eter the n.m.r. spectrum of 3,4-dimethylenetetrahydrofuran (I) in purified carbon tetrachloride containing a drop of tetramethylsilane as an internal standard was obtained at an electromagnet frequency of 60 Mc. Assignment of band positions on the spectrogram was accomplished by use of an audio side band of known frequency. Peak distances on the spectrogram were measured in cycles per second from the tetramethylsilane peak and then converted to τ values (p.p.m.). Three peaks were observed at 4.62, 5.07, and 5.60 p.p.m., with relative peak area ratios of 1:1:2, respectively.

$\Delta^{3a(7a)}$-Hexahydrobenzo[*c*]furan-5,6-dicarboxylic Anhydride (VII).—A small amount (*ca.* 0.5 g.) of the diene-enriched fraction (described above) was added to a small amount (*ca.* 0.3 g.) of sublimed maleic anhydride. Immediately the mixture generated considerable heat and upon cooling deposited a solid material which was collected on a Büchner funnel and washed with copious amounts of anhydrous ether. The solid was recrystallized from an ethyl alcohol–ether mixture (1:9 by volume) and then from a benzene–petroleum ether mixture containing a few drops of acetic anhydride to obtain 0.6 g. of the white, crystalline $\Delta^{3a(7a)}$-hexahydrobenzo[*c*]furan-5,6-dicarboxylic anhydride (VII), m.p. 118–121°.

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 61.85; H, 5.19. Found: C, 61.84; H, 5.34.

$\Delta^{3a(9a),6(7)}$-Octahydronaphtho[2,3-*c*]furan-5,8-dione (VIII).—A small amount (*ca.* 0.5 g.) of the diene-enriched fraction (described above) was added to a small amount (*ca.* 0.5 g.) of *p*-benzoquinone. After the mixture was allowed to stand overnight, crystals which had deposited were collected on a Büchner funnel and washed with anhydrous ether to give approximately 0.4 g. of the 1:1 adduct of *p*-benzoquinone and 3,4-dimethylenetetrahydrofuran, $\Delta^{3a(9a),6(7)}$-octahydronaphtho[2,3-*c*]furan-5,8-dione (VIII), m.p. 129–131°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.93. Found: C, 70.80; H, 6.20.

$\Delta^{3a(12a),6a(9a)}$-Tetradecahydroanthra[2,3-*c*:6,7-c′]difuran-5,11-dione (IX).—When the filtrate from which the 1:1 adduct of *p*-benzoquinone and 3,4-dimethylenetetrahydrofuran (I) had been isolated was cooled, an additional adduct (*ca.* 0.1 g.) was deposited as the 1:2 adduct, $\Delta^{3a(12a),6a(9a)}$-tetradecahydroanthra-[2,3-*c*: 6,7-*c*′]difuran-5,11-dione (IX), which sublimed at 185° (cor.).

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.18; H, 7.00.

Paracyclophane Derivatives by the Dieckmann Cyclization

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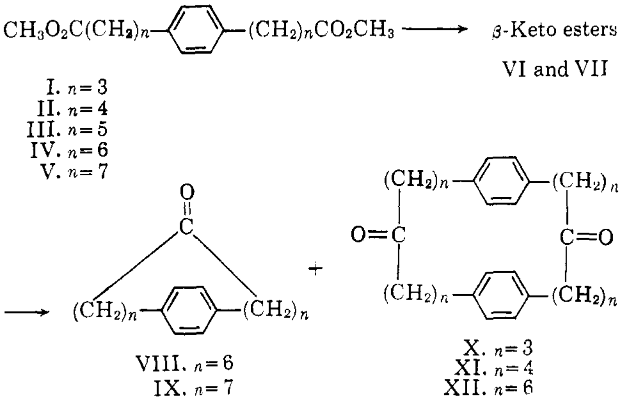
The Dieckmann condensation under conditions of high dilution has been used with the esters of *p*-phenylenedicarboxylic acids. The products, several ketone derivatives of [*n*]paracyclophanes and [*n.n*]paracyclophanes, are described.

Ever since it was shown that macrocycles could be prepared by the Dieckmann cyclization,[2,3] we have wondered if this reaction might be used to prepare derivatives of paracyclophanes. This reaction appeared to be desirable for making compounds with odd-numbered carbon bridges from symmetrical *p*-phenylenedicarboxylic esters, which have led to compounds with even-numbered carbon bridges in the acyloin cyclization.[4] Moreover, it was believed that dimeric derivatives might be made in cases where intramolecular cyclization proved to be impossible.

Precursor diesters were prepared by standard methods; each of the previously known diesters possessed physical properties which agreed with those earlier described.[5–7] *p*-Bis(3-carboxypropyl)benzene was prepared from 4-(*p*-succinylphenyl)butyric acid by the catalytic method of Horning and Reisner.[8] Methyl esters were made by the method of Clinton and Laskowski.[9] *p*-Bis(4-carboxybutyl)benzene was prepared by the action of sodium cyanide on *p*-bis(4-bromobutyl)benzene followed by hydrolysis. *p*-Bis(5-carboxypentyl)benzene was prepared by a malonic ester synthesis with *p*-bis(4-bromobutyl)benzene. In order to prepare *p*-bis(6-carboxyhexyl)benzene, it was necessary to treat *p*-bis(5-carbomethoxypentyl)benzene with lithium aluminum hydride, treat the glycol with hydrogen bromide, allow the dibromide to react with cyanide, and then hydrolyze the dinitrile. This same dibromide was part of a malonic ester synthesis to produce *p*-bis-(7-carboxyheptyl)benzene.

It was found possible to prepare ketone derivatives of paracyclophanes by the method of Dieckmann, although in low yields. From the mixtures, following hydrolysis and decarboxylation of the β-keto esters formed during the reactions, four products were obtained by fractional crystallization and one product was obtained by distillation. No attempts were made to isolate the intermediates VI ($C_{9+2n}H_{6+4n}O_3$) and VII ($C_{18+4n}H_{12+8n}O_6$). From I was produced 4,17-diketo[7.7]paracyclophane (X) in 11.1% yield; from II was produced 5,20-diketo[9.9]paracyclophane (XI)



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[2] N. J. Leonard and C. W. Schimelpfenig, *J. Org. Chem.*, **23**, 1708 (1958). Earlier examples are cited in this article.

[3] A. Lüttringhaus and H. Prinzbach, *Ann.*, **624**, 79 (1959); N. J. Leonard, T. W. Milligan, and T. W. Brown, *J. Am. Chem. Soc.*, **82**, 4075 (1960); C. G. Overberger, P. Barkan, A. Lusi, and H. Ringsdorf, *ibid.*, **84**, 2814 (1962).

[4] A summary of macrocyclic systems is presented by J. Sicher in "Progress in Stereochemistry," Vol. 3, P. B. D. de la Mare and W. Klyne, ed., Butterworths, Inc., Washington, D. C., 1962, pp. 202–263.

[5] D. J. Cram and H. U. Daeniker, *J. Am. Chem. Soc.*, **76**, 2743 (1954).

[6] D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954).

[7] A. T. Blomquist, R. E. Stahl, Y. C. Meinwald, and B. H. Smith, *J. Org. Chem.*, **26**, 1687 (1961).

[8] E. C. Horning and D. B. Reisner, *J. Am. Chem. Soc.*, **71**, 1036 (1949).

[9] R. O. Clinton and S. C. Laskowski, *ibid.*, **70**, 3135 (1948).

in 8.2% yield; from IV were produced 7-keto[13]-paracyclophane (VIII) in 36.8% yield and 7,26-diketo-[13.13]paracyclophane (XII) in 1.2% yield; and from V was produced 8-keto[15] paracyclophane (IX) in 11.7% yield. No pure product could be isolated by fractional crystallization of the reaction mixture from III, although several solid fractions had infrared spectra characteristic of ketones and esters.

Because of the possibility of transannular interaction between carbonyl and aromatic portions of these compounds, it was of interest to interpret their infrared spectra. Of the ketones, only X exhibited an absorption band which indicated such an interaction. Of the paracyclophanes with only ketonic functional groups which have been previously prepared,[5,10] the keto[9]paracyclophanes,[10g] the keto[10]paracyclophanes,[5] and the benzoyl type[10e] were reported with infrared spectra data. The carbonyl stretching frequencies of these keto[9]paracyclophanes and the keto-[10]paracyclophanes appeared in the range 1703–1709 cm.$^{-1}$. Compounds of the benzoyl type exhibited absorption dependent upon coplanarity of the carbonyl group and the aromatic ring. With respect to spectral identification of transannular effects, such compounds are not analogous to those with the carbonyl group flanked by two methylene groups and situated above the plane of aromatic ring carbons.

Experimental

***p*-Bis(3-carboxypropyl)benzene by Catalytic Hydrogenation.**—Into a 500-ml. reaction bottle was placed a boiling solution of 31.7 g. (0.12 mole) of 4-(*p*-succinylphenyl)butyric acid[6] and 300 ml. of acetic acid. Two grams of 10% palladium-on-charcoal catalyst was added and the bottle was fitted into a shaker-type hydrogenation apparatus[11] which was equipped with a 200-watt electric bottle heater.[11] The reaction mixture was heated (40–50 v. applied to the bottle heater) while hydrogenation was effected during a 4-hr. period. The reaction mixture was filtered and the filtrate was poured into 600 ml. of water. The suspension was digested; then the solid was removed by filtration. The solid was dried *in vacuo* over phosphoric anhydride. There was obtained 27 g. of *p*-bis(3-carboxypropyl)benzene with m.p. 174–176° (lit.,[6] m.p. 176–177°).

Procedure for Cyclization.—The general method for cyclization has been described.[2] In every case the catalyst was prepared from 44.4 g. (0.6 mole) of *t*-butyl alcohol and 9.35 g. (0.24 g.-atom) of potassium. In each case 0.05 mole of ester was used. Following the removal of esters by distillation from the reaction products, the ketones were obtained by fractional crystallization except for VIII, which was separated by distillation.

4,17-Diketo[7.7]paracyclophane (X).—From 13.92 g. of I was obtained 1.043 g. of X with m.p. 141–142.2° (colorless needles from ethanol).

Anal. Calcd. for $C_{26}H_{32}O_2$: C, 82.93; H, 8.57; mol. wt., 376.5. Found: C, 83.04; H, 8.70; mol. wt., 406 (Rast, camphor).

5,20-Diketo[9.9]paracyclophane (XI).—From 15.32 g. of II was obtained 0.89 g. of XI with m.p. 124.5–126° (colorless platelets from ethanol).

Anal. Calcd. for $C_{30}H_{40}O_2$: C, 83.28; H, 9.32; mol. wt., 432.6. Found: C, 83.06; H, 9.75; mol. wt., 411 (Rast, camphor).

***p*-Bis(6-hydroxyhexyl)benzene.**—To a cold suspension of 38 g. of lithium aluminum hydride and 500 ml. of tetrahydrofuran was added dropwise 84.57 g. (0.253 mole) of *p*-bis(5-carbomethoxypentyl)benzene. After the reaction mixture had been stirred for 40 hr., 65 ml. of ethyl acetate was added. This suspension was slowly transferred to a beaker which contained 1 l. of water. Concentrated hydrochloric acid was added until the mixture became acidic. Then the mixture was heated to remove all tetrahydrofuran. As the mixture cooled to 20°, crystals appeared. These were removed by filtration, washed with water, and dried. The *p*-bis(6-hydroxyhexyl)benzene weighed 71.8 g. and had m.p. 59–62°. The analytical sample, recrystallized from benzene, had m.p. 61.5–62.5°.

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.84; H, 10.76.

***p*-Bis(6-bromohexyl)benzene.**—For 4.5 hr. hydrogen bromide was bubbled through 69.6 g. (0.25 mole) of *p*-bis(6-hydroxyhexyl)benzene which was being stirred and heated at 110–115° with a wax bath. The reaction mixture was extracted with ether. The ether solution was extracted successively with water, sodium bicarbonate solution, and water. The ether solution was dried with magnesium sulfate. The ether was removed from the solution by evaporation. The residue was recrystallized from ethanol. There was obtained 75.4 g. of *p*-bis(6-bromohexyl)benzene with m.p. 36.8–38°. The analytical sample, colorless platelets from ethanol, had m.p. 37.4–38.3°.

Anal. Calcd. for $C_{18}H_{28}Br_2$: C, 53.48; H, 6.98. Found: C, 53.44; H, 7.04.

***p*-Bis(6-carboxyhexyl)benzene.**—To a stirred and refluxing solution of 100 ml. of ethanol, 40 ml. of water, and 43 g. of potassium cyanide was added during a 20-min. period a suspension of 40.4 g. (0.1 mole) of *p*-bis(6-bromohexyl)benzene and 50 ml. of ethanol. Stirring and refluxing were continued for 13 hr. The reaction mixture was extracted with benzene. The benzene solution was clarified by filtration through paper. Then the benzene was removed by evaporation. The brown residue was added to a solution of 400 ml. of ethanol, 100 ml. of water, and 20 g. of sodium hydroxide. This solution was refluxed until the evolution of ammonia ceased. The ethanol was then removed by distillation, during which time there was added in small portions 400 ml. of hot water. The hot aqueous solution was cooled and acidified. The colorless solid product weighed 26.8 g. and had m.p. 144–155°. The analytical sample, prepared by recrystallization from acetic acid and then from ethyl acetate, was composed of colorless needles with m.p. 155.5–157.5°.

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.93; H, 8.96.

***p*-Bis(6-carbomethoxyhexyl)benzene (IV).**—A solution of 26.6 g. (0.08 mole) of *p*-bis(6-carboxyhexyl)benzene, 32 g. of absolute methanol, 200 ml. of methylene chloride, and 1 ml. of concentrated sulfuric acid was heated to reflux for 30 hr. The solution was extracted successively with water, sodium bicarbonate solution, and water. The methylene chloride solution was dried with magnesium sulfate. After the methylene chloride had been removed by evaporation, the residue was distilled. The colorless IV distilled at 212–213° (0.35 mm.) and weighed 20.6 g.

Anal. Calcd. for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 73.00; H, 9.39.

7-Keto[13]paracyclophane (VIII) and 7,26-Diketo[13.13]-paracyclophane (XII).—From 18.1 g. of IV were obtained 5.09 g. of VIII and 0.16 g. of XII.

VIII was a colorless liquid with b.p. 170–172° (0.8 mm.) and m.p. 33–35°.

Anal. Calcd. for $C_{19}H_{28}O$: C, 83.77; H, 10.36; mol. wt., 262.4. Found: C, 83.95; H, 10.42; mol. wt., 224 (Rast, camphor).

XII, colorless platelets from methanol, possessed m.p. 84–84.7°.

Anal. Calcd. for $C_{38}H_{56}O_2$: C, 83.77; H, 10.36; mol. wt., 524.9. Found: C, 83.67; H, 10.21; mol. wt., 484 (Rast, camphor).

***p*-Bis(7-carboxyheptyl)benzene.**—To a stirred and heated solution of 160 ml. of absolute ethanol, 12.3 g. of sodium and 90.6 g. of diethyl malonate was added during a period of 75 min. a warm suspension of 32.4 g. (0.08 mole) of *p*-bis(6-bromohexyl)benzene and 20 ml. of ethanol. The suspension was stirred and heated to reflux for 30 min. After the suspension cooled, to it were added 53 g. of potassium hydroxide and 150 ml. of water. This solution was stirred and heated. The ethanol was

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(10) (a) E. Fourneau and P. M. Baranger, *Bull. soc. chim. France*, [4] **49**, 1161 (1931); (b) K. Wiesner, D. M. MacDonald, R. B. Ingraham, and R. B. Kelly, *Can. J. Research*, **B28**, 561 (1950); (c) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73**, 5691 (1951); (d) D. J. Cram and H. Steinberg, *ibid.*, **74**, 5388 (1952); (e) W. M. Schubert, W. A. Sweeney, and H. K. Latourette, *ibid.*, **76**, 5462 (1954); (f) R. Huisgen, W. Rapp, I. Ugi, H. Walz, and I. Glogger, *Ann.*, **586**, 52 (1954); (g) D. J. Cram and M. F. Antar, *J. Am. Chem. Soc.*, **80**, 3109 (1958); (h) R. Huisgen and I. Ugi, *Chem. Ber.*, **93**, 2693 (1960).

(11) Available from Parr Instrument Co., Moline, Ill.

removed by distillation, during which time 200 ml. of hot water was added in small portions. The residual solution was cooled and made acidic with hydrochloric acid. The acidic suspension was extracted with ether. The ether extracts were combined and dried with magnesium sulfate. The ether was removed by evaporation and the residue was heated to 230°. The acid was allowed to cool and then was dissolved in sodium hydroxide solution. The basic solution was filtered and the filtrate was acidified. The solid was removed by filtration and was recrystallized from acetic acid. The solid weighed 16.8 g. and possessed m.p. 110–116°. The analytical sample, colorless platelets from benzene, had m.p. 119.5–120.5°.

Anal. Calcd. for $C_{22}H_{34}O_4$: C, 72.89; H, 9.45. Found: C, 73.05; H, 9.36.

p-Bis(7-carbomethoxyheptyl)benzene (V).—*p*-Bis(7-carboxyheptyl)benzene was treated with methanol, methylene chloride, and sulfuric acid in the manner described for the preparation of IV. From 84.7 g. (0.234 mole) of *p*-bis(7-carboxyheptyl)benzene there was obtained 56.8 g. of V with b.p. 264–269° (4 mm.). The analytical sample, colorless platelets from benzene, had m.p. 51–52°.

Anal. Calcd. for $C_{24}H_{38}O_4$: C, 73.81; H, 9.81. Found: C, 74.01; H, 9.74.

8-Keto[15]paracyclophane (IX).—From 19.52 g. of V was obtained 1.76 g. of IX with m.p. 68.5–69.5° (colorless platelets from methanol).

Anal. Calcd. for $C_{21}H_{32}O$: C, 83.94; H, 10.74; mol. wt., 300.5. Found: C, 83.92; H, 10.68; mol. wt., 303 (Rast, camphor).

Infrared Spectra.—Spectra of the new ketones were recorded with the Perkin–Elmer Model 21 spectrophotometer. A summary of the carbonyl stretching frequencies follows: VIII, 1706 cm.$^{-1}$ (liquid film); IX, 1703 cm.$^{-1}$ (KBr disk); X, 1695 cm.$^{-1}$ (KBr disk); XI, 1705 cm.$^{-1}$ (KBr disk); and XII, 1708 cm.$^{-1}$ (KBr disk). Each spectrum had only one absorption band (located between 1892 cm.$^{-1}$ and 1911 cm.$^{-1}$) in the 1800–2000-cm.$^{-1}$ region, the characteristic display for a *p*-disubstituted benzene.[12] Moreover, each ketone exhibited a characteristic medium-intensity absorption band in the range 794–819 cm.$^{-1}$, confirming the *para* orientation.

Acknowledgment.—Our sincere appreciation is given to the Robert A. Welch Foundation for generous financial support. We are indebted to Dr. J. J. Spurlock for aid with infrared instrumentation.

[12] C. W. Young, R. B. DuVall, and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

The Synthesis and Rearrangement of 2-Hydroxyalkyl 3-Thienyl and 2-Hydroxyalkyl 2-Naphthyl Sulfides

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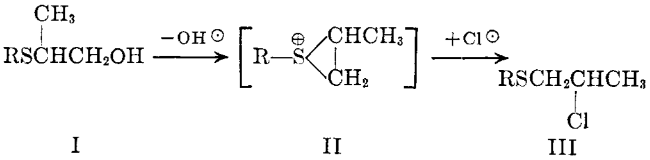
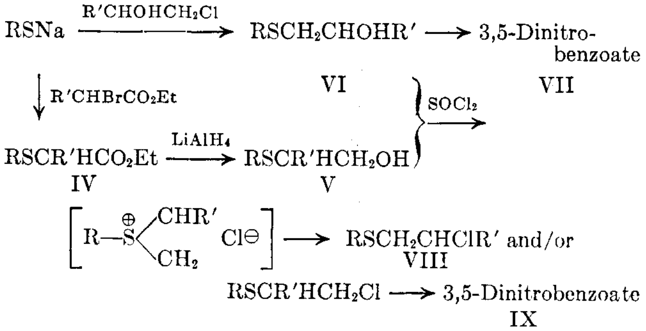
Three 2-hydroxy-*sec*-alkyl 3-thienyl sulfides and a 2-hydroxy-*sec*-alkyl 2-naphthyl sulfide were prepared and converted to their corresponding alkyl chlorides. In the case of the hydroxy heterocyclic sulfides it was found that the chlorides obtained were mixtures of isomers resulting from the intermediate formation of an unsymmetrical sulfonium ion.

The participation of neighboring sulfur atoms in the rearrangement of 2-hydroxyalkyl sulfides has been reported by Fuson and co-workers.[3–5] Specifically, these investigators showed that nucleophillic displacement of the hydroxy group of 2-hydroxyisopropyl sulfides (I) by chloride ion resulted in rearrangement to the *n*-propyl structure (III). They postulated the rearrangement proceeded through a cyclic sulfonium intermediate (II).[3,5] Formation of the *n*-propyl structure requires that displacement by chloride ion occur at the most substituted carbon atom; *i.e.*, the carbon having the methyl group attached to it.



R = alkyl or phenyl

The present investigation was undertaken to study some additional cases of displacement–rearrangement reactions involving aromatic and heterocyclic hydroxy sulfides. Four 2-hydroxyalkyl sulfides (V, compounds **5B**, **6B**, **7B**, and **8B**, Table I) were prepared by reduction of the esters, (IV), and the structures of the chlorides, (VIII), obtained from the reaction of these alcohols with thionyl chloride, were investigated. The isomeric 2-hydroxy-*n*-alkyl sulfides (VI, compounds, **9C**, **10C**, **11C**, and **12C**, Table I) were also prepared and converted to the chlorides with thionyl chloride. These chlorides were converted to 3,5-dinitrobenzoate derivatives (IX) and compared with the 3,5-dinitrobenzoates (VII), obtained from the 2-hydroxy-*n*-alkyl sulfides (VI).



R = 3-thienyl or naphthyl; R′ = methyl, ethyl or *n*-propyl

Thus, 2-hydroxy-*n*-propyl 3-thienyl sulfide (**9C**) was treated with thionyl chloride in pyridine to obtain 2-chloro-*n*-propyl 3-thienyl sulfide (**13D**). The 3,5-dinitrobenzoate of this chloro sulfide was prepared by reaction of the chloride with sodium 3,5-dinitrobenzoate and was found to be identical with the 3,5-dinitrobenzoate prepared from 2-hydroxy-*n*-propyl 3-thienyl sulfide (**9C**) and 3,5-dinitrobenzoyl chloride.

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[1] Abstracted in part from the Masters thesis of F. J. McCarty, Michigan State University.

[2] The Wm. S. Merrell Company, Cincinnati, Ohio.

[3] R. C. Fuson, C. C. Price, and D. M. Burness, *J. Org. Chem.*, **11**, 475 (1946).

[4] R. C. Fuson and A. J. Speziale, *J. Am. Chem. Soc.*, **71**, 1582 (1949).

[5] R. C. Fuson and J. H. Koehneke, *J. Org. Chem.*, **14**, 706 (1949).