

showed absorption bands at 2.85 (—N—H), 3.00 (—O—H), 6.15, 6.30, 6.43, and 6.57 μ (aromatic ring). Since **7a** was insoluble in chloroform, a proton magnetic resonance spectrum was run on a dioxane solution in order to observe the aromatic proton signals. A noisy base line obscured the fine structure. Signals were seen at about 9.0 (—N—H , very broad), 6.58 (=C—H at 2'), and 5.93 p.p.m. (=C—H at 3').

Anal. Calcd. for $\text{C}_{21}\text{H}_{31}\text{NO}$: C, 80.46; H, 9.97; N, 4.47. Found: C, 80.73; H, 10.10; N, 4.50, 4.56.

17-Methyl-5 α -androstano[3,2-*b*]pyrrol-17 β -ol (7b).—Lithium (2.4 g., 0.34 g.-atom) was added in small pieces during 10 min. to a stirred slurry of **6b** (7.02 g.) in tetrahydrofuran (dried over alumina, 35 ml.) and liquid ammonia (140 ml.). The mixture was stirred for 50 min. under a Dry Ice condenser. Ammonium chloride (21.4 g., 0.400 mole) was added with continued stirring during 10 min. After most of the ammonia had evaporated, the mixture was diluted with water and the resulting mixture was extracted with methylene dichloride (130 ml.). The methylene dichloride extracts were washed with water, dried over sodium sulfate, filtered, and concentrated with ethyl acetate. The product crystallized from ethyl acetate as irregular prisms containing 0.25 mole of ethyl acetate (confirmed by the infrared spectrum) and having adsorbed red-orange color: 3.78 g., 13.2% yield based on **1b**, m.p. (evacuated capillary) 213–214.5°. Two further recrystallizations gave the final product: 2.59 g., dried at 80° at 0.01 mm., m.p. (evacuated capillary) 214–215°. The infrared spectrum showed absorption bands at 2.78 (shoulder), 2.87, 3.02, and 3.06 μ (sh) (—N—H and —O—H), 5.75 ($\text{CH}_3\text{—COOC}_2\text{H}_5$), 6.10, 6.26, and 6.56 (μ) (aromatic ring), and 8.0 μ

($\text{CH}_3\text{COOC}_2\text{H}_5$). The proton magnetic resonance spectrum of **7b** showed signals at 8.09 (broad multiplet, —N—H), 6.95 (triplet, =C—H at 2'), 6.30 (triplet, =C—H at 3'), 4.6 (quartet, $\text{—CH}_2\text{—}$ of $\text{CH}_3\text{COOC}_2\text{H}_5$), 2.52 (singlet, CH_3 of $\text{CH}_3\text{COOC}_2\text{H}_5$), 1.72 (singlet, CH_3 at C-17), 1.37 and 1.28 p.p.m. (C-18 H_3 and C-19 H_3).

Anal. Calcd. for $\text{C}_{22}\text{H}_{33}\text{N—O} \cdot 0.25\text{CH}_3\text{COOC}_2\text{H}_5$: C, 79.03; H, 10.09; N, 4.01. Found: C, 78.95; H, 10.16; N, 3.90.

In another run, two recrystallizations from ethyl acetate of the crude product of the debenzoylation of 8.99 g. of **6b** gave 4.85 g. of **7b**, which was dried at 84° at 0.01 mm. and had m.p. (evacuated capillary) 215.5–216° and no ethyl acetate of crystallization.

Anal. Calcd. for $\text{C}_{22}\text{H}_{33}\text{NO}$: C, 80.68; H, 10.15; N, 4.28. Found: C, 80.74; H, 10.29; N, 4.42.

Acknowledgment.—The authors wish to thank the following members of the staff of the Sterling-Winthrop Research Institute for their contributions to this work: Mr. K. D. Fleischer and co-workers for microanalyses, Dr. F. C. Nachod and Miss C. M. Martini and co-workers for spectral determinations, Dr. R. K. Kullnig for assistance in the interpretation of proton magnetic resonance spectra, Mr. A. V. R. Crain and co-workers for the preparation of thin layer chromatographic plates, Mr. H. P. Warrington for the vapor phase chromatographic analysis, and Drs. R. L. Clarke and J. W. Dean for their criticisms of the manuscript.

The Oxidation of Gossypol. I. Early Stages in the Reaction of Gossypol and Oxygen

EKKEHARD W. SCHEIFFELE AND DAVID A. SHIRLEY¹

Department of Chemistry, University of Tennessee, Knoxville, Tennessee

Received June 8, 1964

The oxidation of gossypol (I) in alkaline solution by oxygen proceeds *via* 1,1',6,6'-tetrahydroxy-5,5'-diisopropyl-3,3'-dimethyl(2,2'-binaphthalene)-7,7',8,8'-tetrone (II) which is formed by a Dakin-type reaction. This labile *o*-binaphthoquinone was isolated and characterized along with several of its derivatives.

It has been long known² that gossypol (I), the common pigment of the cottonseed, is rapidly attacked in alkaline solution by atmospheric oxygen yielding deep purple, labile compounds of intense color. The presence and fixation of such oxidation products in cottonseed oil has been suspected as a causative agent in the formation of off-color oils, but few data are available which bear directly on this problem. We have undertaken an investigation of the nature of the route(s) by which gossypol is degraded by oxygen and hydrogen peroxide in alkaline solution.

Prior work on oxidation of gossypol is confined to studies of ozonization, made as a part of the original work on structure determination,^{3,4} the reported isolation of a crystalline product from the methylation of the reaction mixture from a 500-hr. treatment with oxygen of gossypol in alkaline solution,⁵ and an investigation in this laboratory (to be published later) on the oxidation of gossypol with alkaline hydrogen peroxide.⁶

Principal attention in this work has been given to the isolation and characterization of labile, highly colored intermediates formed in the early stages of the reaction between oxygen and gossypol in alkaline solution. The techniques of paper and thin layer chromatography were used to monitor experiments designed to develop reaction conditions which would yield maximal amounts of the colored compounds. It was observed that uptake of 1.0–1.7 moles of oxygen/mole of gossypol corresponded to maximum production of a red-brown (neutral) or deep purple (alkaline) compound, and at this point there were also present unreacted gossypol and light-colored compounds probably representing later stages of oxidation. Workable quantities of the colored compound (II) were first obtained from column chromatographic separation of the reaction products on polyamide powder,⁷ and larger amounts were later obtained directly by crystallization of a fraction of the reaction product.

The colored intermediate (II) was found to be an *o*-binaphthoquinone of the structure shown in the accompanying chart. The n.m.r. spectrum of the quinone II is summarized in Table I, and the assignments of bands given in the table are straightforward with the

(1) To whom communications concerning this paper should be addressed.

(2) L. Marchlewski, *J. prakt. Chem.*, **60**, 84 (1899).

(3) P. Karrer and E. Tobler, *Helv. Chim. Acta*, **15**, 1204 (1932).

(4) R. Adams, T. A. Geissman, W. R. Dial, and J. T. Fitzpatrick, *J. Am. Chem. Soc.*, **63**, 2439 (1941).

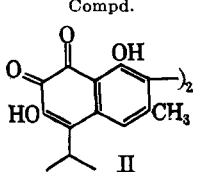
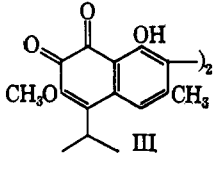
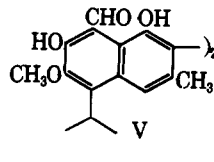
(5) A. Ismailov and A. S. Sadykov, *Uzbeksk. Khim. Zh.*, **34** (1959).

(6) (a) L. Farmer, Doctoral Dissertation, University of Tennessee, 1963.

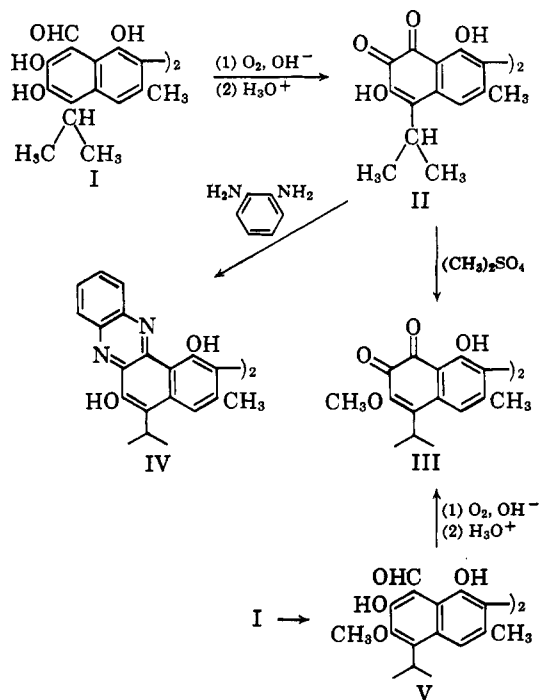
(b) P. W. Alley, unpublished study.

(7) H. Endres and E. Hoermann, *Angew. Chem.*, **75**, 288 (1963).

TABLE I
 N.M.R. ABSORPTION BANDS^a

Compd.	Signal position, p.p.m.	Relative intensity	Multiplicity	Proton assignment
 II	1.45	6	Doublet	CH ₃ of isopropyl
	2.16	3	Singlet	Ring CH ₃
	3.38	1	Multiplet	CH of isopropyl
	6.55	1	Singlet	OH of 6-position
	7.26	1	Singlet	Ring H
	12.86	1	Singlet	OH of 1-position
 III	1.43	6	Doublet	CH ₃ of isopropyl
	2.17	3	Singlet	Ring CH ₃
	3.41	1	Multiplet	CH of isopropyl
	3.91	3	Singlet	CH ₃ of methoxyl
	7.22	1	Singlet	Ring H
	12.86	1	Singlet	OH of 1-position
 V	1.55	6	Doublet	CH ₃ of isopropyl
	2.16	3	Singlet	Ring CH ₃
	3.91	1	Multiplet	CH of isopropyl
	3.96	3	Singlet	CH ₃ of methoxyl
	6.13	1	Singlet	OH of 7-position
	7.83	1	Singlet	Ring H
	11.13	1	Singlet	CHO
	14.46	1	Singlet	OH of 1-position

^a Measured in deuteriochloroform relative to tetramethylsilane as internal standard (TMS = 0).



possible exception of the 12.86-p.p.m. band as the proton of the hydroxyl group of the 1-position. It was suspected that this proton was strongly and intramolecularly hydrogen bonded to the carbonyl oxygen of the 8-position and should appear at a low-field position. This was made more certain by an examination of the n.m.r. spectrum of juglone (8-hydroxy-1,4-naphthoquinone) which gives a signal at 11.86 p.p.m. best assigned to the hydroxyl proton. Other support for the structure of II lies in the infrared spectrum, the ultraviolet spectrum, elemental analyses, and the formation of a phenazine-type derivative (IV) by reaction with *o*-phenylenediamine. The latter reaction (77% yield) is particularly diagnostic of an *o*-quinone structure.

Adams and Geissman report⁸ the oxidation of a gossyp-

pol dimethyl ether (V) in alkaline solution with air to a maroon crystalline substance, m.p. 246°. The compound was decolorized by reaction in solution with sodium hydrosulfite and they suggest that the oxidation product was a quinone, but no further data were given except carbon and hydrogen analyses. The similarity of reaction conditions used by Adams and Geissman with those used in this work suggested that their product had structure III and indeed the analytical figures given in the earlier work check satisfactorily for III. We repeated the procedure of Adams and Geissman and isolated the product of the properties reported by them. Also the methylation of II with methyl sulfate under mild conditions gave an identical product. The n.m.r. spectrum of III, summarized in Table I, supports the assigned structure as do infrared and ultraviolet spectra, elemental analyses, and the formation of a phenazine derivative with *o*-phenylenediamine.

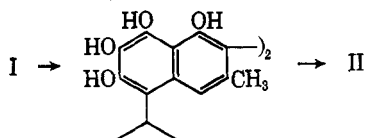
An alternative possibility for the structure of the quinone II could be formulated as a 6,6',7,7'-binaphthoquinone, and this is not rigorously excluded by the preceding data. Aside from the fact that such naphthoquinones have never been isolated, this possibility is eliminated by the clear cut indication from Adams' work⁹ that gossypol dimethyl ether does not have the two methoxyl groups in the 1,1'-positions. Such a dimethyl ether structure would be required for oxidation to a 6,6',7,7'-binaphthoquinone identical with an oxidation-methylation product of gossypol.

Attempted methylation of II with diazomethane and acetylation with acetic anhydride were not successful, yielding mixed products of nonquinoid structure. Reductive acetylation (zinc dust and acetic anhydride) of II produced a mixture of colorless polyacetyl derivatives with less acetyl content (shown by n.m.r. spectra) than the expected octaacetyl derivatives. Reacetylation did not produce the completely acetylated product.

(8) R. Adams and T. A. Geissman, *J. Am. Chem. Soc.*, **60**, 2165 (1938).

(9) R. Adams, T. A. Geissman, and J. D. Edwards, *Chem. Rev.*, **60**, 565 (1960).

It seems likely that the transformation of gossypol into the quinone II is *via* a Dakin reaction,¹⁰ although this hydroxy deformylation process of *o*- and *p*-hydroxyaldehydes usually requires alkaline peroxide and there is apparently no prior record of the operation of a Dakin reaction with oxygen. The Dakin reaction would produce formate ion, and we examined the acidified reaction mixture for formic acid by steam distilla-



tion and determination of formic acid in the distillate by the reduction of HgCl_2 . We found 45–60% of the theoretical amount of formic acid, assuming all of the oxygen consumed was for the production of II.

It was of interest to determine if other *o*-hydroxynaphthaldehydes could be converted by oxygen into *o*-naphthoquinones. Alkaline solution of 2,8-dihydroxy-1-naphthaldehyde showed rapid uptake of oxygen and formic acid (46%) was found in the acidified filtrate; however, it was not possible to isolate the expected 8-hydroxynaphthalene-1,2-dione. High molecular weight products were apparently formed and this may have occurred *via* oxidative coupling at the open positions *ortho* and *para* to the hydroxyl group. These positions contain groups or are blocked by neighboring groups in gossypol. 2-Hydroxy-1-naphthaldehyde showed quite slow oxygen uptake (several days *vs.* about 15 min. for gossypol and 2,8-dihydroxy-1-naphthaldehyde) and over 50% of the unreacted aldehyde was recovered.

Experimental¹¹

1,1',6,6'-Tetrahydroxy-5,5'-diisopropyl-3,3'-dimethyl-(2,2'-binaphthalene)-7,7',8,8'-tetrone (II).—A suspension of 4.62 g. (8.0 mmoles) of gossypol acetic acid in 43 ml. of absolute ethanol was stirred in a closed system connected to a gas buret filled with oxygen. The mixture was cooled to 5–10° and 8 ml. of 20% aqueous sodium hydroxide solution was added at once through a dropping funnel. A brown solution was obtained which quickly absorbed oxygen and changed to a deep blue-violet color and a blue-violet precipitate was formed. Stirring was continued for 15 min. during which time 200 ml. (8.3 mmoles) of oxygen was absorbed. The oxygen was replaced with nitrogen, the mixture was cooled to 0° and filtered under nitrogen, and the residue was washed several times with cold absolute ethanol and ether to yield 1.2 g. of deep blue-violet sodium salt of II. The salt was immediately dissolved in 300 ml. of oxygen-free water, and the solution was layered with benzene and then acidified with dilute acetic acid. The solution was extracted with three 500-ml. portions of benzene, and the combined extracts were washed with water, 5% aqueous sodium bicarbonate solution, and twice again with water. The benzene solution was dried over sodium sulfate and the benzene was removed by distillation *in vacuo* with a bath temperature of below 35°. The brown residue was crystallized from ether (30 ml.) and *n*-hexane (100 ml.) at 5° and there was obtained 400 mg. of brown solid. Concentration of the mother liquor yielded another 140 mg. and both of these materials melted

at 238–240°. Another crystallization gave brown crystals, m.p. 240–242°.

Anal. Calcd. for $\text{C}_{28}\text{H}_{26}\text{O}_8$: C, 68.56; H, 5.34. Found: C, 68.25, 68.47; H, 5.44, 5.53.

The above product gave a single spot of R_f 0.71 in a thin layer chromatogram on polyamide (ethanol–water, 3:2) and of R_f 0.58 on Silicagel G (benzene–dioxane–acetic acid, 45:8:4). The absorption maxima in the visible and ultraviolet range were $\lambda_{\text{max}}^{\text{EtOH}}$ 550 μ ($\log \epsilon$ 3.97), 445 (4.23), 310 (4.11). The infrared spectrum showed bands in the carbonyl stretch region at 6.00 and 6.08 μ . The infrared bands as well as the visible absorption at 550 μ are characteristic of *o*-quinones.¹² The n.m.r. spectral data are presented in Table I.

The solid sodium salt of II, isolated as described above, could not be stored, but the quinone is stable upon storage in the absence of light.

The alkaline solution above remaining after removal of the sodium salt was acidified with phosphoric acid and filtered, and the filtrate was steam distilled. The distillate was made slightly alkaline with sodium hydroxide and concentrated on the steam bath. The residue was acidified with acetic acid and heated under reflux with 120 ml. of 5% aqueous mercuric chloride solution. There were precipitated 2.26 g. of mercurous chloride representing 220 mg. of formic acid.

Reaction of the Quinone II with *o*-Phenylenediamine.—A solution of 100 mg. of the quinone II in 8 ml. of pyridine was mixed with 200 mg. of *o*-phenylenediamine in 2 ml. of pyridine, and the resulting solution was allowed to remain at room temperature for 20 hr. The solution was warmed, water was added, and upon cooling there was precipitated 100 mg. (77%) of red solid. This was recrystallized from dioxane–water. The melting point of the product IV was greater than 350°.

Anal. Calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_4$: C, 75.69; H, 5.40; N, 8.83. Found: C, 75.50, 75.71; H, 5.57, 5.35; N, 9.00, 8.92.

Thin layer chromatograms of the above product showed single spots of R_f 0.73 (polyamide with ethanol–water, 3:2) and R_f 0.75 (Silicagel G, with benzene–methanol, 95:5). The product showed the following ultraviolet and visible absorption maxima: 290 μ ($\log \epsilon$ 4.84), 315 (4.66), 430 (4.10), and 490 (4.25).

1,1'-Dihydroxy-6,6'-dimethoxy-5,5'-diisopropyl-3,3'-dimethyl-(2,2'-binaphthalene)-7,7',8,8'-tetrone (III). A. **By Oxidation of Gossypol Dimethyl Ether (V).**—The preparation of gossypol dimethyl ether (V) was by the selective demethylation of gossypol hexamethyl ether according to the procedure of Adams.⁸

A suspension of 546 mg. (1.0 mmole) of gossypol dimethyl ether in 15 ml. of ethanol was stirred under oxygen and treated with 3 ml. of 20% aqueous sodium hydroxide solution as described earlier for the oxidation of gossypol. In 15 min., 45 ml. of oxygen were absorbed and further oxygen uptake was much slower. The mixture was cooled in an ice bath and the precipitated violet sodium salt was removed. The salt was washed with cold ethanol, suspended in water, and layered with ether, and the mixture was acidified with aqueous sodium dihydrogen phosphate and then extracted with ether. The ether extracts were washed with water, 5% aqueous sodium bicarbonate, and again with water, and dried over sodium sulfate; the ether was evaporated. The residue was crystallized from ether–*n*-hexane to yield 220 mg. (42%) of deep red prisms, m.p. 245°. A thin layer chromatogram on Silicagel G showed a single spot of R_f 0.60 (benzene–dioxane–acetic acid, 45:8:4).

The filtrate from the removal of the sodium salt was treated as described earlier for determination of the amount of sodium formate present. The mercurous chloride collected represented 45% of the calculated amount of formic acid.

B. By Methylation of II.—A solution of 900 mg. of the sodium salt of II in 35 ml. of methanol was treated under nitrogen with 2 ml. of 30% aqueous sodium hydroxide solution. Nitrogen was passed through the solution as it was cooled to 5° and treated dropwise with 4.5 ml. of freshly distilled methyl sulfate. The temperature was then allowed to rise to 25° and after 1 hr. warmed to 40° and held at this temperature until the color of the mixture changed from dark blue to red. Aqueous sodium hydroxide (4%) was added to bring the volume of the mixture to about 200 ml. The mixture was extracted twice with 300 ml. of ether and a voluminous precipitate (sodium salt of III) was formed in the

(10) (a) H. D. Dakin, *Am. Chem. J.*, **42**, 477 (1909); (b) D. H. Rosenblatt and R. Rosenthal, *J. Am. Chem. Soc.*, **75**, 4607 (1953); (c) L. Horner and K. H. Weber, *Ber.*, **96**, 1568 (1963).

(11) Infrared spectra are from KBr pellets taken on a Perkin-Elmer Infracord. Nuclear magnetic resonance spectra were determined in CDCl_3 on a Varian A-60 instrument. Ultraviolet spectra were taken in 95% ethanol or chloroform on a Cary Model 14 instrument. Thin layer chromatograms were with 300- μ layers of Woelm polyamide powder or Merck Silicagel G. Column chromatography was on BASF. Ultramid, BM228. Elemental analyses are by Galbraith Laboratories, Knoxville, Tenn.

(12) S. Goldschmidt and F. Graef, *Ber.*, **61B**, 1858 (1928); H. J. Teuber and G. Staiger, *ibid.*, **88**, 802 (1955); W. Otting and G. Staiger, *ibid.*, **88**, 828 (1955).

aqueous layer. The precipitate was removed and suspended in water and the suspension was acidified with dilute acetic acid and extracted with ether. The ether solution was worked up as described in A to yield 32 mg. of red-violet prisms, melting at 234°. Two recrystallizations raised the melting point to 242°. The infrared spectrum of this product was identical with the product from A and a mixture of the two products showed no depression in melting point. The carbonyl stretch bands appeared at 5.97 and 6.12 μ .

Anal. Calcd. for $C_{30}H_{30}O_8$: C, 69.48; H, 5.83. Found: C, 69.43, 69.66; H, 5.72, 5.90.

The ultraviolet and visible spectrum of the quinone III gave the following maxima in ethanol: 265 m μ (log ϵ 4.44), 303 (3.99), 450 (4.13), 535 (sh) (3.90).

The quinone III (50 mg.) was converted to a phenazine-type derivative by reaction with 100 mg. of *o*-phenylenediamine by the procedure described above. The product was 53 mg. (80%) of

bright red crystals which melted at 327–328° after crystallization from water–pyridine.

Anal. Calcd. for $C_{42}H_{38}N_4O_4$: C, 76.11; H, 5.78; N, 8.45. Found: C, 76.14; H, 5.90; N, 8.56.

Acknowledgment.—The authors would like to acknowledge financial support by the U. S. Department of Agriculture under Contract 12-14-100-5783(72). The contract is administered by the Southern Utilization Research and Development Division at New Orleans, Louisiana, and we should like to acknowledge helpful discussions with Dr. V. L. Frampton of that organization. The authors would like to thank BASF of Ludwigshafen, Rhine, for a generous sample of Ultramid BM228.

Organo-Iron Complexes. IV. Reactions of Substituted Dienes with Iron Pentacarbonyl

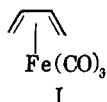
G. F. EMERSON, J. E. MAHLER, R. KOCHHAR, AND R. PETTIT

Department of Chemistry, The University of Texas, Austin 12, Texas

Received July 23, 1964

The reaction of conjugated and nonconjugated dienes with iron pentacarbonyl leads to the formation of diene-iron tricarbonyl complexes with rearrangement of the diene ligand in many cases. These rearrangements appear to take a course providing the less sterically crowded complexes. A compilation of n.m.r. data for these complexes is presented.

The reaction of butadiene with iron pentacarbonyl to produce butadiene-iron tricarbonyl (I) was first re-



ported in 1930,¹ but only recently has the reaction been extended.²⁻⁴ It now appears that the reaction between dienes and $Fe(CO)_5$ may take one of several routes depending on the nature of the diene. These reactions may be briefly summarized as follows.

Conjugated dienes frequently react to give the corresponding diene- $Fe(CO)_3$ complexes, in several cases accompanied by iron complexes of dimers of the diene. Notable exceptions are the reactions of cyclopentadiene and its derivatives which lead to the formation of cyclopentadienyl-iron carbonyl complexes.⁵ Also in a few instances, for example in the case of 1,3-cyclooctadiene, no reaction occurs presumably because the two double bonds cannot become sufficiently coplanar.⁶

Nonconjugated dienes, both cyclic and acyclic, can also react with $Fe(CO)_5$ to furnish diene-iron tricarbonyl complexes in which the ligand is an isomeric conjugated hydrocarbon; for example, 1,4-cyclohexadiene reacts to produce 1,3-cyclohexadiene-iron tricarbonyl and 1,4-pentadiene gives the *trans*-piperylene- $Fe(CO)_3$ complex.⁷ Exceptions again are seen in the cases of

bicycloheptadiene⁸ and bicyclooctatriene^{9,10} derivatives which afford the corresponding nonconjugated diene- $Fe(CO)_3$ complexes. Isolated cases of other types of rearrangements have also been noted; for example, prolonged heating of cycloheptatriene with $Fe(CO)_5$ produces fair yields of the cycloheptadiene- $Fe(CO)_3$ ¹¹ complex while cyclooctatriene leads to the formation of bicyclooctadiene- $Fe(CO)_3$ ¹² and 1,5,9-cyclododecatriene gives a dihydrobenzocyclooctene- $Fe(CO)_3$ complex.¹³

Several aspects of the reaction of $Fe(CO)_5$ with dienes remain to be clarified. The present paper deals with the reaction of acyclic dienes with $Fe(CO)_5$ and is mainly concerned with the question as to when rearrangements may be expected and, in cases where isomerization to different isomers is possible, which is the preferred direction of reaction.

Results and Discussion

Reaction of Dienes with $Fe(CO)_5$.—As indicated in the following scheme the reaction of *cis*-1,3-pentadiene, 1,4-pentadiene, or *trans*-1,3-pentadiene with $Fe(CO)_5$ leads to the formation of *trans*-1,3-pentadiene-iron tricarbonyl (II). Under the same reaction conditions, in the absence of $Fe(CO)_5$, the first two of these hydrocarbons do not undergo isomerization to *trans*-1,3-pentadiene; furthermore, the *cis*-1,3-pentadiene-iron tricarbonyl complex, which can be prepared by an indirect route,¹⁴ does not isomerize to the *trans* complex II under these conditions.

(8) (a) R. Burton, M. L. H. Green, E. W. Abel, and G. Wilkinson, *Chem. Ind. (London)*, 1592 (1958); (b) R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

(9) R. B. King, *ibid.*, **84**, 4705 (1962).

(10) T. A. Manuel and F. G. A. Stone, *ibid.*, **82**, 366 (1960).

(11) H. J. Dauben and D. J. Bertelli, *ibid.*, **83**, 497 (1961).

(12) T. A. Manuel and F. G. A. Stone, *ibid.*, **82**, 366 (1960).

(13) T. A. Manuel, E. Tornqvist, R. Kochhar, and R. Pettit, *in press*.

(14) J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).

(1) H. Reihlen, A. Gruhl, G. von Hessling, and O. Pfrengle, *Ann. Chem.*, **482**, 161 (1930).

(2) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

(3) E. O. Fischer and H. Werner, "Metall- π -Komplexe mit di- und oligoolefinischen Liganden," Verlag Chemie, Weinheim, 1963.

(4) R. Pettit and G. F. Emerson in "Advances in Organometallic Chemistry," R. West and F. G. A. Stone, Eds., Academic Press, New York, N. Y., 1964.

(5) P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960).

(6) J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2955 (1961).

(7) R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).