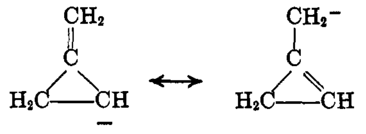

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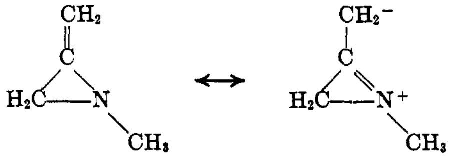

10

It remains to be determined if an exocyclic methylene will impart sufficient stability to a cyclopropylcarbonium ion or a cyclopropyl carbon undergoing an SN2 reaction to allow nucleophilic substitution to occur at cyclopropyl carbon without rupture of the three-membered ring.

Appendix

Kinetic Treatment for the Deuterioxide-Catalyzed Exchange of 2^{2-} with Deuterium Oxide.—Scheme I was assumed. It was further assumed that 3^{2-} undergoes no observable exchange under the reaction conditions, and that the trianion intermediate in the reaction is converted to 2^{2-} and 3^{2-} at essentially equal rates, *i.e.*, $k = k'$. Justification for the latter two assumptions is given in the text.

With k, k', and E as defined previously, and A_0 = the initial concentration of nondeuterated 2^{2-}, A = the concentration of nondeuterated 2^{2-} at time t, B = the concentration of monodeuterated 2^{2-} at time t, C = the concentration of monodeuterated 3^{2-} at time t, and X = the concentration of the first trianion intermediate at time t, rate equations for A, B, and C are

$$\frac{dA}{dt} = -2k_2A$$

$$\frac{dB}{dt} = kX - k_2\left(\frac{E+1}{E}\right)B$$

$$\frac{dC}{dt} = kX$$

A steady-state approximation may be applied for X to give

$$2k_2A + \frac{k_2}{E}B - 2kX = 0$$

The last four equations were solved for A, B, and C by the operator method[17] to obtain

$$A = A_0e^{-2k_2t}$$

$$B = \frac{2E}{2E-1}A_0e^{-2k_2t}\left[e^{\frac{2E-1}{2E}k_2t} - 1\right]$$

$$C = A_0\left[\frac{1+E}{1+2E} + \frac{1-E}{2E-1}e^{-2k_2t} - \frac{2E}{(2E-1)(2E+1)}e^{-\frac{(2E+1)}{2E}k_2t}\right]$$

Now

$$\frac{(\alpha\text{-H})}{(exo\text{-H})} = \frac{2A + B + C}{2A_0}$$

but instead of solving directly for k_2, it was found more convenient to express (α-H)/(*exo*-H) in terms of A/A_0, thereby obtaining eq. 3 (see Results).

Equation 3 was solved by machine computation for each value of (α-H)/(*exo*-H), and ln (A/A_0) was plotted against t to obtain k_2.

[17] N. M. Rodiguin and E. N. Rodiguina, "Consecutive Chemical Reactions," D. Van Nostrand Co., New York, N. Y., 1964.

Synthesis of *cis*- and/or *trans*-Dispiro[3.1.3.1]decane-2,8-dicarboxylic Acid[1]

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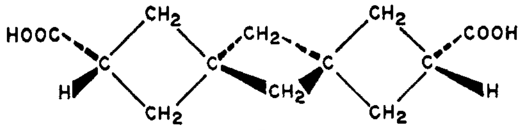
The *cis* and/or *trans* isomers of dispiro[3.1.3.1]decane-2,8-dicarboxylic acid (I) have been synthesized for use in future physical organic studies. Pentaerythritol was converted in three steps into a new compound, 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane (II), *via* the intermediates, 2,2-bis(bromomethyl)-1,3-propanediol, 2-phenyl-5,5-bis(bromomethyl)-1,3-dioxacyclohexane, and diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate. Reaction of II with excess *p*-toluenesulfonyl chloride gave 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane tetra-*p*-toluenesulfonate which was then condensed with 2 moles of diethyl malonate to give tetraethyl dispiro[3.1.3.1]decane-2,2,8,8-tetracarboxylate (III). Saponification of III led to dispiro[3.1.3.1]decane-2,2,8,8-tetracarboxylic acid which, when heated under reduced pressure at a temperature above its melting point (210°), underwent decarboxylation to give *cis*- and/or *trans*-dispiro[3.1.3.1]decane-2,8-dicarboxylic acid.

The isomeric compounds *cis*- and/or *trans*-dispiro[3.1.3.1]decane-2,8-dicarboxylic acids have been synthesized as intermediates for conversion into compounds of interest for physical organic studies. It is hoped that the unique, fixed, geometrical relationships in 2,8-disubstituted dispiro[3.1.3.1]decanes will permit a study of group interactions where the inductive and resonance effects have been minimized and where spacial orientations can be calculated with a reasonable degree of confidence. The primary purpose of this paper is to report the synthesis of *cis*- and/or *trans*-dispiro[3.1.3.1]decane-2,8-dicarboxylic acids (I).



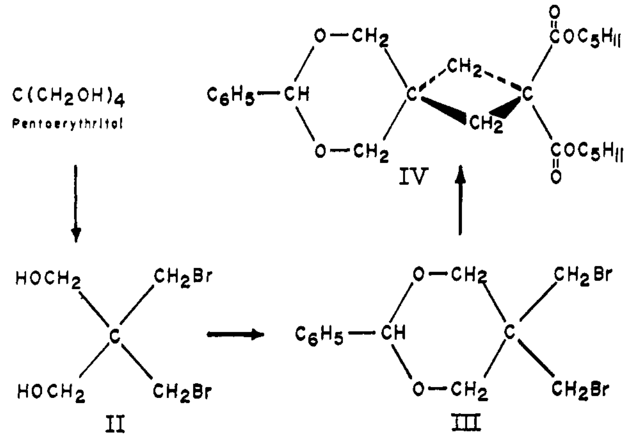
I

Successful synthesis of I was accomplished using methods of synthesis developed earlier by Buchman

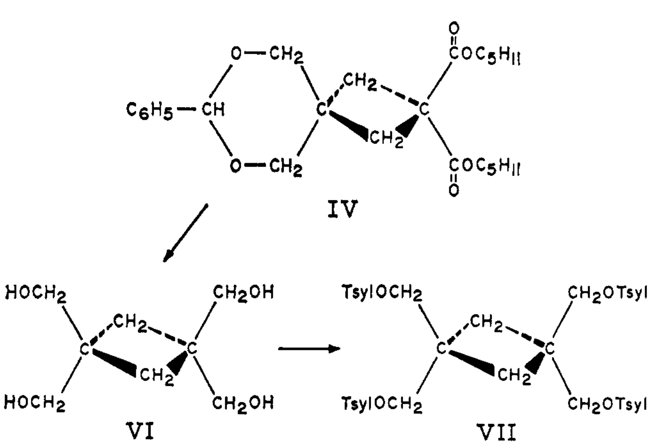
[1] Presented to the Organic Chemistry Division at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964; Abstracts, p. 9S.

and his collaborators[2] and more recently by Buchta and his co-workers.[3-5]

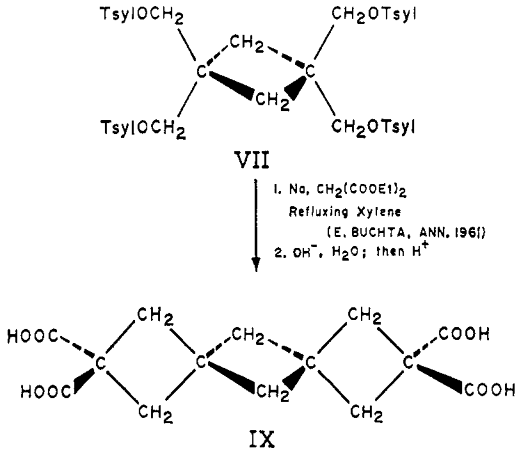
Pentaerythritol was converted by 66% hydrobromic acid in acetic acid into 2,2-bis(bromomethyl)-1,3-propanediol (II). The 1,3-diol group of II was protected by formation of the benzaldehyde acetal to give 2-phenyl-5,5-bis(bromomethyl)-1,3-dioxacyclohexane (III). Formation of the first cyclobutane ring was accomplished by condensation of diethyl malonate and the bromomethyl groups of acetal III. The reaction was carried out in refluxing isoamyl alcohol according to Buchman's directions. The resulting solid product was isolated and identified as diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate (IV) in agreement with the original reports of Buchman.[2]



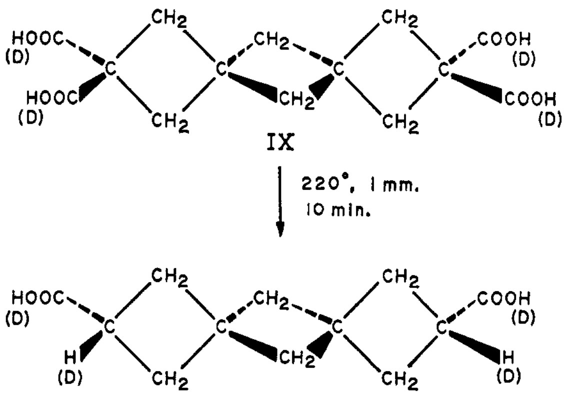
The reduction of IV with lithium aluminum hydride in diethyl ether followed by acidic hydrolysis of the intermediate, 2,2-bis(hydroxymethyl)-7-phenyl-6,8-dioxaspiro[3.5]nonane (V), gave the previously unreported 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane (VI), a water-soluble crystalline white solid, m.p. 183–184°. N.m.r. and infrared spectra of VI were in agreement with the assigned structure. Conversion of VI into the corresponding tetratosylate was accomplished after an extended reaction time of 4 days. The structure of the product, 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane tetra-*p*-toluenesulfonate (VII) was confirmed by infrared and n.m.r. spectra.



Formation of the dispiro[3.1.3.1]decane system was accomplished using methods developed by Buchta.[3] A double ring closure was effected on tetratosylate VII by heating it under reflux in xylene solution with a slight stoichiometric excess of sodium diethyl malonate and an excess of diethyl malonate. A mixture of the product, tetraethyl dispiro[3.1.3.1]decane-2,2,8,8-tetracarboxylate (VIII), and side reaction products, including polymer, was obtained. Reasonably pure VIII was obtained by distillation as indicated by subsequent saponification to dispiro[3.1.3.1]decane-2,2,8,8-tetracarboxylic acid (IX).



The tetracarboxylic acid was characterized as completely as possible. All data obtained were in agreement with the assigned structure. The neutralization equivalent of 70.3 (70.1 theoretical) confirmed the presence of four carboxylic acid groups. The n.m.r. spectrum at 60 Mc.p.s. showed only three kinds of protons at 7.49, 2.67, and 2.21 p.p.m. relative to tetramethylsilane (TMS) with relative intensities in the ratio 1:2:1 (4:8:4). These unsplit peaks are assigned, respectively, as being due to four equivalent carboxyl group hydrogens, eight equivalent end-ring methylene hydrogens, and four center-ring methylene hydrogens. The n.m.r. spectrum of IX in deuterium oxide does not have carboxyl hydrogens. Instead, owing to exchange, a typical water absorption at 4.88 p.p.m. was observed. Singlet methylene peaks at 2.67 and 2.21 p.p.m. were present with area ratios of 2:1 (8:4). Decomposition of IX in a thermal balance under atmospheric pressure showed quantitative loss of 2 moles of carbon dioxide when the temperature was greater than the melting point of IX. The product resulting from loss of two



cis and *trans*

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(2) E. R. Buchman and D. H. Deutsch, "Spirane Hydrocarbons," ONR Technical Report, California Institute of Technology, 1951.

(3) E. Buchta and K. Geibel, *Ann.*, **648**, 36 (1961).

(4) E. Buchta and W. Merk, *Naturwissenschaften*, **50** (12), 441 (1963).

(5) E. Buchta and O. Neuner, *Ann.*, **666**, 81 (1963).

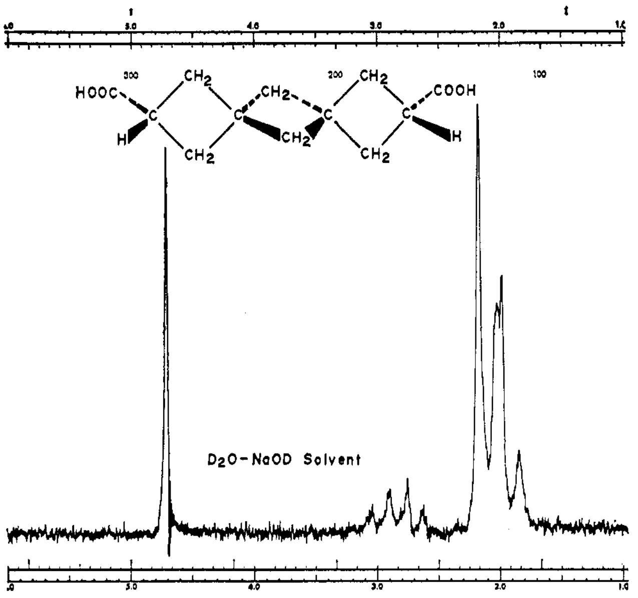

Figure 1.—The n.m.r. spectrum of dispiro[3.1.3.1]decane-2,8-dicarboxylic acid.

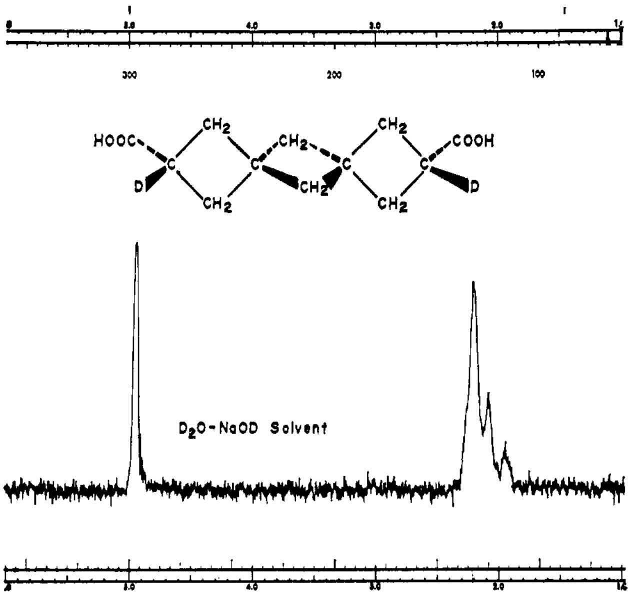

Figure 2.—The n.m.r. spectrum of 2,8-dispiro[3.1.3.1]decane-2,8-dicarboxylic-2,8-d_2 acid.

carbon dioxide molecules was assigned the structure of mixed *cis-* and *trans*-dispiro[3.1.3.1]decane-2,8-dicarboxylic acid (I). When carefully crystallized from ethanol–water, an acid fraction was obtained, m.p. 174–175° (softens at 170°), which is probably mixed *cis* and *trans* isomers. Work to this date to separate and identify, unequivocally, both the *cis* and *trans* isomers of I has been unsuccessful. It may well be that only one isomer is formed in the decarboxylation step. Some of the observed physical properties such as the sharpness of n.m.r. lines and the melting point could be interpreted to argue for the presence of only one isomer.

The n.m.r. spectra of 2,8-dispiro[3.1.3.1]decanedicarboxylic acid (I) and of 2,8-dispiro[3.1.3.1]decane-2,8-dicarboxylic-2,8-d_2 acid (I-D) are shown in Figure 1 and Figure 2, respectively. In Figure 1 the hydrogens on the 2,8-positions of I are clearly observable as a multiplet at 3.04, 2.91, 2.86, and 2.63 p.p.m. downfield from tetramethylsilane reference. In Figure 2, there are no peaks at these positions due to the deuterium substitution. By comparison with spectra of some derivatives, the highest peak in each spectrum of Figures 1 and 2 at about 2.20 p.p.m. can be assigned as the methylene hydrogens in the 5,10-positions of the center cyclobutane ring. The sharp high peak at about 2.20 p.p.m. would have to result from both the *cis* and *trans* isomers. For the *trans* isomer all 5,10-hydrogens are equivalent. This is not the case for the *cis* isomer, in which hydrogens in the 5-position differ from those in the 10-position. If both *cis* and *trans* isomers are present, it is assumed that the chemical shifts of the 5,10-methylene hydrogens are identical. The peaks occurring at 2.18 (underneath larger peak), 2.05, 2.00, and 1.95 p.p.m. are assigned the cyclobutane methylene hydrogens on the outside cyclobutane rings in the 1-, 3-, 7-, and 9-positions.

The n.m.r. spectra of I and I-D are still under investigation. A detailed study and analysis of the n.m.r. spectra of substituted dispiro[3.1.3.1]decanes will be presented separately.

Experimental Section

Melting points were observed on a Fisher-Johns hot stage and are corrected. N.m.r. spectra were observed on a Varian spectrometer, model A-60. Infrared spectra were observed on a Perkin-Elmer Infracord.

2,2-Bis(bromomethyl)propane-1,3-diol (II).—The procedure of Buchman and Deutsch was followed.[2] Pentaerythritol (180 g., 1.32 moles) was heated under reflux in 66% hydrobromic acid in acetic acid for 18 hr. After work-up the crude brown II was crystallized from benzene and then water to give 235 g. (0.898 mole, 67.6%) of II, m.p. 109–110°, lit.[2] m.p. 109–110°.

The infrared spectrum of II observed in a Nujol mull had the following absorption bands: 3210 (vs), Nujol 2840 (vs), Nujol 1460 (s), Nujol 1380 (s), 1295 (w), 1285 (s), 1230 (s), 1195 (s), 1130 (w), 1110 (w), 1065 (s), 1050 (vs), 1030 (vs), 966 (m), 890 (ms), 852 (w), 844 (s), 772 (m), 727 (w), and 692 (s) cm.$^{-1}$.

2-Phenyl-5,5-bis(bromomethyl)-1,3-dioxacyclohexane (III).—This procedure is essentially that described by Buchman and Deutsch.[2] A mixture of 223 g. (0.856 mole) of 2,2-bis(bromomethyl)propane-1,3-diol, 100 g. (0.953 mole) of benzaldehyde, 1.0 g. of *p*-toluenesulfonic acid, and 400 ml. of benzene was heated to distillation temperature and the water–benzene azeotrope was distilled off. When no additional water distilled (12 g. of water recovered), the reaction solution was washed twice with 200 ml. of aqueous sodium carbonate solution and dried over anhydrous potassium carbonate. After filtration to remove potassium carbonate, solvent was distilled off under reduced pressure. Recrystallization of the residue twice from methanol at −15° gave 262 g. (0.748 mole, 87.5%) of III, m.p. 68.0–68.5°, lit.[2] m.p. 68.0–68.3°.

The infrared spectrum of a Nujol mull of III had the following absorption bands: 1495 (w), Nujol 1460 (s), 1475 (−), 1430 (w), 1380 (s), 1335 (vw), 1320 (w), 1280 (m), 1260 (m), 1240 (m), 1220 (m), 1175 (w), 1160 (w), 1125 (s), 1090 (m), 1085 (w), 1055 (m), 1045 (w), 1035 (s), 996 (s), 988 (w), 981 (m), 943 (m), 934 (w), 886 (w), 866 (m), 846 (m), 792 (w), 747 (s), 696 (s), and 685 (m) cm.$^{-1}$.

Diisoamyl 7-Phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate (IV).—The procedure of Buchman and Deutsch[2] was followed. From 34.0 g. (1.48 moles) of sodium, 322 g. (2.0 moles) of diethyl malonate, and 235 g. (0.672 mole) of 2-phenyl-5,5-bis(bromomethyl)-1,3-dioxacyclohexane in 1400 ml. of 3-methyl-1-butanol was prepared 175 g. (0.396 mole, 60.5%) of crude IV, b.p. 190–242° (1–4 mm.). Crystallization of crude IV from methanol at −30° gave 125 g. (0.283 mole, 42.2%) of purified IV, m.p. 42.0–44.5°, lit.[2] m.p. 44.5–45.0°.

The infrared spectrum of IV observed in a Nujol mull had strong absorption bands at 1725 (ester carbonyl) and 698 and 761 cm.$^{-1}$ (aromatic C–H deformations). Bands observed in the range 1300–900 cm.$^{-1}$ are as follows: 1310 (s), 1280 (vs), 1270 (vs), 1230 (w), 1220 (w), 1190 (s), 1155 (s), 1150 (s), 1120 (m), 1070 (s), 1025 (m), 1010 (w), 998 (w), 971 (m), 959 (m), 931 (w), and 916 (m) cm.$^{-1}$.

The n.m.r. spectrum at 60 Mc.p.s. was observed in carbon tetrachloride solution. The following peaks were observed expressed in parts per million downfield from a tetramethylsilane reference: aromatic hydrogens, 7.27 (observed area 5.05/theoretical area 5.0); acetal hydrogen, 5.24 (1.04/1.0); dioxacyclohexane ring methylene hydrogens as a quartet, 4.19, 4.09, 3.97, and 3.87 (3.92/4.0); oxygen-bonded methylene hydrogens of isoamyl groups as a triplet, 3.81, 3.64, and 3.47 (3.92/4.0); cyclobutane ring methylene hydrogens, 2.64 and 2.08 (4.36/4.0); secondary methylene and tertiary hydrogens of isoamyl groups, complex multipeaks from 1.48 to 1.39 (5.88/6.0); and methyl-group hydrogens, 0.92 and 0.82 (11.78/12.0) p.p.m.

1,1,3,3-Tetrakis(hydroxymethyl)cyclobutane (VI).—Diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate (50.5 g., 0.117 mole) was reduced by lithium aluminum hydride (7.40 g., 0.185 mole) in an ether–benzene slurry. After cautious hydrolysis by aqueous ammonium chloride solution and separation of the organic phase, crude 2,2-bis(hydroxymethyl)-6,8-dispiro[3.5]nonane (V) was concentrated by removal of volatile solvents at reduced pressure. Crude V was hydrolyzed by excess dilute hydrochloric acid solution (2 ml. of 37% HCl in 300 ml. of water) at the temperature required to steam distil benzaldehyde (15 ml. recovered). The aqueous residue from steam distillation was neutralized with sodium hydroxide and 200 g. of sodium carbonate was added to salt out the crude product, 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane (VI). Recrystallization of VI from water gave 8.2 g. (0.047 mole, 40%) of purified VI, m.p. 213.3–213.8°.

Anal. Calcd. for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.34; H, 9.43.

The infrared spectrum was observed for both a Nujol mull and a potassium bromide pellet. The spectra were essentially the same in both media; each spectrum showed extensive hydrogen bonding in the solid state with no free hydroxyl bands observable. The spectrum of the potassium bromide pellet of VI had the following absorption bands: 3280 (vs), 2900 (m), 2850 (m), 1460 (w), 1445 (vw), 1435 (m), 1410 (s), 1370 (w), 1300 (w), 1285 (m), 1215 (m), 1105 (s), 1080 (vw), 1025 (vs), 1015 (vs), 943 (w), 891 (w), 858 (m), 762 (vw), and 690 (s) cm.$^{-1}$.

The n.m.r. spectrum of VI in deuterium oxide at 60 Mc. was exceedingly simple and consisted of three sharp peaks at 5.08, 4.10, and 2.08 p.p.m. downfield from TMS. The 4.10 and 2.08 peaks had area ratios of 2.0:1.0 corresponding, respectively, to the two hydrogens on each methanol group and the cyclobutane-ring methylene hydrogens. The peak at 5.08 was identified as a water peak (spiking with water) arising from water impurity in deuterium oxide and from the hydroxyl hydrogens of VI which exchanged with deuterium oxide.

The tetraacetate derivative of VI was prepared in 10 min. by heating under reflux a mixture of 0.20 g. of VI, 4.0 g. of pyridine, and 4.0 g. of acetic anhydride. When the mixture was poured into water, an oil formed which required 12 days to crystallize. Recrystallization from acetone at −25° gave 0.16 g. of white crystalline 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane tetraacetate, m.p. 113.2–113.5°.

Anal. Calcd. for $C_{16}H_{24}O_4$: C, 56.08; H, 7.11. Found: C, 55.80; H, 7.11.

The 60-Mc.p.s. n.m.r. spectrum of the tetraacetate in deuteriochloroform consisted of three sharp peaks at 4.13, 2.08, and 1.88 p.p.m. downfield from tetramethylsilane with a ratio of areas of 2:3:1, respectively, corresponding to the acetoxy-substituted methylene hydrogens, acetate methyl hydrogens, and cyclobutane methylene hydrogens, respectively.

2,2-Bis(hydroxymethyl)-6,8-dioxaspiro[3.5]nonane (V).—Preparation of V was made as described in the preceding procedure for VI. From 60.2 g. (0.136 mole) of diisoamyl 7-phenyl-6,8-dioxaspiro[3.5]nonane-2,2-dicarboxylate was prepared 10.2 g. (0.045 mole, 33%) of impure V. Repeated efforts to purify V by recrystallization were not highly successful; however, repeated recrystallizations from ethanol–water gave about 1.0 g. of V, m.p. 132.0–133.5°. This sample of V was successfully converted into a product identical with 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane (VI) by a procedure similar to that used for VI described above. The infrared spectrum of V in methylene chloride solution was consistent with the structure assigned for V.

1,1,3,3-Tetrakis(hydroxymethyl)cyclobutane Tetra-*p*-toluenesulfonate (VII).—To a stirred and cooled (−10°) solution of 7.0 g. (0.040 mole) of 1,1,3,3-bis(hydroxymethyl)cyclobutane (VI) in 100 ml. of pyridine was added 36.0 g. (0.189 mole) of *p*-toluenesulfonyl chloride. The mixture was warmed to room temperature and, after 19 hr., heated for 3.0 hr. at 60°. The mixture was cooled and then poured into 200 ml. of chilled (0°) 18% hydrochloric adid. Solids were separated by filtration and washed twice with 50-ml. portions of cold 2-propanol and twice with 50-ml. portions of boiling 2-propanol. Solid VII amounted to 24.2 g. (0.308 mole, 77%) and had m.p. 183–184°. No satisfactory solvent for recrystallization was found. A sample of VII had m.p. 186.0–186.5° after recrystallization from acetone–ethanol.

Anal. Calcd. for $C_{36}H_{40}O_{12}S_4$: C, 54.53; H, 5.09. Found: C, 54.60; H, 5.41.

The infrared spectrum of VII was observed in Nujol mull, in a potassium bromide pellet, and in methylene chloride solution. The spectrum of a potassium bromide pellet had the following bands: 3010 (vvw), 2890 (w), 1640 (w), 1580 (m), 1490 (w), 1455 (m), 1450 (w), 1365 (vs), 1285 (w), 1230 (vw), 1205 (vw), 1180 (vs), 1170 (vs), 1040 (w), 1015 (w), 968 (vs), 956 (s), 912 (w), 839 (vs), 823 (vs), 819 (s), 808 (s), 790 (s), 767 (s), and 704 (w) cm.$^{-1}$.

The n.m.r. spectrum of VII was observed in hexadeuterioacetone and in methylene chloride. Slight solvent shifts in the positions of hydrogen absorptions were observed. The n.m.r. spectrum in methylene chloride with internal TMS standard had the following peaks expressed in parts per million downfield from TMS: aromatic hydrogens at 7.90, 7.76, 7.54, 7.39 (total observed area ratio 4.16/theoretical area ratio 4.0); hydroxymethyl hydrogens at 3.84 (2.16/2.0); aromatic methyl hydrogens at 2.48 (3.00/3.0); and cyclobutane ring hydrogens at 1.70 (1.00/1.0) p.p.m.

Dispiro[3.1.3.1]decane-2,2,8,8-tetracarboxylic Acid (IX).—The procedure used for the double ring closure on 1,1,3,3-tetrakis(hydroxymethyl)cyclobutane tetra-*p*-toluenesulfonate (VII) to form the title product IX is similar to the procedure developed by Buchta for the single ring closure to form spirocyclobutanes.[3] Diethyl malonate (20.8 g., 0.13 mole), freshly cut sodium (2.52 g., 0.110 g-atom), and 100 ml. of azeotropically dried xylene were allowed to remain at room temperature in a system protected from moisture until all of the sodium had reacted (4.5 hr.). To this mixture was added 15.0 g. (0.0189 mole) of VII, and the new mixture was heated for 86 hr. under gentle reflux. To the cooled mixture was added 100 ml. of 2-propanol to dissolve the product and reduce the viscosity. Salts were removed by filtration and then washed twice with 20-ml. portions of diethyl ether. The organic phases were combined and the volatile solvents removed by distillation at 30° by gradually reducing the pressure of the system from 760 to 7.0 mm. The residue was taken up in diethyl ether. The ether solution was washed with water and the ether was then evaporated. The crude product at this point was the tetraester, tetraethyl dispiro[3.1.3.1]decane-2,2,8,8-tetracarboxylate (VIII). The crude tetraester VIII was saponified with 12 g. of potassium hydroxide dissolved in 160 ml. of 95% ethanol. After saponification, 60 ml. of water was added and ethanol was distilled off. The resulting aqueous solution was acidified with concentrated hydrochloric acid and extracted six times with 50-ml. portions of diethyl ether. Ether was evaporated from the solution to give 7.90 g. of crude product which was treated with 20 ml. of boiling acetone. The hot acetone solution was filtered to remove insoluble material. The acetone solution was brought to a gentle boil and boiling benzene (7.3 ml.) was added to bring the resulting solution to near the cloud point. The solution was stored at −5° overnight; during this time discolored crystalline product formed. Recrystallizations, first from acetone–benzene and then from hot water (charcoal decolorized), gave 3.97 g. (0.0127 mole, 67%) of analytically pure dispiro[3.1.3.1]decanetetracarboxylic acid (IX), m.p. 210° dec.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 53.84; H, 5.17; neut. equiv. 70.1. Found: C, 53.90; H, 5.07; neut. equiv., 70.3.

A 91.9-mg. sample of IX was heated on a thermal balance. A weight loss of 26.6 ± 1.0 mg. was observed. For a loss of two carbon dioxide molecules from IX the theoretical weight loss from a 91.9-mg. sample would be 25.9 mg.

The infrared absorption spectrum of IX was observed in a Nujol mull and a potassium bromide pellet. Spectra were nearly identical and were consistent with the structure assigned for

IX. Infrared absorption bands were found as follows: three broad peaks at 2900 (vs), 2660 (s), 2570 (s); two broad peaks at 1710 (vs) and 1680 (vs); 1460 (s), 1410 (s), 1380 (m), 1300 (vs), 1280 (m), 1255 (w), 1245 (w), 1220 (vw), 1205 (s), 1125 (w), 1095 (w), 1075 (w), 1040 (w), 1030 (vw), 948 (w); two broad peaks at 918 (vs) and 908 (vs); 825 (w), 808 (m), 784 (s), 748 (vw), 732 (m), 720 (vw), and 676 (s) cm.$^{-1}$.

The n.m.r. spectrum of IX was observed in acetone, water, and deuterium oxide at 60 Mc. and chemical shifts were recorded in parts per million relative to TMS. In deuterium oxide a water peak due to exchange of carboxylic acid protons was observed at 4.88 p.p.m. The end-cyclobutane-ring methylene hydrogens were observed as a sharp singlet at 2.67 p.p.m., area ratio corresponding to eight hydrogens. The center-cyclobutane-ring methylene hydrogens were observed as a sharp singlet at 2.21 p.p.m., area ratio corresponding to four hydrogens. In acetone-d_6 the n.m.r. spectra of IX had three peaks occurring at approximately 8.3, 2.7, and 2.2 p.p.m. in a ratio of 1:2:1 (4:8:4) corresponding to carboxyl hydrogens, end-ring methylene hydrogens, and center-ring methylene hydrogens.

The anilide of IX prepared directly from the reaction of aniline and IX at 180° had m.p. 212.2–213.0° when recrystallized twice from ethanol–water. The analysis indicated that decarboxylation of IX had occurred and that the derivative was the dianilide of dispiro[3.1.3.1]decanedicarboxylic acid (I).

Anal. Calcd. for $C_{38}H_{36}N_4O_4$, the tetraanilide of IX: C, 74.49; H, 5.92; N, 9.14. Calcd. for $C_{24}H_{26}O_2N_4$, the dianilide of I: C, 76.9; H, 7.03; N, 7.48. Found: C, 77.60; H, 7.18, N, 7.52.

cis- and *trans*-**Dispiro[3.1.3.1]decanedicarboxylic Acids (I).**—The title acids, I, were initially obtained as a mixture of the *cis* and *trans* isomers by thermal balance decarboxylation of dispiro-[3.1.3.1]decanetetracarboxylic acids (IX) as described above for the characterization of IX. Synthesis of I on a preparative scale was carried out in a semimicro sublimation apparatus with an internal cold finger. Tetraacid IX (400 mg., 1.28 mmoles) was put into the sublimer and the system was flushed with dry nitrogen. The sublimer was heated 10 min. in an oil bath at 220° after which time gas evolution ceased. The pressure on the system was gradually reduced to 1 mm. at which pressure white product I rapidly sublimed. The sublimate amounted to 272 mg. (1.21 mmoles, 94.5%), m.p. 174–175° (softening at 171°). Recrystallization from water did not raise the melting point.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 63.87; H, 7.15. Found: C, 64.27; H, 7.19.

The infrared spectrum of diacid I was observed in a potassium bromide pellet. The spectrum of I was clearly that of a carboxylic acid and was greatly simplified from the spectrum of the precursor of I, the tetraacid IX. The simplification in the spectrum is presumably due to absence of intramolecular hydrogen bonds in I relative to IX. The infrared spectrum of I had absorption bands as follows: 3310 (m), 2940 (w), 2860 (s), 2780 (w), 2690 (w), 2595 (w), 2520 (w), 1692 (vs), 1450 (w), 1410 (s), 1330 (m), 1257 (s), 1245 (w), 1207 (w), 1177 (w), 1115 (broad, w), 1043 (w), 1020 (w), 858 (broad, w), 807 (broad, w), 757 (m), and 727 (w) cm.$^{-1}$.

The 60-Mc.p.s. n.m.r. spectrum of the sodium salt of I in deuterium oxide solution is shown as Figure 1. The spectrum of I is interpreted to be in agreement with the structure assigned.

2-8-Dispiro[3.1.3.1]decane-2,8-dicarboxylic-2,8-d_2 Acid (I-D).—N.m.r. spectra of 2,2,8,8-dispiro[3.1.3.1]decanedicarboxylic acid (IX) were observed in deuterium oxide solution. Recovery of IX and further equilibration with deuterium oxide gave IX tetrasubstituted by deuterium at the carbonyl groups of IX. Decarboxylation of tetradeuterated IX (2,2,8,8-dispiro[3.1.3.1]-decanedicarboxylic acid-d_4) by the procedure described above for I gave 2,8-dispiro[3.1.3.1]decane-2,8-dicarboxylic-2,8-d_2 acid (I-D). The 60-Mc.p.s. n.m.r. spectrum of the sodium salt of I-D is shown in Figure 2.

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Additions of a Phosphorane to Dimethyl Acetylenedicarboxylate

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Triphenylphosphorylideneacetophenone forms two adducts with dimethyl acetylenedicarboxylate, one in methanol (protic solvent) involving a simple *trans* Michael addition (**3**), the other in dry ether (aprotic solvent) involving a four-membered phosphorane ring intermediate and thus a 1,3 shift of the triphenylphosphorus group, in effect **10**. An isomer (**7**) of the first adduct, formed in acid, and other chemical transformations of the two are described, including chemical and physical evidence in confirmation of the assigned structures. A rationalization of the preference for four-centered intermediates involving phosphorus is presented, and the various adducts are shown to conform to the expected modes of additions to acetylenedicarboxylate.

In connection with studies on the preparation and properties of phosphoranes with five single P–C bonds, we considered the possibility of a Diels–Alder reaction between a dienophile and a ketophosphorane such as **1**. When triphenylphosphorylideneacetophenone (**1**) was boiled in methanol with dimethyl acetylenedicarboxylate, a pale yellow crystalline product was, in fact, formed. The empirical composition and physical properties were consistent with its formulation[2] as the expected adduct 2 (see Chart I), as was the formation on bromination of a monobromo compound of very similar properties. The infrared spectra of the two compounds showed the conjugated ester absorption of 5.83 μ and bands at 6.2, 6.3, 6.6, and 6.95 μ assigned to olefinic and aromatic absorptions. The n.m.r. spectrum of the adduct showed two ester methoxyl singlets of three protons each at τ 6.67 and 6.97, a complex multiplet of 20 protons at τ 2–3, and a single proton as a doublet (J = 3 c.p.s.)[3] at τ 4.81 which disappeared on bromination.

Our concurrent experiments with the nature of additions to acetylenedicarboxylate esters,[5] however, suggested another formulation in the isomeric *trans* Michael adduct **3**. Pyrolysis of the adduct led to quantitative yields of triphenylphosphine oxide and the acetylenic ester **4** identified by analysis, infrared absorptions at 4.49 (C≡C), 5.78 ($COOCH_3$), and 6.20 μ (C=C), and hydrogenation and saponification to the known[6] β-phenylethylsuccinic acid, which formed

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[2] Reported in a preliminary communication: J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 2018 (1961).

[3] The splitting of the proton signal by the proximate phosphorus nucleus led us to explore a series of phosphorus compounds as models.[4]

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