Some Reactions Involving 9,10-Phenanthroquinodimethane as an Intermediate

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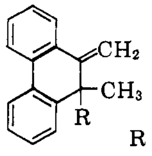
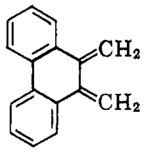
The dehydration of *trans*-9,10-dihydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (I) over alumina at 400° gave 9,10-dimethylphenanthrene. Upon treatment with acetyl chloride, I rearranged to give 10,10-dimethyl-9(10*H*)-phenanthrone and 9-hydroxymethyl-10-methylphenanthrene or, under more vigorous conditions, 9-acetoxymethyl-10-methylphenanthrene. The pyrolysis of 9-acetoxymethyl-10-methylphenanthrene afforded 9,10-dimethylphenanthrene, 9-hydroxymethyl-10-methylphenanthrene, polymeric material, and 1,2,5,6-bis-(9,10-phenanthro)cyclooctadiene (XXI). The pyrolysis of 3,4-(9,10-phenanthro)-2,5-dihydro-1,1-dioxathiophene and 2-methylene-3,4,5,6-dibenzo-3′,4′-(9,10-phenanthro)spirobicyclohexane also gave III. The intermediate 9,10-phenanthroquinodimethane II has been trapped as a Diels–Alder adduct in the pyrolysis of both 9-acetoxymethyl-10-methylphenanthrene and 3,4-(9,10-phenanthro)-2,5-dihydro-1,1-dioxathiophene.

Recent papers[1-3] describing the rearrangement reactions of *trans*-9,10-dimethyl-9,10-dihydroxy-9,10-dihydrophenanthrene (I) (Chart I) have postulated the 9-methylene intermediate II which rearranges to 9,10-disubstituted phenanthrene derivatives. Our own efforts to synthesize 9,10-phenanthroquinodimethane (III) also have disclosed an interesting series of similar reactions.



R = Cl
OCOCH₃

II



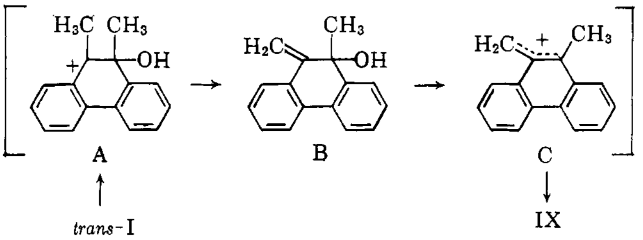
III

When the diol I was distilled under reduced pressure into a column of alumina heated to 400°, 9,10-dimethylphenanthrene (IV) and 9-methylfluorene (V) were formed. When the reaction was run at 200° only low molecular weight poly(9,10-phenanthroquinodimethane (VI) and V were obtained. The formation of V may be explained by a pinacol–pinacolone rearrangement[4] of I on the acid alumina to 9-acetyl-9-methylfluorene which splits out ketene readily by thermal pyrolysis.[5]

Since at 200° the dehydration of I produced poly-(9,10-phenanthroquinodimethane) (VI), the 9,10-dimethylphenanthrene (IV) could be formed by thermal pyrolysis at 400° of the polymer followed by a hydrogen abstraction reaction. Such a reaction is known to occur in the preparation of 1,2-benzoquinodimethane.[6] When the diol I was heated with aniline hydrobromide at 170° polymeric material was obtained, but at 350° IV was again produced. In both the alumina dehydration reactions and the acid-catalyzed dehydration, apparently the polymer VI is formed first from the intermediate quinodimethane III, but higher temperatures are needed for the thermal cracking and subsequent hydrogen abstraction to produce IV.

Treatment of diol I with acetyl chloride and pyridine gave *trans*-9-acetoxy-10-hydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (VII) and 10,10-dimethyl-9(10*H*)-phenanthrone (VIII). Even with a twentyfold excess of acetyl chloride and pyridine only the monoacetate VII was formed.

Treatment of I with acetyl chloride in the absence of pyridine again gave the ketone VIII, 9-hydroxymethyl-10-methylphenanthrene (IX), and the *cis* form of diol I or, under more vigorous conditions, VIII and 9-acetoxymethyl-10-methylphenanthrene (X). The formation of these products may be accounted for by the generation of ion A which may suffer a pinacol–pinacolone rearrangement or produce intermediate B. The allylic alcohol B may then generate IX through ion C. A similar mechanism must be involved when I reacts with acetic anhydride or thionyl chloride.[2,3]



When I was heated to the reflux temperature with acetic anhydride in the presence of maleic anhydride, none of the Diels–Alder adduct, 1,2,3,4-tetrahydro-2,3-triphenylene-*cis*-dicarboxylic anhydride (XI), was formed although a similar pinacol, 1,2-dihydroxy-1,2-dimethylacenaphthene is known to give a 70% yield of the adduct, tetrahydrofluoroanthene-11,12-dicarboxylic anhydride, under even less vigorous conditions.[7]

9,10-Phenanthroquinodimethane (III) formed by the pyrolysis of acetate X, was trapped with maleic anhydride and after hydrolysis gave the Diels–Alder adduct, 1,2,3,4 - tetrahydro - 2,3 - triphenylene - *cis* - dicarboxylic acid (XII), although the yield was very low (Chart II). Apparently III polymerizes readily on condensation.

Since the Diels–Alder adduct XI was isolated in a very low yield, the compound was synthesized by the following route.

The reaction of 9-chloromethyl-10-bromomethylphenanthrene (XIII) with sodium sulfide gave a 40% yield of 3,4-(9,10-phenanthro)-2,5-dihydrothiophene (XIV) and the remainder of the product was a sulfur containing material which appeared polymeric.

Oxidation of sulfide XIV with cold peracetic acid gave an 87% yield of 3,4-(9,10-phenanthro)-2,5-dihydro-1,1-dioxathiophene (XVII). The pyrolysis of

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(1) P. D. Gardner and H. Sarrafizadeh R., *J. Am. Chem. Soc.*, **82**, 4287 (1960).

(2) S. Hauptmann, *Chem. Ber.*, **93**, 2604 (1960).

(3) W. E. Adcock, *J. Org. Chem.*, **26**, 4141 (1961).

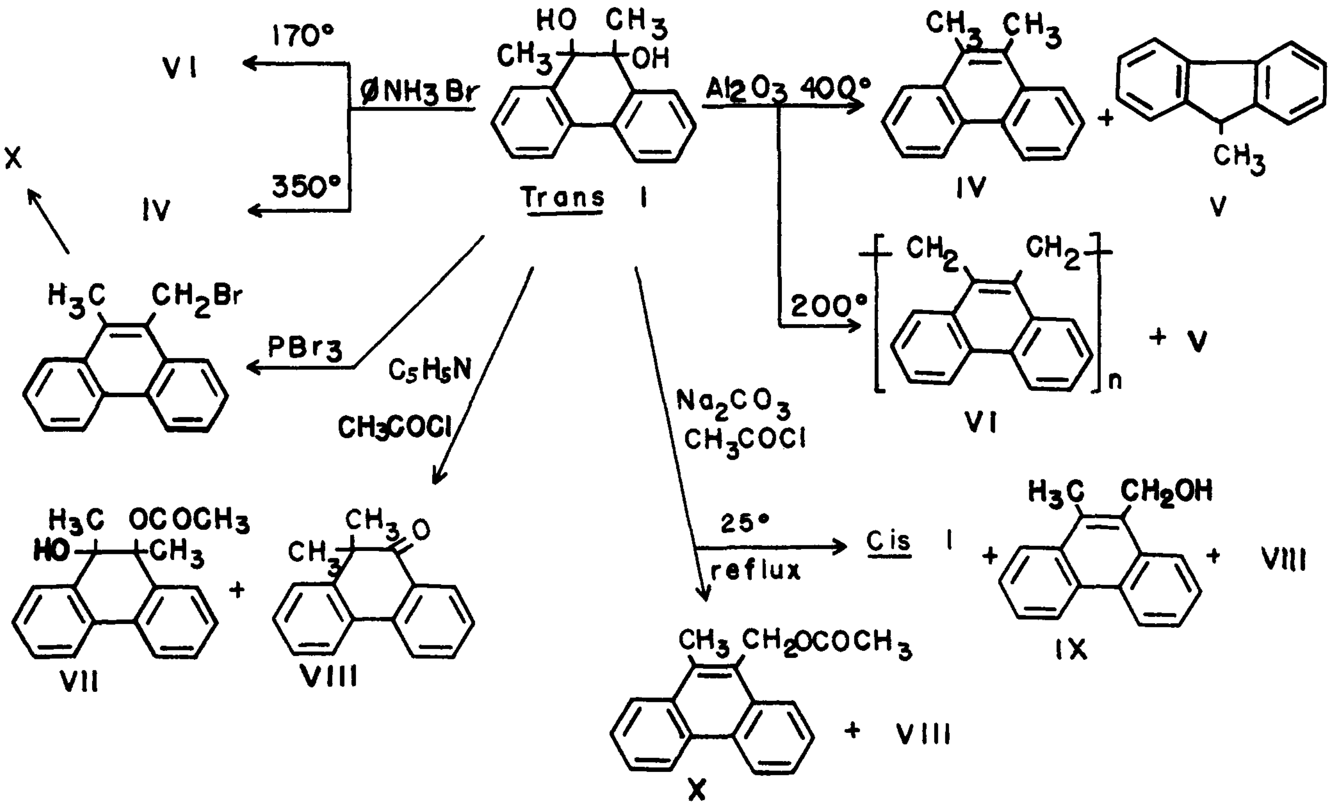
(4) E. J. Greenhow, D. McNeil, and E. N. White, *J. Chem. Soc.*, 986 (1952).

(5) H. Meerwein, F. Kremers, and R. Splittegarb, *Ann.*, **396**, 241 (1913).

(6) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4267 (1959).

(7) N. Campbell, R. S. Gow, and H. Wang, *Nature*, **162**, 857 (1948); *J. Chem. Soc.*, 1555 (1949).

CHART I



sulfone XVII in the presence of maleic anhydride in diethyl phthalate gave a 90% yield of 1,2,3,4-tetrahydro-2,3-triphenylene-*cis*-dicarboxylic anhydride (XI) which upon hydrolysis by base and acidification gave acid XII.

Further proof of the structure of the Diels-Alder adduct XI was shown by the conversion of the anhydride to triphenylene XVIII and by dehydrogenation of XI to 2,3-triphenylenedicarboxylic anhydride (XIX).

When the halogen compound XIII was converted to the 9,10-bis(iodomethyl)phenanthrene (XV) with sodium iodide in acetone, it was found that the iodo compound XV lost iodine readily in refluxing acetone, forming 2-methylene-3,4,5,6-dibenzo-3′,4′-(9,10-phenanthro)spirobicyclohexane (XVI) in good yield. Solutions of XV in ethanol or chloroform liberated iodine so rapidly, especially when exposed to light, that a suitable ultraviolet spectrum could not be obtained. The n.m.r. spectrum of XVI was entirely consistent with the proposed Diels-Alder structure.[1]

The pyrolysis of acetate X at 550° in the absence of maleic anhydride gave impure IV.

The pyrolysis of acetate X at 500° afforded a light yellow, crystalline solid which could be sublimed at 500° in air without decomposition. The elemental analysis and the molecular weight (mass spectrometer) are consistent for a dimer of III. Since the spiro compound XVI is known,[1] the structure 1,2,5,6-bis(9,10-phenanthro)cyclooctadiene (XXI) was assigned to the compound. The high melting point, the simplicity of the infrared spectrum, the lower mass fragments in the mass spectrum, and the stability of the compound are further support of a highly symmetrical molecule. The n.m.r. spectrum showed a singlet at 7.07 τ, characteristic of benzyl protons. An analogous compound 1,2,5,6-dibenzocyclooctadiene shows a band at 6.98 τ,[8] and the spiro dimer XVI exhibits its benzylic peak at 7.17 τ.

It is known that pyrolysis of 1,3-dihydroisothianaphthene 2,2-dioxide in diethyl phthalate[6] gives 1,2,5,6-dibenzocyclooctadiene, and also that spirodi-*o*-xylylene rearranges readily to form the same product.[8] In a similar manner it was found that when sulfone XVII or spiro dimer XVI were pyrolyzed in diethyl phthalate the dimer XXI was formed. These results lend further support to the structure XXI.

The fact that the ultraviolet spectrum of dimer XXI shows a bathochromic shift of 38 mμ compared to a phenanthrene derivative, is probably a result of the dimer XXI existing in a tub form rather than in the crown form. The tub form allows considerable overlap of the π-electrons of the phenanthrene nuclei. *p,p′*-Dimethylene-1,3-diphenylethane shows a bathochromic shift of about 20 mμ compared to the open-chain compound 4,4′-dimethylbibenzyl. This shift also have been attributed to π-electron overlap in the aromatic rings.[9] Conformational possibilities in such systems have been discussed by Baker[10] for 1,2,5,6-dibenzocyclooctadiene.

Experimental[11]

Alumina Dehydration of *trans*-9,10-Dimethyl-9,10-dihydroxy-9,10-dihydrophenanthrene (I).[12]—Ten grams (0.041 mole) of diol

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[8] L. A. Errede, *J. Am. Chem. Soc.*, **83**, 949 (1961).

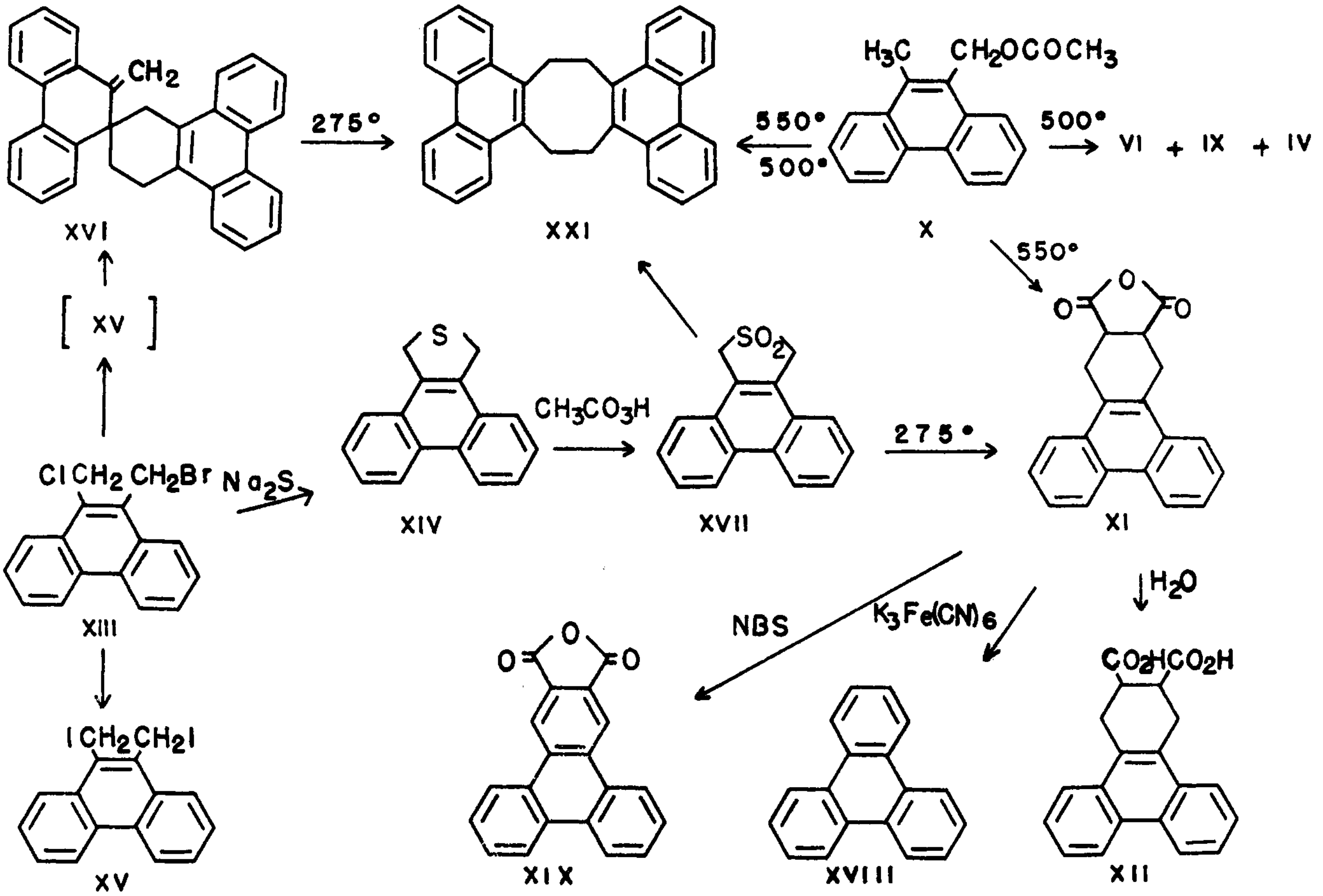
[9] D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954).

[10] W. Baker, R. Banks, D. R. Lyon, and F. G. Mann, *J. Chem. Soc.*, 27 (1945).

[11] All melting points are corrected. The infrared spectra were obtained with a Perkin-Elmer Model 21 infrared spectrophotometer. The ultraviolet spectra were obtained with a Cary Model 14 recording spectrophotometer. The molecular weights were determined with a Mechrolab Model 301 vapor pressure osmometer using chloroform as a solvent. The alumina used in the elution chromatography was Woelm neutral, activity I. The alumina for dehydration experiments was Fisher Scientific, acid washed.

[12] The diol I was prepared by addition of methylmagnesium bromide to 9,10-phenanthrenequinone in an 83% yield by a procedure similar to the one reported by T. Zincke and W. Tropp, *Ann.*, **362**, 242 (1908).

CHART II



I was distilled at 200° (0.5 mm.) in an atmosphere of nitrogen, into a furnace packed with 8–14-mesh alumina and heated to 400°. After 1 hr. a yellow oil began to condense in the receiver. After 4 hr. all of diol I had distilled and the system was swept with nitrogen for an additional hour. The oily product was crystallized from hexane to give 6.0 g. of crude material, m.p. 120–134°. Recrystallization of this material from ethanol gave 5.0 g. (58%) of 9,10-dimethylphenanthrene (IV), m.p. 146–147° (lit.[13] m.p. 147–148°); picrate, m.p. 190–192° (lit.[14] m.p. 192°).

The mother liquors from the recrystallizations were combined, evaporated to dryness at reduced pressure, and the residue placed on a column of 200 g. of alumina. Elution of the column with hexane, and evaporation of the fractions to dryness gave 0.5 g. (6.6%) of 9-methylfluorene (V), m.p. 44–45° (lit. m.p. 45–46°). The infrared (melt) and ultraviolet spectra (ethanol) of V were identical to those of an authentic sample.[15] The melting point of a mixture of V and an authentic sample was not depressed.

Further elution of the column with benzene–hexane mixtures gave a small amount of IV.

When the reaction was repeated with a furnace temperature of 200°, only 0.42 g. of V was collected in the receiver. The furnace was cooled and the alumina was deactivated with water, and washed with ethanol, followed by benzene. The solvent was removed under reduced pressure and the residue (5.4 g.) chromatographed on 200 g. of alumina. Elution of the column gave only 1.4 g. (16.2%) of a low-molecular weight polymer of 9,10-phenanthroquinodimethane (VI). The ultraviolet spectrum showed a phenanthrene nucleus, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 260 mμ (ϵ 3.5 × 10^4). The number average molecular weight was 1400 in chloroform. The infrared spectrum (film) showed a weak band at 3640 cm.$^{-1}$ which is probably due to OH end groups. The material could be reprecipitated from benzene by the addition of hexane.

Anal. Calcd. for $(C_{16}H_{12})_n$: C, 94.12; H, 5.92. Found: C, 92.26; H, 6.45.

Dehydration of I with Aniline Hydrobromide.—A mixture of 10 g. (0.041 mole) of I and 2.2 g. of aniline hydrobromide was heated under reduced pressure at 170°. A considerable amount of water distilled. The temperature was raised to 350° and white material distilled, b.p. 180–200° (0.2 mm.), and solidified in the receiver. Recrystallization of this material from ethanol gave 3.2 g. (38%) of IV, m.p. 135–142°. The melting point of a mixture of this sample and an authentic sample was undepressed. The infrared spectra (carbon disulfide and carbon tetrachloride) of the two samples were identical.

The same mixture was heated to 170° for 1 hr. The residue was dissolved in benzene and poured with vigorous stirring into hexane to give a white precipitate which melted over a range (77–120°) and appeared polymeric. The hexane solution yielded no crystalline products.

A mixture of 2.0 g. (0.0083 mole) of I, 1 g. of maleic anhydride, and 30 mg. of aniline hydrobromide was heated at 200° for 1.5 hr. The mixture was cooled and then treated with 25 ml. each of benzene and water and stirred overnight. The water solution was extracted with benzene, and the combined extracts evaporated to dryness at reduced pressure. The residue was extracted with hexane leaving a small amount of noncrystalline material. The hexane solution was reduced to a small volume and cooled to give 1.52 g. (82.5%) of material melting at 66–70°. Recrystallization of this material from hexane gave 0.92 g. of 10,10-dimethyl-9(10*H*)-phenanthrone (VIII), m.p. 74–75° (lit.[12] m.p. 74°). Infrared spectrum showed a maximum at 1690 cm.$^{-1}$ (C=O str.). VIII formed a 2,4-dinitrophenylhydrazone although it is reported[16] that VIII would not react with 2,4-dinitrophenylhydrazine.

2,4-Dinitrophenylhydrazone of VIII.—To a solution of 0.20 g. (0.90 mmole) of VIII in 20 ml. of glacial acetic acid was added a solution of 0.23 g. (0.90 mmole) of 2,4-dinitrophenylhydrazine in 15 ml. of 95% ethanol. The solution was evaporated on a steam bath to approximately 25 ml. and cooled to give 0.25 g. (69.5%) of long orange needles, m.p. 163–168°. The material was recrystallized from ethanol to provide an analytical sample, m.p. 168–169°.

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[13] E. J. Greenhow and D. McNeil, *J. Chem. Soc.*, 3204 (1956).

[14] R. W. Rimmer, R. G. Christiansen, R. K. Brown, and R. B. Sandin, *J. Am. Chem. Soc.*, **72**, 2298 (1950).

[15] E. J. Greenhow, E. N. White, and D. McNeil, *J. Chem. Soc.*, 2848 (1951).

[16] R. L. Shriner and L. Geipel, *J. Am. Chem. Soc.*, **79**, 228 (1957).

Anal. Calcd. for $C_{22}H_{18}N_4O_4$: C, 65.66; H, 4.51. Found: C, 65.62; H, 4.98.

***trans*-9-Acetoxy-10-hydroxy-9,10-dimethyl-9,10-dihydrophenanthrene (VII) and VIII.**—To a solution of 20 g. (0.082 mole) of diol I in 250 ml. of dry benzene, containing 26 g. (0.328 mole) of dry pyridine, heated to the reflux temperature was added 25.8 g. (0.328 mole) of acetyl chloride over a period of 1 hr. The mixture was then heated at the reflux temperature for an additional 24 hr., filtered to remove the pyridine salts, and the solvent was removed under reduced pressure. The semisolid residue was placed on a column of 250 g. of alumina. Elution of the column with benzene-hexane mixtures and evaporation of the fractions gave 5.0 g. (27.6%) of VIII, m.p. 74–75°.

Further elution of the column with ethyl acetate–ethanol mixtures and evaporation of the fractions to dryness and recrystallization of the resulting solid from a mixture of benzene–hexane gave 10 g. (35%) of VII, m.p. 123–124° (lit.[3] m.p. 122–123°). Infrared spectrum (carbon disulfide) showed maxima at 3395 cm.$^{-1}$ (OH str.) and 1721 cm.$^{-1}$ (C=O str.). The ultraviolet spectrum (ethanol) showed a dihydrophenanthrene nucleus; $\lambda_{\max}^{CHCl_3}$ 272 (ϵ 1.8 × 10^4).

Reaction of Diol I with Acetyl Chloride. A. At Reflux Temperature.—A solution of 10 g. (0.042 mole) of I in 100 ml. of benzene was stirred in an atmosphere of nitrogen with 45 g. (0.84 mole) of anhydrous sodium carbonate while 66 g. (0.84 mole) of acetyl chloride was added. The mixture was heated at the reflux temperature for 12 hr. The benzene and acetyl chloride were removed under reduced pressure and the residue was treated with 100 ml. of water. The mixture was extracted with carbon disulfide, and the carbon disulfide was removed under reduced pressure. The residue was placed on a column of 200 g. of alumina. Elution of the column with carbon disulfide and recrystallization of residue from hexane gave 2.7 g. (29%) of VIII.

Further elution of the column with benzene and ether, evaporation of the eluate to dryness, and recrystallization of the residue from hexane gave 2.5 g. (21.5%) of material melting at 109–110°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.91; H, 6.00.

Recrystallization of the material from carbon disulfide gave 9-acetoxymethyl-10-methylphenanthrene (X), m.p. 131–132° (lit.[2] m.p. 132.5°). The infrared (carbon disulfide and carbon tetrachloride) and ultraviolet spectra (ethanol) of the two compounds were identical. When the lower melting form was melted or heated at 80° for 24 hr., it was converted to the higher melting form.

The melting point of a mixture of X and an authentic sample[2] showed no depression. The lower melting form could also be obtained from authentic sample by recrystallization from hexane.

When the reaction was run in the absence of sodium carbonate the products were the same.

B. At Room Temperature.—A solution of 10 g. (0.042 mole) of I in 100 ml. of benzene was stirred, in an atmosphere of nitrogen, with 45 g. (0.840 mole) of anhydrous sodium carbonate, and 66 g. (0.840 mole) of acetyl chloride was added. The mixture was stirred at room temperature for 3 days. The solvent was removed at reduced pressure to give a yellow viscous oil. The residue was dissolved in benzene–hexane and placed on a column of 200 g. of alumina. The column was eluted with benzene–hexane, solvents were evaporated at reduced pressure, and white solid was recrystallized from hexane to give 3.7 g. (40%) of VIII.

Further elution of the column with ethyl acetate–ethanol mixtures gave a white crystalline solid, melting at 199–200°. Recrystallization of this material from benzene gave 3.3 g. (35%) of 9-hydroxymethyl-10-methylphenanthrene (IX), m.p. 169–170° (lit.[1] m.p. 170–171°). The infrared spectrum (Nujol mull) showed a maximum at 3280 cm.$^{-1}$ (OH str.).

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.34; H, 6.34. Found: C, 86.53; H, 6.21.

Elution of the column with ethanol and removal of the solvent under reduced pressure afforded a substance melting at 95–100°. After recrystallization of this material from carbon disulfide, 0.3 g. (3%) of the *cis* isomer of diol I, m.p. 104–105° (lit.[17] m.p. 103–104°), was obtained. The infrared (carbon disulfide) and ultraviolet (ethanol) spectra of this isomer were identical to those of the *trans* isomer.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 80.11; H, 6.63.

9-Acetoxymethyl-10-methylphenanthrene (X).—To a solution of 4.0 g. (0.0295 mole) of sodium acetate trihydrate in 90 ml. of glacial acetic acid was added 2.7 g. (0.0095 mole) of 9-bromomethyl-10-methylphenanthrene[1] and the mixture was heated at the reflux temperature for 6 hr. The mixture was allowed to stand for 18 hr., then poured into water. The water solution was extracted with benzene and the extracts were combined. The benzene was removed under reduced pressure, and the white residue was recrystallized from hexane to give 1.8 g. of acetate X as light yellow needles, m.p. 131.7–132°. Further evaporation and cooling produced 0.6 g. of acetate X, m.p. 107–108°. The combined yield was 96.0%.

Reaction of Diol I with Acetic Anhydride in the Presence of Maleic Anhydride.—A solution of 0.66 g. (0.0027 mole) of I, 4 g. (0.041 mole) of maleic anhydride, and 40 ml. of acetic anhydride was heated at the reflux temperature for 18 hr. The cooled solution was stirred with water for 1 hr. then extracted with benzene. The benzene was removed at reduced pressure and the brown residue was recrystallized from hexane to give 0.12 g. (17%) of acetate X, m.p. 100–108°. The infrared spectrum was identical to that of an authentic sample. Further evaporation of the hexane filtrate gave 0.21 g. (35%) of impure VIII, m.p. 60–71°. The infrared spectrum (carbon disulfide) showed this sample to be mostly VIII contaminated with small amounts of X.

Dehydration of I in the Presence of Maleic Anhydride with Potassium Bisulfate.—A mixture of 2.0 g. (0.0083 mole) of I, 1 g. of maleic anhydride, and 0.1 g. of powdered, freshly fused, potassium bisulfate, was heated at 200° for 1 hr. The mixture was cooled and stirred with 100 ml. of water for 15 min. The water solution was extracted with benzene, the extracts were combined, and the solvent was removed under reduced pressure. The viscous residue was dissolved in hexane, and the hexane was cooled to precipitate a small amount of polymeric material. The hexane solution was filtered and the mother liquor reduced to approximately 15 ml. to give 1.10 g. (59.1%) of VIII, m.p. 71–73°. The infrared spectrum was identical to that of an authentic sample.

Pyrolysis of 9-Acetoxymethyl-10-methylphenanthrene (X).—A solution of 5.0 g. (0.019 mole) of X in 50 ml. of benzene was allowed to drop slowly, under an atmosphere of nitrogen, into a furnace packed with Pyrex helices and heated to 550°. After all the solution had been added the column was swept for 10 min. longer with a slow stream of nitrogen. The volume of the pyrolysate solution was reduced and the solution was passed through a column of 200 g. of neutral alumina. Elution of the column with hexane–benzene mixtures and evaporation of the solvents to dryness gave 1.3 g. (33.2%) of IV, m.p. 120–129°. Repeated recrystallization of this material from hexane or ethanol failed to raise the melting point. The melting point of a mixture of an authentic sample and this product was 132–136°. The infrared spectrum (carbon disulfide and carbon tetrachloride) was identical to that of an authentic sample of IV. Further elution of the column with benzene and ethyl acetate gave only polymeric material. Considerable charring occurred during the pyrolysis.

Pyrolysis of 5.0 g. (0.019 mole) of ester X at 500°, followed by chromatography of the pyrolysate gave 0.28 g. (7.1%) of IV and 0.95 g. of polymeric material. Further elution of the column with ethanol afforded 0.61 g. (14.2%) of IX. Titration of the acetic acid showed that 73.6% of the ester had been pyrolyzed.

The end of the pyrolysis tube contained a crystalline, yellow compound which was insoluble in most common solvents. The material was sublimed at 325° (0.5 mm.) and then placed in a Soxhlet extractor and extracted with refluxing xylene. Cooling the xylene produced 0.3 g. of material melting at 433–440°. When the end of the pyrolysis tube was raised back into the hot portion of the furnace the material would sublime unchanged on the cooler end of the tube even under a stream of air. The compound was insoluble in most low boiling organic solvents, and was soluble to the extent of 2.5 g./100 ml. in refluxing α-chloronaphthalene.

An analytical sample of the material was prepared by one recrystallization from refluxing diethyl phthalate or α-chloronaphthalene, followed by washing several times with benzene; m.p. 438–440° subl.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92; mol. wt., 408. Found: C, 94.16; H, 5.85; mol. wt. (mass spectrometer), 408.

The sample was charged into the mass spectrometer at 427° through a sintered disk. Prominent *m/e* values of 78, 128, 152, 234, 378, and 408 were observed. At low ionizing voltage, *m/e* values of 408, 378, and 234 were observed. The infrared spectrum

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(17) R. Criegee, E. Hogar, G. Huber, P. Kruck, F. Marktocheffel, and H. Schellenberger, *Ann.*, **599**, 81 (1956).

(Nujol mull) revealed no unsaturation other than the aromatic bands characteristic of a phenanthrene nucleus. The ultraviolet spectrum (chloroform) showed maxima at 260, 271, 295, 305, and 333 mμ with extinction coefficients of 4.47, 5.18, 9.60, 7.26, and 3.81 × 10^4, respectively. The n.m.r. spectrum in pyridine at 110° showed a singlet at 7.07 τ. The concentration was too low to show any definite splittings.

1,2,3,4-Tetrahydro-2,3-triphenylene-*cis*-dicarboxylic Acid (XII) from the Pyrolysis of X.—A solution of 5.0 g. (0.019 mole) of X in 50 ml. of benzene was pyrolyzed in a nitrogen atmosphere at 550°, and the pyrolysate vapor was directed into a flask containing maleic anhydride in benzene. The resulting solution was stirred with water for 12 hr., then the benzene solution was separated, and the benzene was removed under reduced pressure. The residue was extracted with hexane to remove unpyrolyzed acetate and hydrocarbons. The residue was recrystallized from benzene to give 25 mg. of acid XII, m.p. 272–275° dec. subl. The melting point of a mixture of this material and a sample made from anhydride XI was not depressed, and the infrared (Nujol mull) and ultraviolet (ethanol) spectra of the two samples were also identical.

The hydrocarbon XXI also was present in the end of the pyrolysis tube after this run.

Evaporation of the hexane solution from the extraction gave 0.2 g. of a white powder, m.p. 133.5–135°. Recrystallization of this material from carbon disulfide gave pure mono(9-hydroxymethyl-10-methylphenanthrene) maleate, m.p. 138–139°.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.98; H, 5.03. Found: C, 75.30; H, 5.28.

The infrared spectrum (carbon disulfide) showed maxima at 1725 and 1755 cm.$^{-1}$ (C=O str.).

A solution of 0.10 g. of mono(9-hydroxymethyl-10-methylphenanthrene) maleate, 10 ml. of water, and 0.2 g. of potassium hydroxide was stirred at room temperature for 1 hr. The white precipitate was extracted with benzene and the volume was reduced to give 0.05 g. of alcohol IX, m.p. 161–163°. The infrared spectrum (Nujol mull) was identical to the spectrum of an authentic sample.

9-Bromomethyl-10-chloromethylphenanthrene (XIII).—To a solution of 10.0 g. (0.0416 mole) of 9-methyl-10-chloromethylphenanthrene[2] and 250 ml. of carbon tetrachloride was added 7.40 g. (0.0416 mole) of N-bromosuccinimide and 0.1 g. of benzoyl peroxide. The mixture was heated at the reflux temperature for 2 hr., and allowed to stir for 16 hr. at room temperature. The precipitate (m.p. 195–205°), of some succinimide and product, was removed, and the mother liquor was evaporated to dryness to give additional material (m.p. 205–212°). These crude fractions were leached with hot ethanol to remove the succinimide, and the precipitate was collected to afford 11.8 g. (86.5%) of dihalide XIII, m.p. 215–218°. The melting point of a mixture of this material and an authentic sample[2] showed no depression. Cooling the ethanol extracts gave an additional 0.5 g. of pure XIII, m.p. 219.5–220.5°. The combined yield was 89.6%.

9,10-Bis(iodomethyl)phenanthrene (XV).—To a solution of 2.00 g. (0.625 mmole) of XIII in 260 ml. of acetone was added 3.30 g. of sodium iodide in 100 ml. of acetone. The solution was stirred for 2 hr. at 30° then allowed to stand overnight at 0°. The precipitate was collected and stirred with water. The organic material was extracted with benzene and the volume of the solution was reduced to give 0.47 g. of light yellow needles of iodide XV, m.p. 130–133° dec.

The mother liquor was evaporated to dryness at reduced pressure. The residue was shaken with benzene and water, the layers were separated, and the water solution was extracted with benzene. The benzene extracts were combined and concentrated, to give 1.21 g. (42.1%) of XV, m.p. 128–130° dec.

Anal. Calcd. for $C_{16}H_{12}I_2$: C, 41.95; H, 2.64; mol. wt., 458. Found: C, 42.26; H, 2.31; mol. wt., 442.

2-Methylene-3,4,5,6-dibenzo-3′,4′-(9,10-phenanthro)spirobicyclohexane (XVI).—A mixture of 4.10 g. (0.0125 mole) of halide XIII, 6.68 g. of sodium iodide, and 200 ml. of acetone was heated at the reflux temperature for 2 hr. on a steam bath. The mixture was poured into water and the water solution was extracted with cyclohexane. The cyclohexane extracts were shaken with 5% sodium thiosulfate to remove the iodine and the cyclohexane solution was reduced to a small volume to give 0.091 g. of XVI, m.p. 228–229° dec. An analytical sample was prepared by one recrystallization from cyclohexane, m.p. 228.5–229° dec.

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92; mol. wt., 408. Found: C, 94.49; H, 6.19; mol. wt., 393.

Further evaporation of the cyclohexane solution produced 1.83 g. of XVI, m.p. 241–246° dec. This material was recrystallized according to the literature to give pure XVI, m.p. 250–251 dec. (lit.[1] m.p. 252–253°).

Combined yield of dimers was 74.8%. The infrared spectra (carbon disulfide) of both crystal forms were identical showing two strong bands at 893 and 898 cm.$^{-1}$ (=CH_2). In a Nujol mull the compound melting at 250° showed a maximum at 898 cm.$^{-1}$ while the compound 228–229° showed a maximum at 913 cm.$^{-1}$. The ultraviolet spectra (ethanol) of both forms showed the characteristic bands reported.[1]

The n.m.r. spectrum in deuteriochloroform using tetramethylsilane as an internal standard shows peaks at 4.76 and 4.98 (=CH_2), a singlet at 6.16 (-CH_2- isolated), and triplets at 7.17 and 8.10 τ (-CH_2-) which is consistent with the proposed structure.[1] Spin decoupling experiments showed that the olefinic doublet is not a spin multiplet coupled to protons in the aromatic region and must be due to nonequivalent =CH_2 protons.

3,4-(9,10-Phenanthro)-2,5-dihydrothiophene (XIV).—To a solution of 19.0 g. (0.102 mole) of sodium sulfide nonahydrate in 500 ml. of refluxing absolute ethanol was added 5.00 g. (0.0151 mole) of halide XIII by extraction from a Soxhlet apparatus over a period of 2 days. The mixture was poured into water with stirring to afford a white precipitate. The precipitate was extracted with hot ethanol and the ethanol solution was concentrated to give 0.89 g. of sulfide XIV, m.p. 155–170°. Further evaporation gave 0.59 g. of material, m.p. 145–165°. The combined yield was 40.1%. The remainder of the material appeared to be polymeric. The analytical sample was recrystallized from ethanol containing a small amount of benzene, m.p. 164–166°.

Anal. Calcd. for $C_{16}H_{12}S$: C, 81.38; H, 5.12; mol. wt., 236. Found: C, 81.24; H, 5.21; mol. wt., 251.

The ultraviolet spectrum showed a phenanthrene nucleus with $\lambda_{\max}^{\text{EtOH}}$ 255 mμ (ϵ 5.57 × 10^4).

3,4-(9,10-Phenanthro)-2,5-dihydro-1,1-dioxathiophene (XVII).—To a stirred suspension of 2.82 g. (0.0119 mole) of crude XIV in 42 ml. of glacial acetic acid, cooled to 0°, was added dropwise a solution of 6.8 g. of peracetic acid[18] in 7.0 ml. of glacial acetic acid over a period of 30 min. The mixture was allowed to stir at room temperature for 18 hr. The white precipitate which had formed was washed with water, and dried to give 2.76 g. (87%) of sulfone XVII, m.p. 255–265° dec. The material was best recrystallized by dissolving the product in dimethylformamide (50 ml.) and adding 200 ml. of chloroform. The sulfone (2.65 g.) crystallized as white needles, m.p. 268–270° dec. The infrared spectrum (Nujol mull) showed maxima at 1310 and 1125 cm.$^{-1}$ characteristic of sulfones. The ultraviolet spectrum showed a phenanthrene nucleus with $\lambda_{\max}^{\text{EtOH}}$ 256 mμ (ϵ 7.13 × 10^4).

Anal. Calcd. for $C_{16}H_{12}SO_2$: C, 71.62; H, 4.51. Found: C, 71.40; H, 4.38.

1,2,3,4-Tetrahydro-2,3-triphenylene-*cis*-dicarboxylic Anhydride (XI).—A solution of 1.00 g. (0.00331 mole) of sulfone XVII and 1.30 g. of maleic anhydride in 10 ml. of diethyl phthalate was heated at the reflux temperature for 20 min. The solution was cooled to afford white needles, which were washed with cold benzene, m.p. 313–315° subl. One recrystallization from benzene afforded 1.02 g. (90.2%) of XI, m.p. 315–317.5° subl.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 79.28; H, 4.57.

The infrared spectrum (Nujol mull) showed maxima at 1798 and 1865 cm.$^{-1}$ (anhydride). The ultraviolet spectrum showed a phenanthrene nucleus with $\lambda_{\max}^{\text{EtOH}}$ 254 mμ (ϵ 5.76 × 10^4).

1,2,3,4-Tetrahydro-2,3-triphenylene-*cis*-dicarboxylic Acid (XII) from Anhydride XI.—A mixture of 0.40 g. (1.32 mmoles) of XI and a solution of 60 ml. of water containing 0.50 g. of potassium hydroxide was heated until a clear solution was obtained. The solution was filtered and acidified with 15 ml. of concentrated hydrochloric acid. After the addition of 60 ml. of ethanol the fluffy white precipitate was collected to give 0.42 g. (99%) of XII. One recrystallization from a 1:1 mixture of ethyl acetate and ethanol afforded pure material.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.98; H, 5.03. Found: C, 74.77; H, 4.84.

The cubic crystals began to sublime to needles at 270° and finally melted at 279–282° dec. forming long needles of the corresponding anhydride, m.p. 308–313° subl. The infrared

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(18) The peracetic acid was approximately 45% prepared from 90% hydrogen peroxide and glacial acetic acid according to J. d'Ans and W. Frey, *Chem. Ber.*, **45**, 1845 (1912).

spectrum of XII (Nujol mull) showed a maximum at 1698 cm.$^{-1}$ (C=O str.). The ultraviolet spectrum shows a phenanthrene nucleus with λ_{max}^{EtOH} 255 mμ (ϵ 6.03 × 10^4).

2,3-Triphenylenedicarboxylic Anhydride (XIX).—A solution of 0.285 g. (0.943 mmole) of XI. 0.340 g. (1.91 mmoles) of N-bromosuccinimide and 15 mg. of benzoyl peroxide in 10 ml. of chloroform was heated at the reflux temperature for 12 hr. The mixture was cooled to 0° and 0.012 g. of light yellow crystals were collected, m.p. 338–345° subl. The mother liquor was heated with 20 ml. of 10% potassium hydroxide and filtered. The solution was acidified with concentrated hydrochloric acid to give a white precipitate. Two recrystallizations from diethyl phthalate followed by washing with benzene gave 0.090 g. (32%) of pure anhydride XIX, m.p. 349–350° subl.

Anal. Calcd. for $C_{20}H_{10}O_3$: C, 80.52; H, 3.37. Found: C, 80.21; H, 3.66.

The ultraviolet spectrum had the same general shape as triphenylene with λ_{max}^{EtOH} 266, 257 mμ (ϵ 6.20 and 4.82 × 10^4, respectively).

Triphenylene (XVIII).—A mixture of 0.25 g. (0.836 mmole) of XI and 30 ml. of 10% sodium hydroxide was heated until a clear solution was obtained. This solution was poured into a solution of 2.25 g. of potassium ferricyanide in 10 ml. of water and the solution heated at the reflux temperature for 24 hr., during which time a small amount of white needles had sublimed on the condensor walls. The mixture was cooled and the water solution was extracted with benzene. The combined benzene extracts were evaporated to dryness at reduced pressure to give 0.019 g. (9.7%) of triphenylene (XVIII), m.p. 190–195°, after one recrystallization from ethanol. The material showed no melting point depression when mixed with an authentic sample of triphenylene (Aldrich Chemical Co.). The ultraviolet spectrum was identical to the authentic sample.

1,2,5,6-Bis(9,10-phenanthro)cyclooctadiene (XXI). A. By Pyrolysis of Sulfone XVII in Diethyl Phthalate.—A solution of 0.700 g. (0.00265 mole) of XVII in 10 ml. of diethyl phthalate was heated at the boiling point until approximately half of the diethyl phthalate had distilled. The residue was cooled to room temperature and light yellow crystals precipitated. The crystals were washed with benzene to give 0.11 g. (20.9%) of XXI, m.p. 430–435° subl. The material was recrystallized from diethyl phthalate to give pure material, m.p. 438–440°. The melting point of a mixture of this sample and the sample obtained from the pyrolysis of acetate X was not depressed.

Addition of ethanol to the mother liquor gave material which melted over a range and appeared polymeric.

B. By Pyrolysis of Dimer XVI in Diethyl Phthalate.—A solution of 0.104 g. (0.254 mmole) of XVI, m.p. 228–229°, in 10 ml. of diethyl phthalate was heated at the boiling point until approximately half of the diethyl phthalate was distilled. The residue was cooled, and 0.032 g. (33%) of XXI, m.p. 430–438° subl., precipitated as a yellow powder. This product was shown to be the same as the hydrocarbon obtained from the pyrolysis of sulfone XVII and acetate X by comparison of the infrared and ultraviolet spectra and by the fact that the melting points of a mixture of these samples was undepressed.

Hydrolysis of the diethyl phthalate solution by stirring 2 days with 30% sodium hydroxide produced no crystalline products from the basic solution.

A similar result was obtained when the higher melting form of XVI was pyrolyzed under the same conditions. Attempts to trap the quinodimethane III as a possible intermediate in this rearrangement as the maleic anhydride adduct XI resulted only in the isolation of XXI.

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Alumina: Catalyst and Support. XX.[1] Aromatization of *n*-Octane-4-C^{14} over Chromia–Alumina Catalyst. Contribution to the Mechanism of Aromatization[2]

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The aromatization of *n*-octane-4-C^{14} over chromia–alumina catalyst was investigated in order to demonstrate that cyclooctane adsorbed species participates in the aromatization reaction. Only a C_8-ring intermediate will lead to ethylbenzene having a labeled ethyl group in the α- and β-position. The present study provides evidence that at least 30% of the ethylbenzene produced at the beginning of the reaction proceeds *via* a 1,8-ring closure. The radioactivity distribution in the *m*- and *p*-xylene is in agreement with the proposed mechanism suggesting the participation of 1,7- and 1,8-ring in the transition state.

The aromatization of *n*-octane presents an interesting mechanistic problem. Herington and Rideal[3] reported the formation of ethylbenzene, and *o*-, *m*-, and *p*-xylene when *n*-octane was passed over chromia–alumina catalyst at elevated temperatures. Ethylbenzene and *o*-xylene could be explained by simple 1,6-ring closure, but this mechanism precludes the formation of *m*- and *p*-xylene. In order to account for their formation, Herington and Rideal proposed the formation of bicyclo[3.2.1]octane and bicyclo[2.2.2]-octane intermediates.

In studying the aromatization of *n*-octane-1-C^{14} over "nonacidic" chromia–alumina catalyst, Pines and Chen[4] have shown that no combination of mechanisms which contain the bicyclic intermediates of Herington and Rideal would fit their data. Pines and Chen explained their data by a combination of mechanisms involving 1,6-ring closure and the presence of 1,7- and 1,8- adsorbed species in the transition state.

The fact that methylcycloheptane has been isolated from the selectively hydrogenated reaction mixture from the aromatization of *n*-octane over "nonacidic" chromia–alumina catalyst[5] provides good evidence for the existence of a cycloheptane adsorbed species.

In order to demonstrate the existence of a cyclooctane adsorbed species, *n*-octane-4-C^{14} was synthesized and aromatized under conditions described previously.[6]

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(1) For paper XIX, see J. Herling and H. Pinesin, *Chem. Ind.* (London), 984 (1663).

(2) (a) Paper XI of the series "Aromatization of Hydrocarbons"; for paper X see S. M. Csicsery and H. Pines, *J. Am. Chem. Soc.*, **84**, 3939 (1962); (b) this research was supported by the U. S. Atomic Energy Commission, contract AT(11-1)-1046.

(3) E. F. G. Herington and E. R. Rideal, *Proc. Roy. Soc.*, **184A**, 434, 447 (1945).

(4) Proceedings from the Second International Congress in Catalysis, Paris, 1960, pp. 367–387, edited by TECHNIP, Paris, 1961.

(5) S. M. Csicsery, Ph.D. thesis, "Contribution to the Mechanism of Dehydrogenation, Dehydrocyclization and Dehydroisomerization of Hydrocarbons over Chromia–Alumina Catalysis," Northwestern University (1962), Table XLVIII.

(6) H. Pines and S. M. Csicsery, *J. Catalysis*, **1**, 313 (1962).