was stirred with 7.5 moles of bromine at 20° for 70 hr., giving 2.0 g. (92%) of dithioxanthylium perbromide.

Anal. Calcd. for $C_{26}H_{16}Br_6S_2$: Br, 55.8; S, 8.4. Found: Br, 55.6; S, 8.1.

9-Hydroxythioxanthylium Perbromide.—A filtered solution of 3.28 g. (0.02 mole) of thioxanthone in 1250 ml. of carbon tetrachloride was saturated with dry hydrogen bromide at 25°. The yellow solution became hazy orange, but nothing precipitated. A solution of 20 moles of bromine in carbon tetrachloride was added at one time; after 40 hr., the red solid was collected on a filter and washed with carbon tetrachloride, giving 4.7 g. (58% yield).

Anal. Calcd. for $C_9H_9Br_3OS$: C, 26.7; H, 2.2; Br, 59.2; S. 7.9. Found: C, 27.0; H, 2.4; Br, 57.8; S, 8.2.

The Synthesis of Some Bicyclo[3.3.0]octane Derivatives[1]

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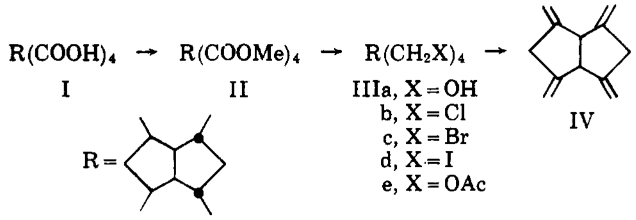
In an earlier communication,[2] the synthesis and characterization of *cis*-bicyclo[3.3.0]octane-*cis,cis*-2,4-*trans,trans*-6,8-tetracarboxylic acid (I) was reported and the suggestion was made that this acid might serve as a readily obtainable intermediate for an attempted synthesis of pentalene. We wish to report the results of some of the work directed along these lines.



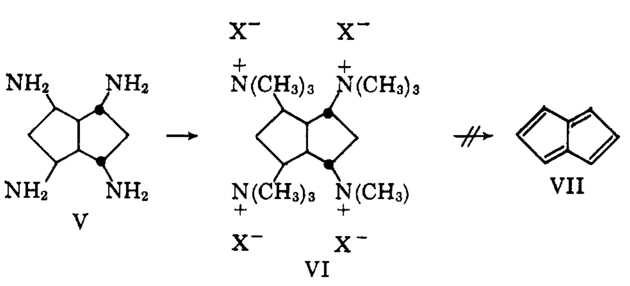
The preparation of tetramethyl *cis*-bicyclo[3.3.0]-octane-*cis,cis*-2,4-*trans,trans*-6,8-tetracarboxylate (II) can be accomplished from the tetraacid chloride of I or by the direct methylation of I. The reduction of II with lithium aluminum hydride gave the tetraalcohol IIIa.[3]

The tetrabromide IIIc was prepared in a 26% yield by the reaction of IIIa with phosphorus tribromide. The reaction of IIIa with potassium iodide in 95% phosphoric acid afforded *cis,cis*-2,4-*trans,trans*-6,8-tetra(iodomethyl)-*cis*-bicyclo[3.3.0]octane (IIId). The n.m.r. spectra of the tetraalcohol IIIa, the tetrabromide IIIc, and the tetraiodide IIId all show the $-CH_2X$ protons as multiplets in the region τ 6.2–7.0, centered near 6.6 (relative to tetramethylsilane). The ratio of these protons to the remainder of the ring protons (from τ 7.4 upfield) exhibited the correct 8:6 ratio. Since the structure of the tetraalcohol IIIa is unambiguous, the halides isolated from the reaction of this alcohol with the halogenating agents must possess the unrearranged skeleton R. Although the corresponding tetrachloride IIIb[3] was allowed to react with sodium iodide in acetone for 1 hr. at the reflux temperature, the starting materials were recovered in quantitative yields.

Dehydrohalogenation of the tetrabromide IIIc or the tetraiodide IIId to obtain 2,4,6,8-tetramethylene-*cis*-bicyclo[3.3.0]octane (IV) was accomplished by warming the halide in an alcoholic solution of potassium hydroxide. The product IV could be recrystallized from methanol to give long colorless needles, but prolonged exposure to light even in the solid state caused a change in the compound. The compound was assigned the *exo*-methylene structure on the basis of the nature of the reaction which produced it, the elemental analysis, the infrared, ultraviolet, and n.m.r. spectrum. The n.m.r. spectrum exhibited two different vinyl protons centered at τ 4.70 and 4.93 (ratio 4:4) with the remainder of the ring protons above 7.5 (ratio 6).

The pyrolysis of *cis,cis*-2,4-*trans,trans*-6,8-tetra(acetoxymethyl)-*cis*-bicyclo[3.3.0]octane afforded a mixture of olefins whose spectrum indicated that both *endo*- and *exo*-methylene unsaturation were present. The vapor phase chromatography of the mixture indicated at least seven different olefins were present.

The thermal decomposition of both the quaternary ammonium hydroxide VI (X = OH) and the corresponding tertiary amine oxide have been shown to be ineffective for the preparation of pentalene.[3] Although pentalene may be formed under these circumstances, it is questionable whether or not it would survive the rough treatment encountered in these reactions. In addition, the stereochemistry of the compound is such that three of four of the amine functions are situated to provide either facile *trans* or *cis* elimination, respectively, while the fourth amine function would be forced into an elimination which is not generally associated with that function. Mixtures of *cis* and *trans* isomers of cyclooctene have been obtained, however, from cyclooctane trimethylammonium bromide with the reagents potassium amide in liquid ammonia (−33°) and phenyl lithium in ether (20°).[4] Because the quaternary salt VI requires that both *cis* and *trans* eliminations occur in the formation of pentalene and the conditions of temperature are mild, these modifications of the Hofmann elimination seemed to be especially inviting.



Treatment of *cis*-bicyclo[3.3.0]octane-*cis,cis*-2,4-*trans,trans*-6,8-tetra(trimethylammonium bromide) (VI, X = Br) with phenyl lithium in ether or with potassium amide in liquid ammonia gave red viscous residues. The infrared spectra showed the presence of *cis* double bonds, but no hydrocarbons could be isolated by gas chromatography or by column chromatography.

The tetraacetamide and tetrabenzamide of V were prepared. Treatment of these amides with thionyl

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[1] This research was supported by a grant (NSF G-10472) from the National Science Foundation whose assistance is gratefully acknowledged.

[2] J. K. Stille and D. A. Frey, *J. Am. Chem. Soc.*, **81**, 4273 (1959).

[3] E. R. Hanna, K. T. Finley, W. H. Saunders, Jr., and V. Boekelheide, *ibid.*, **82**, 6342 (1960).

[4] G. Wittig and R. Polster, *Ann.*, **612**, 102 (1958).

chloride and benzoyl chloride, according to the procedure of the von Braun reaction,[5] gave none of the desired 2,4,6,8-tetrachloro-*cis*-bicyclo[3.3.0]octane.

Experimental

***cis,cis*-2,4-*trans,trans*-6,8-Tetra(bromomethyl)-*cis*-bicyclo[3.3.0]octane (IIIc)**.—To 12.0 g. (0.0444 mole) of phosphorus tribromide in 100 ml. of carbon tetrachloride[6] was added 7.15 g. (0.0311 mole) of the tetraalcohol IIIa.[3] The mixture was stirred and heated at the reflux temperature for 12 hr. after which time the solution was cooled and allowed to stand at room temperature for 36 hr. The solvent was removed under reduced pressure and the yellow residue was extracted with methylene chloride. The combined extracts were washed with 5% aqueous sodium carbonate and dried over calcium chloride. The solvent was removed under reduced pressure and the tan residue was recrystallized from acetone to yield 3.92 g. (26.2%) of white crystals: m.p. 119–119.5°; n.m.r. spectrum (deuteriochloroform) multiplet τ 6.1–6.9 (CH_2Br) and multiplets above 7.3 (ring protons), ratio 8:10 (tetramethylsilane internal standard).

Anal. Calcd. for $C_{12}H_{18}Br_4$: C, 29.88; H, 3.73. Found: C, 30.07; H, 3.73.

***cis,cis*-2,4-*trans,trans*-6,8-Tetra(iodomethyl)-*cis*-bicyclo[3.3.0]octane (IIId)**.—To a cooled solution of 95% orthophosphoric acid made from 26 g. (0.183 mole) of phosphoric anhydride and 54 ml. (92.5 g., 0.80 mole) of 85% orthophosphoric acid was added 133 g. (0.80 mole) of potassium iodide and 23.0 g. (0.100 mole) of the tetraalcohol IIIa. The mixture was heated at 100–110°, with stirring, for 16 hr. and then cooled. The mixture was allowed to stand at room temperature for 30 hr. The solid residue was dissolved in 1.5 l. of carbon tetrachloride. The solution was washed with a sodium thiosulfate solution and water, and the solvent was removed under reduced pressure. The dark oily residue was triturated with 150 ml. of cold carbon tetrachloride. The solid residue (13.5 g., 20%) which did not dissolve was recrystallized from heptane to afford 12.4 g. (18.5%) of white crystals: m.p. 140–141°; n.m.r. (deuteriochloroform) multiplet τ 6.3–7.0 ($-CH_2I$) and multiplets above 7.3 (ring protons), ratio 8:10 (tetramethylsilane internal standard).

Anal. Calcd. for $C_{12}H_{18}I_4$: C, 21.49; H, 2.69. Found: C, 21.74; H, 2.34.

An attempt was also made to prepare the tetraiodide IIId directly from the tetrachloride IIIb[3] by reaction with sodium iodide in acetone. After 1 hr. of heating at the reflux temperature the tetrachloride was recovered unchanged.

2,4,6,8-Tetramethylene-*cis*-bicyclo[3.3.0]octane (IV).—To a solution of 4.75 g. (0.0848 mole) of potassium hydroxide in 40 ml. of methanol was added 7.11 g. (0.0106 mole) of the tetraiodide IIId. The mixture was heated at the reflux temperature for 7 hr. The solution was cooled and the solvent was removed under reduced pressure. The dark residue was diluted with water and the mixture was extracted with hexane. The combined hexane extracts were washed with water and dried. After a first crude distillation under reduced pressure, fractional distillation at 80° (0.05 mm.) gave 59 mg. (3.5%) of an oily yellow solid on the cold finger and a polymeric pot residue. (During the first distillation, the pot temperature should not be allowed to go above 50° since in several experiments an exothermic reaction affording a violet compound occurred.) Recrystallization of this solid from methyl alcohol produced white needles, m.p. 59.5–60°. The infrared spectrum of IIId (mull) showed absorption maxima at 1635 (C=C stretching), 883 and 860 ($R_2C{=}CH_2$, C–H out-of-plane deformation), and no maxima below 850 cm.$^{-1}$ characteristic of $R_1R_2C{=}CHR_3$, C—H out-of-plane deformation.[7] There was no absorption in the ultraviolet above 220 mμ. The n.m.r. spectrum (carbon tetrachloride) showed two unresolved peaks at τ 4.70 and 4.93 ($=CH_2$) and multiplets at 7.5–8.2 (ring protons), ratio 8:6 (tetramethylsilane internal standard).

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.47; H, 8.98.

The same compound was obtained in the elimination reaction of the corresponding tetrabromide IIIc.

***cis,cis*-2,4-*trans,trans*-6,8-Tetra(acetoxymethyl)-*cis*-bicyclo[3.3.0]octane (IIIe)**.—To a 50 ml. of benzene was added 13.8 g. (0.060 mole) of the tetraalcohol IIIa and 30.6 g. (0.30 mole) of acetic anhydride. The solution was heated at the reflux temperature for 8 hr. and then cooled. The solvent was removed under reduced pressure. The viscous oily residue was dissolved in benzene, washed with 5% aqueous sodium bicarbonate, and dried over calcium chloride. The volume of the solution was reduced to 25 ml. and the solution was passed down a column of alumina using benzene as the eluent. Concentration of the eluate gave 14.9 g. (62.4%) of a clear viscous oil, which could not be distilled at 0.25 mm. without decomposition; n^{20}_D 1.4812. The infrared spectrum of IIIe (neat) showed absorption maxima at 1750 (C=O stretching) and 1250 cm.$^{-1}$ (C–O acetate).

Anal. Calcd. for $C_{20}H_{30}O_8$: C, 60.30; H, 7.54. Found: C, 59.81; H, 7.30.

Pyrolysis of *cis,cis*-2,4-*trans,trans*-6,8-Tetra(acetoxymethyl)-*cis*-bicyclo[3.3.0]octane (IIIe).—A 15.20-g. (0.0387 mole) sample of the tetraacetate IIIe was dropped at the rate of 1 ml./min. through a column packed with glass helices. The column was heated to 550° at a pressure of 300–400 mm. while a steady flow of nitrogen was maintained. The products, which were collected in a flask cooled in a Dry Ice–acetone bath, were dissolved in benzene and neutralized with a 10% aqueous sodium bicarbonate solution. After washing the benzene solution with water and drying over sodium sulfate, the solvent was removed under reduced pressure and the oily residue was fractionally distilled to afford a fraction, 0.5 g., b.p. 60–80° (1 mm.), which showed little carbonyl absorption in the infrared region.

Vapor fractometry of this fraction showed three major components and at least four minor components. Separation of the three major components by vapor fractometry produced red oils. Only one of the three major components contained no carbonyl. The infrared spectrum (neat) of this component showed absorption maxima at 1655 and 1620 (C=C stretching) and no less than eight maxima between 600 and 1000 cm.$^{-1}$. The compound was not characterized further.

***cis*-Bicyclo[3.3.0]octane-*cis,cis*-2,4-*trans,trans*-6,8-tetra(ammonium chloride)**.—Tetraethyl *cis*-bicyclo[3.3.0]octane-*cis,cis*-2,4-*trans,trans*-6,8-tetracarbamate[3] was heated at the reflux temperature with an excess of concentrated hydrochloric acid. Removal of the solvent under reduced pressure left a white solid residue which was dissolved in water and recrystallized by passing gaseous hydrogen chloride through the solution; m.p. above 300° (lit.[3] m.p. above 300°).

Anal. Calcd. for $C_8H_{22}Cl_4N_4$: C, 30.38; H, 6.96; N, 17.70. Found: C, 30.65; H, 6.99; N, 17.36.

***cis*-Bicyclo[3.3.0]octane-*cis-cis*-2,4-*trans,trans*-6,8-tetraamine (V)**.—To a powdered sample of 4.00 g. (0.0127 mole) of the tetraamine (V) tetrahydrochloride was added 6.0 g. (0.15 mole) of powdered sodium hydroxide. The two were well mixed and then transferred to an apparatus suitable for sublimation. The amine was sublimed at 160–180° (1 mm.) onto a cold finger. The yield of hygroscopic white granules was 1.22 g. (57%), m.p. 75–75.5° (sealed capillary tube). The infrared spectrum of V (melt) showed a maximum at 3450 cm.$^{-1}$ (N–H stretching).

Anal. Calcd. for $C_8H_{18}N_4$: C, 56.47; H, 10.59; N, 32.9. Found: C, 56.03; H, 10.32; N, 32.8.

The tetraamine V was also prepared in the following manner. A mixture of 18 g. (0.28 mole) of sodium azide, 18 g. (1.0 mole) of water, and 100 ml. of chloroform was cooled to 0°. To this was added with stirring 14.8 ml. (27.7 g., 0.283 mole) of 100% sulfuric acid at a rate so that the temperature remained below 10°. The tetracarboxylic acid I (8.6 g.; 0.030 mole) was dissolved in 46 ml. of 100% sulfuric acid. An aliquot of the chloroform solution of hydrazoic acid equivalent to 8.6 g. (0.20 mole) of hydrazoic acid was slowly added with stirring. The temperature was kept between 35 and 45° during addition. After the addition was completed the mixture was warmed for 12 hr. at 40° and then cooled to room temperature. Solid barium carbonate was slowly added to precipitate all the sulfate as barium sulfate which was then removed by filtration and washed with methanol. The washings were added to the filtrate and the solvents were removed under reduced pressure. The solution was steam distilled until the distillate was no longer basic to litmus. The distillate was then made acidic with hydrochloric acid and the solvent was removed under reduced pressure. The solid residue was mixed with pulverized sodium hydroxide and sublimed to give a 2% yield of the amine V.

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(5) W. R. Vaughan and R. D. Carlson, *J. Am. Chem. Soc.*, **84**, 769 (1962).

(6) A. T. Blomquist and J. A. Verdol, *ibid.*, **77**, 1806 (1955).

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 34

cis,cis-**2,4-***trans,trans*-**6,8-(Tetratrimethylammonium bromide)-***cis*-**bicyclo[3.3.0]octane.**—A sealed tube containing 3.0 g. (0.011 mole) of VI,[3] 10 ml. of methyl bromide, and 5 ml. of methyl alcohol was heated at 100–110° for 12 hr. After cooling the tube, the seal was broken and the solvent was decanted from the gummy residue. Drying the residue under reduced pressure in the presence of calcium chloride gave 4.3 g. (61%) of a tan crystalline solid which was soluble in water but insoluble in most organic solvents. This solid slowly yielded a white powder upon continuous extraction with acetonitrile. The powder decomposed above 140°.

Anal. Calcd. for $C_{20}H_{46}Br_4N_4$: C, 36.25; H, 6.95. Found: C, 36.18; H, 6.85.

Attempted Degradation of the Quaternary Bromide of VI with Phenyllithium.—To a suspension of 4.24 g. (0.00640 mole) of the quaternary bromide in 100 ml. of anhydrous ether was added an aliquot of phenyllithium solution containing 0.0256 mole of phenyllithium. The mixture was stirred for 70 hr. at room temperature and then filtered under nitrogen. The filtrate showed a small peak by vapor fractometry which could not be ascribed to ether, benzene, bromobenzene, or biphenyl. The filtrate was washed with water and dried over calcium chloride for 30 min.; the solvent was removed under reduced pressure to yield only trace amounts of an oily red residue. The infrared spectrum of this oil (neat) showed absorption maxima at 1685 and 753 cm.$^{-1}$. Not enough compound was present in any of the runs to identify this product.

Attempted Degradation of the Quaternary Bromide of VI with Potassium Amide.—To 1.64 g. (0.042 mole) of potassium metal in 100 ml. of liquid ammonia was added 5.83 g. (0.0088 mole) of the quaternary bromide. The mixture was stirred for 4 hr. at Dry Ice–acetone temperature. After removing the cooling bath, the solvent was allowed to slowly boil away over an 8-hr. period.

The residue was extracted with ether and the combined extracts were washed with 2% aqueous ammonium chloride and dried. Removal of the solvent left 0.15 g. of a red-brown oil which was dissolved in pentane and chromatographed over Woelm basic alumina using pentane as the eluent. Fractional distillation of the eluate gave 50 mg. of a yellow oil, b.p. 200° (1 mm.), which showed maxima in the infrared region which could be ascribed to carbonyl.

cis,cis-**2,4-***trans,trans*-**6,8-Tetra(acetamido)-***cis*-**bicyclo[3.3.0]-octane.**—To 10.2 g. (0.10 mole) of acetic anhydride was added with stirring 3.4 g. (0.020 mole) of the tetraamine V. The precipitate was separated by filtration and recrystallized from glacial acetic acid to give a quantitative yield of pure product, m.p. above 400°. The infrared spectrum (mull) showed absorption maxima at 3330 and 3125 (N–H stretching), 1652 (C═O stretching), and 1550 cm.$^{-1}$ (C–N stretching).

Anal. Calcd. for $C_{16}H_{26}N_4O_4$: C, 56.80; H, 7.69; N, 16.57. Found: C, 56.97; H, 7.82; N, 16.38.

Attempted Degradation of *cis,cis*-**2,4-***trans,trans*-**6,8-Tetra-(acetamido)-***cis*-**bicyclo[3.3.0]octane.**—A mixture of 20 g. (0.17 mole) of thionyl chloride and 3.92 g. (0.0116 mole) of the tetraacetamide was allowed to stand at room temperature for 20 hr. and then heated at the reflux temperature for 48 hr. Removal of the solvent left a small amount of residue which was recrystallized from hexane to give trace amounts of a white crystalline solid, m.p. 119.5–120°, which was not characterized.

cis,cis-**2,4-***trans,trans*-**6,8-Tetra(benzamido)-***cis*-**bicyclo[3.3.0]-octane.**—The tetraamine (V) tetrahydrochloride (0.637 g., 0.00202 mole) was dissolved in 25 ml. of water and to this solution was added 4 g. (0.10 mole) of sodium hydroxide. The solution was cooled to 10° in an ice bath and 1.4 g. (0.01 mole) of benzoyl chloride was added slowly with stirring, keeping the temperature of the solution below 20°. Stirring was continued an additional hour and the precipitate was then collected by filtration. The white solid was washed with 5% aqueous sodium hydroxide and 5% hydrochloric acid, and dried. The weight of pure product was 1.026 g. (87%), m.p. above 400°. The infrared spectrum (mull) showed absorption maxima at 3330 (N–H stretching) and 1640 cm.$^{-1}$ (C═O stretching).

Anal. Calcd. for $C_{36}H_{34}N_4O_4$: C, 73.72; H, 5.80; N, 9.56. Found: C, 73.84; H, 5.89; N, 9.73.

Attempted Degradation of *cis,cis*-**2,4-***trans,trans*-**6,8-Tetra-(benzamido)-***cis*-**bicyclo[3.3.0]octane by the von Braun Reaction.**—A mixture of 5.82 g. (0.010 mole) of the tetrabenzamide and 12.5 g. (0.060 mole) of phosphorus pentachloride in 75 ml. of carbon tetrachloride was heated at the reflux temperature for 5 days. The excess phosphorus pentachloride was destroyed by the cautious addition of water. The carbon tetrachloride layer was washed with 5% aqueous sodium bicarbonate and dried. Removal of the solvent gave only trace amounts of an oily residue.

The Rearrangement of 1,1-Dicyclopropylethylene

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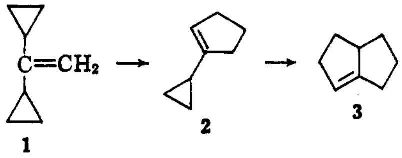
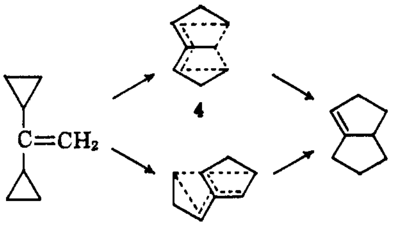
Two examples have been reported of the vinylcyclopropane rearrangement in compounds containing more than one cyclopropyl ring. Doering has studied the pyrolysis of 1-cyclopropyl-2-vinylcyclopropane[1] while Vogel and Erb have described the rearrangement of *cis*- and *trans*-1,2-dicyclopropylethylene.[2] The products in both cases were cyclopropylcyclopentenes which were stable under the conditions of the pyrolyses.

We have studied the pyrolysis of 1,1-dicyclopropylethylene (**1**) because, in this case, the rearrangement of one cyclopropyl ring leads to a product **2** containing a new vinylcyclopropane system. This in turn, would be expected to rearrange to bicyclo[3.3.0]octene-1 (**3**) in a second step. The possibility also exists in this system of the two rings opening in a concerted reaction to give **3** directly without the intermediate formation of 2. Two transition states for the concerted reaction can be formulated, one (**4**) in which the two cyclopropyl groups simultaneously attack the 2-carbon of the vinyl group and another (**5**) in which the one cyclopropyl attacks this carbon while the other attacks the incipient cyclopentene double bond backside.





1,1-Dicyclopropylethylene was prepared from dicyclopropyl ketone by the Wittig reaction. The n.m.r. spectrum of this compound is shown in Figure 1. Pyrolysis in a glass packed tube at 400° gave, on the first pass, a material **6** showing only one major new peak in the gas chromatograph. After continuous passage through the column, **6** had grown to about 40% of the starting material. A second peak **7** began to appear at this point and grew at the expense of **6**. When the peak corresponding to the 1,1-dicyclopropylethylene

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[1] W. von Doering, *Angew. Chem., Intern. Ed. Engl.*, **2**, 115 (1963).

[2] E. Vogel and R. Erb, *ibid.*, **1**, 53 (1962).