 l. A small amount of the salt separated on cooling and this was removed. The filtrate was concentrated again in the same way to 1 l. After separation and removal of a second crop of salt, 40 ml of concentrated ammonia was added to the filtrate. The work-up, carried out as described for the d-acid 6,[15] gave 5–7 g (25–35%) of the l-acid 6 ([Φ]$_{578}$ −6.4°, [Φ]$_{546}$ −7.4°, [Φ]$_{436}$ −12.7°,

(62) The ionization potential for 1, 9.02 eV,[61] is somewhat greater than the values observed for other cyclic olefins and unconjugated cyclic dienes, but on the other hand by comparison with that for cyclobutene, 9.43 eV,[63] there should be an experimental red shift of 0.82 eV with respect to cyclobutene.

(63) P. Bischof and E. Heilbronner, Helv. Chim. Acta, 53, 1677 (1970).

(64) American Petroleum Institute, Research Project 44, Catalogue of Mass Spectral Data, Carnegie Institute of Technology, Pittsburgh, Pa., Serial No. 1775.

(65) H. L. Herzog, "Organic Syntheses," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 753.

(66) E. Buchta and W. Merk, Justus Liebigs Ann. Chem., 694, 1 (1966).

$[\Phi]_{405}$ $-15.3°$, $[\Phi]_{365}$ $-19.9°$ (c 5.1, acetone)) with an optical purity of 75% (based on the maximum optical activity of the d-acid 6 as was determined by Wynberg and Houbiers[15]).

dl-Spiro[3.3]heptane-2,6-diammonium Sulfate (7). To a solution of 64 g (0.35 mol) of *dl*-spiro[3.3]heptane-2,6-dicarboxylic acid (6) in 640 ml of concentrated sulfuric acid stirred at a temperature of 40°, a solution of hydrazoic acid,[67] prepared from 69.2 g of sodium azide in 430 ml of chloroform, was added over a period of 8 hr according to Janson and Pope's procedure.[16] A modification of Wynberg and Houbiers[15] was used during the work-up, which provided that calcium chloride was not added to the combined filtrates. There was obtained 89.8 g of sulfate 7 (mole percentage of sulfate in this salt was variable giving for one specific run a 4.2:1 ratio of amine:sulfate[68]).

d-Spiro[3.3]heptane-2,6-diammonium Sulfate (d-7). Starting from 9.2 g (0.05 mol) of *l*-spiro[3.3]heptane-2,6-dicarboxylic acid (l-6) with $[\Phi]_{578}$ $-6.4°$, $[\Phi]_{436}$ $-12.7°$, $[\Phi]_{365}$ $-19.9°$ (c 5.1, acetone), the same reaction as described in the preceding section for the *dl* mixture was performed in adapted proportions, affording 12.1 g of d-sulfate 7: $[\alpha]_{578}$ $+19.4°$, $[\alpha]_{546}$ $+21.3°$, $[\alpha]_{436}$ $+37.8°$, $[\alpha]_{365}$ $+61.0°$ (c 0.5, water).

dl-Spiro[3.3]heptane-2,6-bis(dimethylamine) (8). Sulfate 7 (86.6 g) was dissolved in 100 ml of distilled water. To this solution 320 ml of a 32% sodium hydroxide solution in water, 1120 ml of formic acid, and 1120 ml of a 35% formaldehyde solution in water were added. The mixture was kept for 36 hr at 100°, allowed to cool, poured into 225 g of concentrated hydrochloric acid, and evaporated under reduced pressure. A solution of 470 g of sodium hydroxide in 1500 ml of water was then added to the residue. This mixture was saturated with sodium chloride and the organic layer was diluted with ether. The crude tertiary amine 8, obtained by continuous ether extraction of the water layer and subsequent drying over potassium hydroxide and removal of the ether, was distilled *in vacuo* from sodium and under nitrogen atmosphere at bp 91–92° (14 mm) yielding 41.7 g (0.23 mol or 68%, calculated on Fecht acid (6)): n^{20}D 1.4582; ir (neat) 2950 (s), 2800 (s), 1450 (s), 1340 (s), 1280 (s), 1195 (s), 1155 (s), 1090 (m), 1040 (s), 930 (m), 900 (m), 860 (w), 830 (w), 700 (w), 660 (m) cm^{-1}; pmr (carbon tetrachloride) δ 1.6–3.1 (broad m, 10 H), 2.0 (s, 12 H).

Anal. Calcd for $C_{11}H_{22}N_2$: C, 72.47; H, 12.16; N, 15.37; mol wt, 182.31. Found: C, 72.9, 72.7; H, 12.2, 12.3; N, 15.2, 15.1.

l-Spiro[3.3]heptane-2,6-bis(dimethylamine) (l-8). From 12.1 g of *d*-spiro[3.3]heptane-2,6-diammonium sulfate (d-7) with $[\alpha]_{578}$ $+19.4°$, $[\alpha]_{436}$ $+37.8°$, $[\alpha]_{365}$ $+61.0°$ (c 0.5, water), *l*-spiro[3.3]heptane-2,6-bis(dimethylamine) (l-8) was prepared in the manner as described in the preceding section, in a yield of 7.2 g (0.04 mol or 80% with respect to the acid l-6): $[\Phi]_{578}$ $-5.5°$, $[\Phi]_{546}$ $-6.4°$, $[\Phi]_{436}$ $-13.1°$, $[\Phi]_{405}$ $-16.7°$, $[\Phi]_{365}$ $-25.1°$ (c 4.8, acetone); $[\Phi]_{578}$ $-4.2°$, $[\Phi]_{546}$ $-5.4°$, $[\Phi]_{436}$ $-10.9°$, $[\Phi]_{365}$ $-21.8°$ (c 6.6, ether); $[\Phi]_{478}$ $+14.7°$, $[\Phi]_{546}$ $+17.5°$, $[\Phi]_{436}$ $+29.5°$, $[\Phi]_{405}$ $+36.0°$ (c 3.6, 2 N sulfuric acid).[70]

dl-Spiro[3.3]heptane-2,6-bis(dimethylamine) dimethiodide (9) was prepared according to the method of Wynberg and Houbiers.[15] Starting from 41.7 g (0.23 mol) of *dl*-spiro[3.3]heptane-2,6-bis(dimethylamine) (8), 106 g (0.23 mol or 99%) of *dl*-spiro[3.3]heptane-2,6-bis(dimethylamine) dimethiodide (9), mp 302° dec, was obtained after one crystallization from methanol in an overall yield of 67% calculated on 6 (lit.[15] 42%).

d-Spiro[3.3]heptane-2,6-bis(dimethylamine) Dimethiodide (d-9). *l*-Spiro[3.3]heptane-2,6-bis(dimethylamine) (l-8) (0.24 g, 1.3 mmol) with $[\Phi]_{578}$ $-5.5°$, $[\Phi]_{436}$ $-13.1°$, $[\Phi]_{365}$ $-25.1°$ (c 4.8, acetone), was converted to 0.5 g (1.1 mmol or 81%) of *d*-spiro[3.3]heptane-2,6-bis(dimethylamine) dimethiodide according to the method described in the preceding section: $[\Phi]_{578}$ $+16.8°$, $[\Phi]_{546}$ $+19.1°$, $[\Phi]_{436}$ $+33.6°$, $[\Phi]_{405}$ $+41.0°$, $[\Phi]_{365}$ $+54.5°$ (c 5.1, water); after three recrystallizations from methanol $[\Phi]_{578}$ $+27.0°$, $[\Phi]_{436}$ $+42.4°$, $[\Phi]_{405}$ $+49.4°$, $[\Phi]_{365}$ $+63.8°$ (c 2.6, water).

dl-Spiro[3.3]hepta-1,5-diene (1) *via* Hofmann's Elimination Process. A solution of 42.4 g (0.09 mol) of *d*-spiro[3.3]heptane-2,6-bis(dimethylamine) dimethiodide (d-9) (after three recrystallizations from methanol: $[\Phi]_{578}$ $+6.1°$, $[\Phi]_{546}$ $+7.5°$, $[\Phi]_{436}$ $+15.5°$, $[\Phi]_{405}$ $+18.8°$, $[\Phi]_{365}$ $+26.3°$ (c 5.0, water) and prepared from 20% optically pure Fecht acid (6)) in 100 ml of water was shaken with 126.7 g (0.55 mol) of freshly prepared silver oxide in 300 ml of water for 12 hr The mixture was filtered and concentrated under reduced pressure at a temperature below 25°. The sirupy quaternary ammonium bishydroxide was added dropwise to a flask heated to 150–160° with an oil bath. The pressure within this flask was maintained at 50–60 mm. The evolved gases were bubbled through a 2 N solution of hydrochloric acid and then condensed in a Dry Ice-cooled trap and thereafter in a trap in series cooled with liquid nitrogen. In the hydrogen chloride bubbler sometimes polymerization occurred. The yields of the diene 1, determined by 60-MHz pmr spectroscopy, were 27–59%. The contents of each trap were diluted with *n*-pentane. The product was purified by glc (8 ft × 0.5 in column with 20% silicon rubber GE-SE-30 on a Diatoport W 60–80 mesh in a F&M 700-0119 F gas chromatograph; oven, injection port, and detector 60°). The diene 1 was a colorless, relatively stable liquid, bp 71.6° (762 mm), and appeared to be optically inactive. The ir spectrum showed absorptions at 3120 (m), 3050 (s), 2940 (s), 2840 (m), 1560 (w), 1320 (m), 1190 (w), 940 (w), 890 (m), and 720 (s) cm^{-1} (this latter absorption is characteristic for a *cis*-HC=CH linkage). The uv spectrum (Cary 15) was taken in the gas phase showing a shoulder at 202 and 199 nm with low gas concentration and at *ca.* 200 nm with higher gas concentration and in the liquid phase (*n*-hexane, Merck, Uvasol) showing a shoulder at 202 nm (ε 7,200)[71] and end absorption to shorter wavelengths. The pmr spectrum (carbon tetrachloride) showed signals at δ 2.70 (AB quartet, $J = 13.5$ Hz, Δν unknown, 4 H), 6.06 (t, $J = 3.1$ Hz, 4 H), and (Varian XL-100, carbon tetrachloride) 2.56, 2.69, 2.70, 2.84 (AB system, $J = -13.3$ Hz, Δν 6.96, 4 H), and 6.00–6.10 (m, 4 H); mass spectrum (70 eV) m/e (rel intensity) 93 (0.7), 92 (31), 91 (100), 90 (1), 89 (2.2), 86 (1.3), 77 (1.2), 66 (7.3), 65 (17.5), 64 (1.6), 63 (5.6), 62 (2.5), 61 (1.2), 58 (1.0), 53 (2.3), 52 (2.1), 51 (5.2), 50 (2.9), 45 (1.8), 43 (1.0), 41 (1.8), 40 (5.5), 39 (17.0), 38 (3.3), 37 (1.4), 31 (2.1), 27 (3.9), 26 (1.0); metastable peaks 90:92 → 91; 46.4:91 → 65.

Anal. Calcd for C_7H_8: C, 91.25; H, 8.75; mol wt, 92.14. Found: C 91.1, 91.4; H, 8.7, 8.7.

Identification of By-Products 10, 11, and 12 of Hofmann's Pyrolysis of 9. On the bottom of the pyrolysis flask there appeared a salt that could be identified as 6-trimethylammoniumspiro[3.3]hept-1-ene iodide (10) from the following properties. It was soluble in water, decolorized a bromine solution in carbon tetrachloride, and reacted with an aqueous solution of silver nitrate resulting in a yellow precipitate: pmr spectrum (deuterium oxide, water signal δ 5.30 used as internal reference) δ 6.81 (m, $J = 1$ Hz, 1 H), 6.64 (d, $J = 3$ Hz, 1 H), 4.66 (quintet, $J = 8$ Hz, 1 H), 3.63 (s, 9 H), and 2.97–3.29 (m, 15 H); ir spectrum (KBr) 1600 (w) cm^{-1} (C=C). Pyrolysis after treatment of 10 with an aqueous solution of silver oxide, using the equipment described in the preceding section, furnished in the Dry Ice-cooled trap a yellow colored unstable product that polymerized to a thin film. In one run the contents of the hydrogen chloride bubbler (see preceding section) were made basic and extracted with pentane. The pentane extracts were dried over potassium hydroxide and distilled from sodium. Glc retention time was identical with an authentic sample of 8. The yield was not determined.

During the purification step of spirene 1 by gas chromatography as described in the preceding section, two compounds were isolated in one particular run. With increasing retention times on the column, compounds 12 and 11, respectively, could be identified in approximately 10% yield. 6-Dimethylaminospiro[3.3]hept-1-ene (11): pmr spectrum (carbon tetrachloride) δ 5.83–6.23 (broad m, 2 H), 2.50 (s, 2 H), 2.02 (s, 6 H), 2.10–2.75 (broad m, 5 H); ir spectrum (neat) 1610 (w) cm^{-1} (C=C); mass spectrum (70 eV) m/e (rel intensity) 137 (30), 122 (43), 93 (40), 92 (68), 91 (100), and 71 (91). Allylidenecyclobutene (12), identification by glc retention time and pmr spectrum; see for more details the following section of the Cope elimination of 14.

dl-Spiro[3.3]heptane-2,6-bis(dimethylamine *N*-oxide) (14). To an

(67) H. Wolff, *Org. React.*, 3, 307 (1964).

(68) Another illustrative example of surprising composition is the barium salt of Fecht acid 6 (C9 H12 O4. C18 H22 O8 Ba. H20),[69] *i.e.*, acid–barium mole ratio is 3.1.

(69) B. van Dijk, L. A. Hulshof, J. L. de Boer, and H. Wynberg, to be submitted for publication.

(70) These data indicate that the optical activity inherent in the dissymmetric 2,6-disubstituted spiro[3.3]heptane system is small compared to allenes or 4-substituted alkylidenecycloalkanes, whereas the influence of the Cotton effect in the visible wavelength region is much more important in the case of the tertiary amine 8 than it is in the case of the allenes (compare with Fecht acid 6[15]).

(71) The uv spectrum we reported earlier[11] is that of the spirodiene (1) probably still contaminated with traces of trimethylamine (*e.g.*, shoulder at 226 nm).[72]

(72) E. Tannenbaum, E. M. Coffin, and A. J. Harrison, *J. Chem. Phys.*, 21, 311 (1953).

ice-cooled, stirred mixture of 30 ml of 30% hydrogen peroxide solution in water 5.6 g (0.03 mol) of spiro[3.3]heptane-2,6-bis(dimethylamine) (8) in 30 ml of methanol was added at such a rate as to keep the reaction mixture below 5°. The solution was allowed to warm to room temperature and left for 1 day. Platinum foil was added to decompose the excess of peroxide and the solution was filtered and concentrated under reduced pressure. Concentration furnished a residue from which 6.6 g (0.03 mol or 100%) of spiro-[3.3]heptane-2,6-bis(dimethylamine N-oxide) (14), mp 220° dec, crystallized: pmr spectrum (deuterium oxide, water signal δ 5.30 used as internal reference) δ 4.24-4.74 (quartet, J = 8 Hz, 2 H), 3.59 (s, 12 H), and 2.70-3.12 (multiplet, 8 H); mass spectrum (70 eV) parent peak at m/e 214 and base peak at m/e 154 (M+ − (CH₃)₂NO).

d-Spiro[3.3]heptane-2,6-bis(dimethylamine N-oxide) (*d*-14). *l*-Spiro[3.3]heptane-2,6-bis(dimethylamine) (*l*-8) (1.0 g, 5.5 mmol) with [Φ]₅₇₈ −5.5°, [Φ]₄₃₆ −13.1°, [Φ]₃₆₅ −25.1° (c 4.8, acetone) was converted to 1.2 g (5.5 mmol or 100%) of *d*-spiro[3.3]heptane-2,6-bis(dimethylamine N-oxide) (*d*-14) according to a method as described in the preceding section: [Φ]₅₇₈ +7.1°, [Φ]₅₄₆ +8.3°, [Φ]₄₃₆ +14.5°, [Φ]₄₀₅ +17.6°, [Φ]₃₆₅ +24.1° (c 5.8, water).

dl-Spiro[3.3]hepta-1,5-diene (1) *via* Cope's Elimination Process. Spiro[3.3]heptane-2,6-bis(dimethylamine N-oxide) (6.6 g, 0.03 mol) (14) was decomposed at 150–190° (50–30 mm) using the same pyrolysis equipment as described above for the Hofmann elimination of 9. The contents of the liquid nitrogen trap were diluted with pentane and purified by glc (same conditions as described above), furnishing 0.37 g (4 mmol or 13%) of spirodiene 1, identified by glc retention time, mass spectrum, and pmr spectroscopy.

Identification of By-Products 8 and 12 from Cope Elimination on 14. During the glc purification step of 1 as described in the preceding section 0.11 g (1.2 mmol or 4%) of allylidenecyclobutene (12) was isolated. Despite the tendency of this material to polymerize the following spectroscopic data could be measured: pmr spectrum (CD₃OD) δ 3.00 (d, J = 3.0 Hz, 2 H), 4.9–6.6 (broad m, 6 H); ir spectrum (neat) 3050 (w), 2900 (w), 1640 (m), 1590 (m), 1410 (w), 1310 (w), 1160 (w), 980 (m), 890 (m), 720 (m), 650 (m) cm⁻¹; uv spectrum, maximum (methanol) 254 nm (ε unknown); mass spectrum (70 eV) m/e (rel intensity) 93 (2.8), 92 (40.4), 91 (100), 90 (1), 89 (2), 86 (0.3), 77 (1.2), 66 (3.7), 65 (16), 64 (1.9), 63 (5.7), 62 (2.3), 61 (1.5), 53 (2.1), 52 (2.8), 51 (5.1), 50 (2.5), 45 (2.2), 43 (0.9), 41 (1.2), 40 (3.1), 39 (13.7), 38 (2.7), 37 (0.9), 27 (3.3), 26 (0.8); metastable peaks 90:92 → 91, 46.4:91 → 65. Small amounts of 8 could be detected in the pyrolysis traps and were characterized by glc retention time.

dl-Spiro[3.3]heptane-2,6-diacetic Acid (6a). A mixture of 10 g (0.054 mol) of spiro[3.3]heptane-2,6-dicarboxylic acid (6) and 15 ml of thionyl chloride was stirred for 1.5 hr at 50°. Excess thionyl chloride was removed at reduced pressure and distillation afforded 10 g (0.045 mol or 84%) of acid chloride, bp 116–117° (1.2 mm) (lit. bp 154° (15 mm),³⁷ 103–107° (0.5 mm)¹⁵). A solution of 10 g (0.045 mol) of the acid chloride in 50 ml of dry diethyl ether was added in 15 min to an excess of a solution of diazomethane⁷³ in dry ether. The mixture was allowed to stand for 1 day at room temperature. Removal of the ether furnished 10.2 g (0.044 mol or 98%) of residual diazoketone. The Arndt–Eistert synthesis was performed in two different ways involving either conversion to the acid or to the ester.

A solution of 10.2 g (0.044 mol) of the diazoketone in 100 ml of dioxane was added dropwise with stirring to a mixture of 6.6 g of anhydrous sodium carbonate, 4 g of sodium thiosulfate, and 2.6 g of silver oxide in 200 ml of water at 50–60°. Stirring was continued for 1 hr after addition was complete, and the temperature of the mixture was raised finally to 90–100°. After 3 hr the solution was cooled, diluted with water, acidified with dilute nitric acid, filtered, and evaporated until precipitation took place, furnishing 2 g (9 mmol or 20%) of spiro[3.3]heptane-2,6-diacetic acid (6a): ir spectrum (KBr) 2300–3600 (COOH), 1700 cm⁻¹ (CO); pmr spectrum (CD₃COCD₃) δ 1.5–2.8 (broad m); mass spectrum (70 eV) m/e (rel intensity) 212 (27), 194 (100); calcd for C₁₁H₁₆O₄, equiv wt, 106.1; mol wt, 212.25, found, 104.0.

To a solution of 7.5 g (0.032 mol) of diazoketone in 150 ml of ethanol at 55–60° a small amount of a freshly prepared slurry of silver oxide was added. As soon as the evolution of nitrogen subsided, more of the silver oxide was introduced and this process was continued until all the slurry (4.5 g) had been added. The mixture was refluxed for 12 hr, filtered, and evaporated, yielding 2.6 g of crude ester. This material was dissolved in a solution of 20 g of potassium hydroxide in 150 ml of ethanol. Acidification after 2

days of this solution with concentrated hydrochloric acid, evaporation of the ethanol, extraction of the residue with ethyl acetate, evaporation of the extracts, and crystallization of this residue from water gave 2 g (9 mmol or 29%) of spiro[3.3]heptane-2,6-diacetic acid (6a), mp 131–134° (lit.³⁷ 134–135°).

dl-Spiro[3.3]heptane-2,6-bis(acetophenone) (15). A mixture of 3 g (14 mmol) of spiro[3.3]heptane-2,6-diacetic acid (6a) and 20 ml of thionyl chloride was stirred for 2 hr at 50°. Excess of thionyl chloride was removed under diminished pressure and distillation afforded 2.3 g (10 mmol or 71%) of the acid chloride, bp 180° (10 mm). A solution of 2.3 g (10 mmol) of the acid chloride in 3 ml of dry benzene was added dropwise to a stirred suspension of 5 g of anhydrous aluminum chloride in 10 ml of dry benzene. The reaction mixture was kept at 6° during this period and was refluxed for 3 hr. After work-up in the usual way for a Friedel–Crafts acylation 2.7 g (8 mmol or 81%) of spiro[3.3]heptane-2,6-bis(acetophenone) (15) was obtained: mp 91–93° (after four recrystallizations from acetone); ir (KBr) almost identical with acetophenone, 1685 cm⁻¹ (CO); mass spectrum (70 eV) m/e (rel intensity) 332 (5), 227 (1), 212 (3), 184 (23), 145 (100), 120 (12), 105 (23), 92 (2), 77 (64); pmr spectrum (CD₃COCD₃) δ 7.92 (m, 4 H), 7.50 (m, 6 H), 3.13 (d, J = 1 Hz, 2 H), 3.03 (s, 2 H), 2.88–1.50 (broad m, 10 H).

dl-Spiro[3.3]heptane-1,5-diene (1) *via* the Norrish Type II Reaction. A solution of 2.7 g (8 mmol) of spiro[3.3]heptane-2,6-bis-(acetophenone) (15) in 150 ml of tetramethylene glycol dimethyl ether was irradiated for 20 hr at room temperature and at 3 mm pressure in a reaction flask attached by means of ground-glass joints to a quartz jacketed medium-pressure Hanau TQ-81 lamp described by Neckers, *et al.*³⁴ In the liquid nitrogen trap 0.2 g (2.2 mmol or 28%) of pure spiro[3.3]hepta-1,5-diene (1) was collected. The product was identified by mass spectrum, pmr spectrum, and glc retention time.

Thermal Isomerization of 1. The thermal isomerization of spirene 1 was performed in a gas chromatograph F & M 700-0119 F. A solution of 64 mg (0.7 mmol) of 1 in 1 ml of *n*-pentane (Merck) was injected repeatedly in quantities of 0.1 ml in a 8 ft × 0.5 in. column with 20% silicon rubber GE-SE-30 on a Diatoport W 60–80 mesh, furnishing 44 mg or 69% of volatile isomerized products condensed in a trap at −100° (oven 155°, injection port and detector 160°). On standing one night at −30° a yellow colored polymer separated: pmr spectrum (CD₃SOCD₃) δ 2.09 (s), 3.42 (broad s), identical with that of the product from a reaction of spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic acid (16) with copper chromite. The supernatant liquid was identified to be allylidenecyclobutene (12) on account of glc retention time and pmr spectrum.

dl-Diethyl 2,6-Dibromospiro[3.3]heptane-2,6-dicarboxylate (18) was prepared according to the method of Backer and Kemper⁴⁰ starting with 18.4 g (0.10 mol) of spiro[3.3]heptane-2,6-dicarboxylic acid (6). The Hell–Volhard–Zelinsky bromination of 6 afforded 27.0 g (0.08 mol or 79%) of 2,6-dibromospiro[3.3]heptane-2,6-dicarboxylic acid (17), mp 181–183°: ir spectrum (KBr) 1685 (CO), 2200–3400 cm⁻¹ (COOH); pmr spectrum (CD₃COCD₃) δ 2.40–3.40 (quintet with fine splitting, 8 H), 11.45 (s, 2 H). Esterification of 27.0 g (0.08 mol) of 2,6-dibromospiro[3.3]heptane-2,6-dicarboxylic acid (17) with ethanol according to the method of Backer and Kemper⁴⁰ gave 22.7 g (0.057 mol or 71%) of diethyl 2,6-dibromospiro[3.3]-heptane-2,6-dicarboxylate (18): pmr spectrum (C₆D₆) δ 2.28–3.22 (quintet with fine splitting, 8 H), 0.93 (t, J = 7 Hz, 4 H), 3.94 (quartet, J = 7 Hz, 6 H).

dl-Spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic Acid (16). According to the method of Campbell and Rydon⁴² 6 g of molten potassium hydroxide was stirred vigorously in 60 ml of refluxing dry toluene, while 3 g (7.5 mmol) of diethyl 2,6-dibromospiro[3.3]-heptane-2,6-dicarboxylate (18) was added dropwise. After separation of solid potassium salts and completion of the addition, heating was continued for 2 hr. After cooling 60 ml of water was added. Work-up of the aqueous solution by separation from the organic layer, washing with 30 ml of *n*-pentane, acidification with 30% w/w sulfuric acid, extraction with ether, and evaporation of the dried extracts gave the crude acid. Two recrystallizations from water furnished 1.2 g (6.5 mmol or 86%) of spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic acid (16), mp 283° dec: ir spectrum (KBr) 3400–2300 (COOH), 1680 (CO), 1600 cm⁻¹ (C=C); uv spectrum max (96% ethanol) 223 nm (ε 15,600), 205 nm (sh, ε 12,100); pmr spectrum (CD₃OD) δ 6.78 (s, 2 H), 2.88 (s, 4 H), (Varian XL-100, CD₃OD) 6.83 (s, 2 H), 3.04, 2.90, 2.77 (AB system, J = 13.5 Hz, Δν unknown, 4 H); mass spectrum (70 eV) m/e (rel intensity) 180 (2), 162 (3), 135 (14), 134 (100), 113 (3), 110 (2), 108 (4), 107 (19), 106 (19), 105 (6), 91 (7), 90 (11), 89 (17).

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(73) J. A. Moore and D. E. Reed, Org. Synth., 41, 16 (1961).

Anal. Calcd for $C_9H_8O_4$: C, 60.00; H, 4.48; mol wt, 180.162. Found: C, 60.1, 60.1; H, 4.6, 4.6.

d-Spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic Acid (*d*-16). The resolution of the *dl* acid was accomplished similarly to a method used by Backer and Schurink[14] for the resolution of Fecht acid. A solution of 0.71 g (3.9 mmol) of *dl*-spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic acid and 3.24 g (7.8 mmol) of brucine in 65 ml of distilled water was refluxed for 1 hr and filtered. After cooling to room temperature over a period of 1 day the supernatant liquid was decanted and the residue (1.1 g) was dissolved again. Rotation of the residue: $[\alpha]_{578}$ −25.3°, $[\alpha]_{546}$ −29.6°, $[\alpha]_{436}$ −68.2° (*c* 1.6, water). After one crystallization the brucine salt with rotation $[\alpha]_{578}$ −23.0°, $[\alpha]_{546}$ −28.6°, $[\alpha]_{436}$ −67.8° (*c* 1.2, water) was dissolved in water and 10 ml of concentrated ammonia was added. Brucine separated and after one night it was filtered over a Büchner funnel. The filtrate was washed three times with chloroform, evaporated to a volume of 30 ml, and acidified with concentrated hydrochloric acid, and the precipitated acid was recrystallized from water, yielding 0.09 g (13%) of the *d*-acid 16 showing a mp, an ir spectrum, and pmr signals identical with those of the starting material and with the rotation $[\Phi]_{578}$ +15.3°, $[\Phi]_{546}$ +17.9°, $[\Phi]_{436}$ +25.4° (*c* 0.7, methanol), $[\theta]_{232}$ +3700 (*c* 4.4 × 10^{-4} mol/l., absolute ethanol).

l-Spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic Acid (*l*-16). The mother liquor obtained after the first crystallization of the brucine salt of *dl*-spiro acid 16 was concentrated by evaporation until the volume (originally 65 ml) was reduced to 35 ml. The separation of a small amount of the salt on cooling was removed and the filtrate was concentrated in the same way to 22 ml. After separation and removal of a second crop of the salt, 11 ml of concentrated ammonia was added to the filtrate. The work-up, in the same way as described for the *d*-acid 16 in the preceding section, gave 0.31 g (44%) of the *l*-acid 16: $[\Phi]_{578}$ −1.1°, $[\Phi]_{546}$ −1.3°, $[\Phi]_{436}$ −3.4° (*c* 3.2, absolute ethanol). The same procedure for the mother liquor, obtained after the second crystallization of the brucine salt of *dl*-acid 16 with rotation $[\alpha]_{578}$ −36.1°, $[\alpha]_{546}$ −42.3°, $[\alpha]_{436}$ −96.7° (*c* 1.9, water), afforded 0.076 g (11%) of the *l*-acid 16: $[\Phi]_{578}$ −3.1°, $[\Phi]_{546}$ −3.9°, $[\Phi]_{436}$ −6.3° (*c* 2.3, absolute ethanol).

Decarboxylation of Acid 16. Spiro[3.3]hepta-1,5-diene-2,6-dicarboxylic acid 16 (0.086 g, 4.8 mmol) and 0.075 g (0.3 mmol) of copper chromite were intensely mixed and gently heated to 180–200° or added to a heated, evacuated flask at 180°. In both cases a vigorous reaction took place and a yellow colored polymer appeared over the entire evacuated system including the liquid nitrogen trap. This material (0.02 g) was dissolved in deuterated DMSO. The pmr spectrum showed the same signals as described in the section on the thermal isomerization of spirene 1.

Attempts to Hydrogenate 1. (a) Spiro[3.3]hepta-1,5-diene (1) (30 mg, 0.3 mmol) was dissolved in 3 ml of pentane. After addition of 150 mg of powdered platinum this solution was hydrogenated in a Parr apparatus under 2 atm of hydrogen pressure for 24 hr. The filtrated solution was analyzed by gc–ms. Employment of this method indicated only the presence of starting material. (b) Spirene 1 (30 mg, 0.3 mmol) was dissolved in 2 ml of acetic acid and 2 ml of pentane adding 200 mg of platinum dioxide catalyst. This solution was hydrogenated at 3 atm of pressure for 3 days using the Parr apparatus. After removal of the catalyst by filtration the reaction mixture was diluted with water and extracted with pentane. The pentane extracts were washed with saturated aqueous sodium bicarbonate solution and with water and dried over magnesium sulfate. Gas chromatography *via* comparison of the retention time with that of an authentic sample of spiro[3.3]heptane prepared by a different method[10b] indicated that the desired product was not obtained. (c) Spirene 1 (0.1 g, 1 mmol) was added to an excess of 1 *M* solution of sodium borohydride in diglyme under nitrogen atmosphere at 0°. To this solution *ca.* 1 ml of boron trifluoride etherate was added. After 5 hr of stirring at 0° 1 ml of water and 10 ml of acetic acid were added. After stirring overnight at room temperature the reaction mixture was extracted with ether. The ether extracts were washed with saturated aqueous sodium bicarbonate solution and with water and dried over magnesium sulfate. Gs–ms of this solution indicated that only unidentifiable products were formed.

Oxidation of Spirene 1. To a stirred solution of 3.06 g (14.3 mmol) of sodium periodate in 11 ml of acetone and 13 ml of water in a reaction vessel flushed with nitrogen 0.17 g (1.8 mmol) of spirene 1 was added at 0° and maintained under a nitrogen atmosphere and at 0° thereafter. To this stirred mixture a solution of 0.09 g (0.6 mmol) of potassium permangate in 4 ml of water was added dropwise with simultaneous dropwise addition of 4 ml of acetone, the temperature being held lower than 5°. After completion of the addition the stirring was continued for 3 days at 0°. The liquid reaction medium was decanted from the residue and filtered through Celite. The acetone was removed under reduced pressure and the residual aqueous phase was extracted three times with ether. The ether extracts were washed once with saturated sodium chloride solution and dried over magnesium sulfate. Removal of the ether afforded the crude tetracarboxylic acid 23 in approximately 10% yield. The structure was established by comparison of the pmr spectrum of the hydrolyzed product of tetraethyl propane-1,2,2,3-tetracarboxylate (EGA): pmr spectrum (CD_3OD) δ 3.20 (s).

Bromination of Spirene 1. To a stirred solution of 0.09 g (1.03 mmol) of spirene 1 in 3 ml of carbon tetrachloride an excess of bromine in carbon tetrachloride was added at 0°. After 4 hr of stirring the decolorized reaction mixture was evaporated affording 0.43 g (1.03 mmol or 100%) of the tetrabrominated product 24: mass spectrum (70 eV) *m/e* 412; pmr spectrum (carbon tetrachloride) δ 4.05–5.1 (m, 4 H), 2.2–3.9 (m, 4 H).