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 mμ (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.

# Organo–Iron Complexes. IV. Reactions of Substituted Dienes with Iron Pentacarbonyl

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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-

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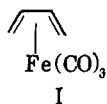
ported in 1930,[1] but only recently has the reaction been extended.[2-4] It now appears that the reaction between dienes and $Fe(CO)_5$ may take one of several routes depending on the nature of the diene. These reactions may be briefly summarized as follows.

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

bicycloheptadiene[8] 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.

(1) H. Reihlen, A. Gruhl, G. von Hessling, and O. Pfrengle, *Ann. Chem.*, **482**, 161 (1930).
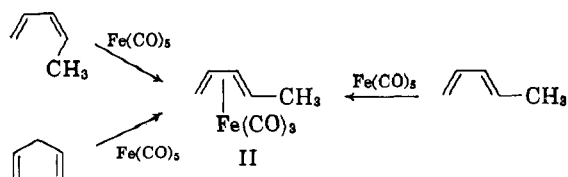
(2) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

(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, Ed., 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).

(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).

Another example of the migration of the double bond similar to that seen in the above reaction with 1,4-pentadiene is found with 1,5-hexadiene. Reaction of this hydrocarbon leads to the formation of *trans*-1,3-hexadiene–iron tricarbonyl (III) possibly with concomitant formation of small amounts of *trans-trans*-2,4-hexadiene–iron tricarbonyl (IV). *trans-trans*-2,4-Hexadiene on the other hand appears to yield the complex IV exclusively when treated with Fe(CO)₅.
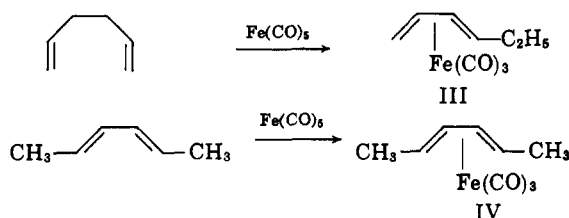

The preference for the formation of *trans*-substituted diene ligands in iron tricarbonyl complexes is further illustrated in the following reactions. 4-Methyl-1,3-pentadiene reacts with Fe(CO)₅ to give what appears to be exclusively *trans*-2-methyl-1,3-pentadiene–iron tricarbonyl (V). Another interesting example is afforded by the cases of 2,5-dimethyl-1,5-hexadiene and 2,5-dimethyl-2,4-hexadiene. As indicated in the following scheme each of these hydrocarbons reacts to produce *trans*-2,5-dimethyl-1,3-hexadiene–iron tricarbonyl (VI).
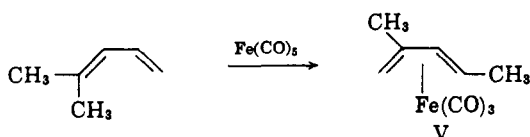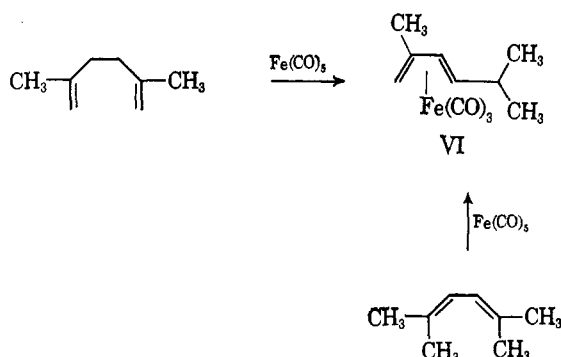

2-Methyl-1,5-hexadiene reacts in an analogous manner to produce 2-methyl-1,3-hexadiene–iron tricarbonyl (VII).
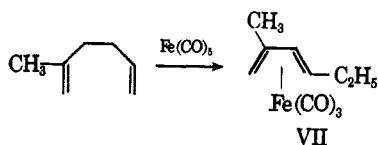
Only in one case studied so far have we obtained a diene–Fe(CO)₃ complex possessing an alkyl group in an

anti position. *cis-trans*-2,4-Hexadiene reacts with Fe(CO)₅ under comparable conditions to those employed in the above reactions to produce *cis-trans*-2,4-hexadiene–iron tricarbonyl (VIII).
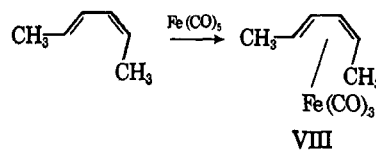
The mechanism of these rearrangements is not established, but it may be concluded that reaction of acyclic dienes with Fe(CO)₅ proceeds to favor end products lacking *cis* (or *anti*) substituents on the diene ligand although such complexes possibily are produced as intermediates. The simplest explanation for this would seem to be that substituents in an *anti* position of the diene ligand experience steric strain and such complexes are less thermodynamically stable than the isomeric complexes having substituents in the *syn* positions. The X-ray data of Mills and Robinson[15] for butadiene–Fe(CO)₃ show that the atoms are distributed as indicated in IX, in particular the four carbons of the diene
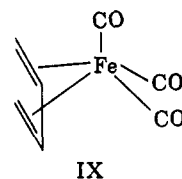
ligand are shown to be held cisoid and coplanar. Using the bond distances found for this system, it is readily seen that repulsion between *anti* substituents themselves or between an *anti* substituent and the iron atom or the adjacent CO group is likely if the diene ligand is to remain nearly planar.

In this regard the n.m.r. spectrum of *cis*-1,3-pentadiene–Fe(CO)₃ is also of interest. As indicated below, the presence of the *anti* methyl group on C-4 has the effect of lowering the absorption of the *syn* hydrogen on C-4 by approximately one τ-unit from the value normally found for such hydrogens in acyclic diene–Fe(CO)₃ complexes lacking substitution in the *anti* position. This hydrogen atom also now absorbs in the region typical of that found for the hydrogens on the terminal diene positions of cyclic diene–iron tricarbonyl complexes[16] which suggests that a similar steric disturbance may be present in these latter systems.

The existence of steric strain in the diene–iron tricarbonyl complexes possessing *anti* substituents may also have some bearing on the question as to which formulation best represents the electronic structure of these systems. Based upon X-ray data taken with triphenyltropone–Fe(CO)₃, cyclooctatetraene–Fe(CO)₃, and cyclooctatetraene–Fe₂(CO)₆, it has been suggested that the terminal carbons of the diene ligand possess a large degree of sp³ character and that the formulation X is more suitable than I for the diene–Fe(CO)₃ structural unit[17,18] in such complexes. These arguments were based upon the fact that there existed a considerable displacement of the ring carbons attached to the ter-

(15) O. S. Mills and G. Robinson, *Acta Cryst.*, **16**, 758 (1963).
(16) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).
(17) D. J. Smith and L. F. Dahl, *J. Am. Chem. Soc.*, **84**, 1743 (1962).
(18) B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

X
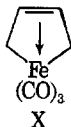
minal carbons of the diene from the plane of the diene system. Since these carbons are in *anti* positions it seems probable that this deformation may be largely steric in origin and in the absence of such interactions, as in butadiene–iron tricarbonyl and its *syn*-substituted derivatives, the ligand becomes more nearly coplanar with the bonding being best represented by structures such as I.

N.m.r. Spectra of Diene–Iron Tricarbonyl Complexes.

—One of the difficulties involved in establishing the structure of a diene–Fe(CO)$_3$ complex involves determination of the structure of the ligand while it is still bonded to the metal. This determination is clearly more desirable than one which first depends on liberation of the ligand by displacement by some other ligand or by oxidative degradation of the complex for such methods always have present the danger of isomerization of the liberated ligand before it is removed from the reaction. For this purpose the n.m.r. technique has proved to be extremely valuable. The n.m.r. data for butadiene–Fe(CO)$_3$ and several cyclic diene–Fe(CO)$_3$ complexes have already been reported by Wilkinson and co-workers.[16] The values of the chemical shifts for the protons in the acyclic diene–iron tricarbonyl complexes mentioned above and for several typical acyclic complexes prepared for other purposes are now listed in Table I.

The positions of the absorptions and the consistent variations with structural changes of the ligand provide a valuable method for identification of an unknown ligand. The pertinent data concerning the chemical shifts may be summarized as follows. The internal protons of the diene ligand (on C-2 and C-3) occur in the region τ 4.6–4.9; this is the same region found by Wilkinson and co-workers for the corresponding protons in several cyclic diene–Fe(CO)$_3$ complexes.[16] The protons on the terminal carbon atoms of the diene system show considerable differences depending on whether they lie in a *syn* or *anti* position with respect to the internal hydrogens. Complexes having a terminal =CH$_2$ group show the *syn* proton of this group in the region τ 8.2–8.4 while the *anti* proton appears at τ 9.5–9.8. A single and significant exception to the latter range is provided by *cis*-1,3-pentadiene–Fe(CO)$_3$ in which the *anti* protons of the =CH$_2$ group appears at τ 8.5–8.6; *trans* substituents at C-4 however have little effect on the chemical shifts of the *anti* protons on C-1. For cyclic diene complexes the hydrogens on the terminal carbons of the diene, which are necessarily in a *syn* position, occur in the region τ 6.6–7.3.

Saturated substituents in a *syn* position on C-4 will cause a hydrogen in the *anti* position of C-4 to move slightly downfield (τ 8.9–9.4). However, in the two cases so far studied, a methyl group in the *anti* position on C-4 causes the *syn* hydrogen on C-4 to appear at the significantly lower value of τ 7.3–7.6; as stated above this is within the region shown for cyclic systems.

Unsaturated substituents such as phenyl or carbomethoxy groups cause the neighboring protons on the diene to shift to lower fields as one might expect.

Experimental

The pertinent n.m.r. data for the complexes reported below is given in Table I.

4-Methyl-1,3-pentadiene.—This was prepared by dehydration of 2-methyl-2,4-pentane diol with 48% hydrobromic acid,[19] n^{23}D 1.4485. V.p.c. analysis showed it to be of 95% purity.

Reaction of 4-Methyl-1,3-pentadiene with Iron Pentacarbonyl. —4-Methyl-1,3-pentadiene (71 g., 0.866 mole) was heated with iron pentacarbonyl (160 g., 0.80 mole) at 90–100° for 140 hr. under a blanket of nitrogen. The mixture was cooled and filtered, and after the removal of unreacted hydrocarbon and iron pentacarbonyl there was obtained 30.5 g. (14.6%) of a deep yellow liquid, b.p. 45° (0.2 mm.), n^{24}D 1.5556. The infrared spectrum (in carbon tetrachloride) of this compound showed strong carbonyl absorption peaks at 1968, 1977, and 2043 cm.$^{-1}$.

Anal. Calcd. for C$_9$H$_{10}$FeO$_3$: C, 48.64; H, 4.50. Found: C, 48.48; H, 4.44.

Reaction of 2,5-Dimethyl-2,4-hexadiene with Iron Pentacarbonyl.—Hydrocarbon (55 g., 0.5 mole) (Matheson Coleman and Bell) was refluxed with 150 g. (0.75 mole) of iron pentacarbonyl for 168 hr. under a blanket of nitrogen. After removal of the unreacted hydrocarbon and iron pentacarbonyl there was obtained 10.0 g. (2.8%) of a yellow liquid, b.p. 48–50° (0.1 mm.), n^{24}D 1.5416. The infrared spectrum of the compound showed intense absorption peaks of the carbonyl groups at 1969, 1979, and 2042 cm.$^{-1}$.

Anal. Calcd. for C$_{11}$H$_{14}$FeO$_3$: C, 52.8; H, 5.60. Found: C, 53.20; H, 5.66.

Reaction of 2,5-Dimethyl-1,5-hexadiene with Iron Pentacarbonyl.—After treatment of the hydrocarbon in a manner similar to 2,5-dimethyl-2,4-hexadiene, there was obtained a clear yellow liquid (6.2% yield) boiling at 40–50° (0.1 mm.), n^{24}D 1.5416. The infrared spectrum of the compound (in carbon tetrachloride) showed strong carbonyl peaks at 1969, 1979, and 2042 cm.$^{-1}$.

Anal. Calcd. for C$_{11}$H$_{14}$FeO$_3$: C, 52.8; H, 5.60. Found: C, 53.10; H, 5.62.

Reaction of 2-Methyl-1,5-hexadiene with Iron Pentacarbonyl. —2-Methyl-1,5-hexadiene (10.0 g.) was refluxed with iron pentacarbonyl (60.0 g.) for 90 hr. After the removal of the volatile material under reduced pressure there was obtained 1.5 g. (6%) of a clear yellow liquid boiling at 35° (0.1 mm.), n^{25}D 1.5520. The infrared spectrum of the compound (in carbon tetrachloride) showed strong carbonyl absorptions at 1967, 1977, and 2043 cm.$^{-1}$.

Anal. Calcd. for C$_{10}$H$_{12}$FeO$_3$: C, 50.84; H, 5.08. Found: C, 50.54; H, 5.06.

Reaction of 1,5-Hexadiene with Iron Pentacarbonyl.—1,5-Hexadiene (82 g., 1.0 mole) and 300 g. (1.5 moles) of iron pentacarbonyl were heated together at 80–90° for 80 hr. under a blanket of nitrogen. After the removal of unreacted hydrocarbon and iron pentacarbonyl there was obtained 16.0 g. (7.2%) of a clear yellow liquid boiling at 40° (0.2 mm.), n^{34}D 1.5588. The infrared spectrum of the compound gave carbonyl peaks at 1970, 1980, and 2048 cm.$^{-1}$.

Anal. Calcd. for C$_9$H$_{10}$FeO$_3$: C, 48.64; H, 4.50. Found: C, 48.68; H, 4.58.
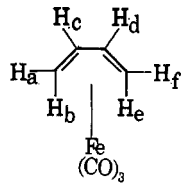
Preparation of *trans-trans*-2,4-Hexadiene.—Hexen-2-ol-4 was dehydrated with hydrobromic acid as described earlier and, after drying, the hydrocarbon layer was distilled. The colorless liquid fraction (b.p. 80–82°) proved to be a mixture of three compounds in the ratio 7:50:43 as shown by v.p.c. analysis using a Carbowax 20M column. The three fractions were separated by preparative scale v.p.c. in the following manner. A 20-ft. (3/8-in. o.d.) aluminum column for the Aerograph A-700 instrument preparative gas chromatograph was packed with 25% (w./w.) Carbowax 20M on 45–60-mesh Chromosorb-P. Under the column conditions at 80° the *cis-cis* isomer had a retention time of 13.5 min., while the *trans-trans* and *cis-trans* isomers came through at 17.2 and 20 min., respectively. Using small injections (0.1 ml.) and judicious cutting of fractions pure *trans-trans* and *cis-trans* compounds were obtained. The *cis-trans* isomer was contaminated with about 10% of the *trans-trans* compound. The infrared spectra of the *trans-trans* and *cis-trans* isomers matched those reported in literature.[20]

Anal. Calcd. for C$_6$H$_{10}$: C, 87.80; H, 12.19. Found (for

(19) G. B. Bachman and C. G. Goebel, *J. Am. Chem. Soc.*, **64**, 787 (1942).

(20) L. K. Montgomery and P. D. Bartlett, *ibid.*, **86**, 627 (1964).

TABLE I

CHEMICAL SHIFTS[a] OF PROTONS IN ACYCLIC DIENE-IRON TRICARBONYL COMPLEXES

Structure of diene ligand	Ref.	H_a	H_b	H_c	H_d	H_e	H_f
(butadiene)	b	8.27	9.78	4.63	4.63	9.78	8.27
CH_3—	c	...	8.92	4.83	4.83	9.78	8.36
CH_3	d	7.33	...	4.70	4.70	8.53	8.25
CH_3—CH_3	c, e	7.64	...	4.90	4.90	8.60	...
CH_3— CH_3	c	...	9.15	4.90	...	9.73	8.32
C_2H_5— CH_3	c	...	9.20	4.90	...	9.74	8.33
C_2H_5—	c	...	8.9	4.9	4.9	9.8	8.3–8.7
CH_3—CH_3	c	...	8.90	5.00	5.00	8.90	...
CH_3, CH_3 CH_3	c	...	9.4	4.90	...	9.77	8.32
CH_3 CH_3—CH_3 CH_3	f	...	8.4	5.0	...	8.8	...
(CH_3 dimer)$_2$	e	...	9.15	4.83	4.83	9.77	8.28
$HOCH_2$—	d	...	8.93	4.71	4.71	9.63	8.22
$HOCH_2$—CH_3	e	...	8.94	4.92	4.92	8.7–9.0	...
CH_3–CH— OH	e	...	9.08	4.69	4.69	9.64	8.23
CH_3–CH— OCH_3	e	...	9.15	4.71	4.71	9.69	8.28
C_6H_5—	g	...	8.02	4.18	4.72	9.48	8.22
C_6H_5—$COOCH_3$	g	...	7.68	4.02	4.02	8.70	...

[a] In τ-units. [b] Ref. 16. [c] This work. [d] J. E. Mahler and R. Pettit, J. Am. Chem. Soc., **85**, 3959 (1963). [e] J. E. Mahler, D. H. Gibson, and R. Pettit, ibid., **85**, 3959 (1963). [f] Prepared by the method described in ref. 7. [g] J. E. Mahler and R. Pettit, unpublished work.

trans-trans): C, 87.70; H, 12.24. Found (for cis-trans): C, 87.62; H, 12.15.

Reaction of trans-trans-2,4-Hexadiene with Iron Pentacarbonyl.—trans-trans-2,5-Hexadiene (4.0 g.) was heated with excess iron pentacarbonyl at 115° for 135 hr. After the removal of the unreacted hydrocarbon and iron pentacarbonyl there was obtained 4 g. (36%) of a clear yellow liquid boiling at 45° (0.3 mm.), $n^{25}D$ 1.5650. The infrared spectrum of the compound showed strong absorption for carbonyls at 1967 (shoulder), 1974, and 2041 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{10}FeO_3$: C, 48.64; H, 4.50. Found: C, 49.29; H, 4.78.

Reaction of cis-trans-2,4-Hexadiene with Iron Pentacarbonyl.—cis-trans-2,4-Hexadiene (3.0 g.) was heated with excess iron pentacarbonyl at 110° for 90 hr. After the removal of the unreacted hydrocarbon and iron pentacarbonyl there was obtained 0.5 g. (yield, 6%) of a clear yellow liquid boiling at 42° (0.25 mm.), $n^{28}D$ 1.5700. The infrared spectrum of the compound showed strong absorption for the carbonyls at 1966 (shoulder), 1977, and 2043 cm.$^{-1}$.

Anal. Calcd. for $C_9H_{10}FeO_3$: C, 48.64; H, 4.50. Found: C, 48.70; H, 4.59.

Reaction of cis-Piperylene with Iron Pentacarbonyl.—Treatment of commercial piperylene with maleic anhydride according

to the procedure of Frank, Emmick and Johnson[21] afforded a mixture indicated by gas chromatography to be free of the *trans* isomer and consisting of 45% *cis*-piperylene and 55% cyclopentene. In a 100-ml. steel autoclave was placed 14.0 g. of the 45% *cis*-piperylene (93 mmoles) with 40.0 g. of iron pentacarbonyl (204 mmoles). The bomb was then heated for 80 hr. at 150–60°. The reaction mixture was first distilled to remove unreacted materials; then a mixture of iron complexes, b.p. 30–80° (1.2 mm.), was obtained. Fractionation gave 1.5 g. (7.8% yield) of the piperylene complex, b.p. 32–36° (1.2 mm.), n^{33}D 1.5460, and 1.0 g. of the piperylene dimer complex, b.p. 67–75°, n^{33}D 1.5340. Gas chromatographic analysis indicated that the unreacted piperylene was entirely the *cis* isomer.

Degradation of the piperylene complex was effected by stirring 1.0 g. with 8.0 g. of ferric chloride dissolved in 20 ml. of 95%

(21) R. L. Frank, *et al.*, *J. Am. Chem. Soc.*, **69**, 2313 (1947).

ethanol with ice cooling. After 1 hr., gas evolution ceased. The mixture was then diluted with water and extracted with 5 ml. of ether. The ether layer was washed with water and dried over sodium sulfate. Gas chromatographic analysis indicated the presence of *trans*-piperylene while none of the *cis* isomer could be detected. Under subjection to the conditions of this degradation, a 4-ml. sample of the 45% *cis*-piperylene remained unchanged.

A 10.0-g. sample of the *cis*-piperylene–cyclopentene mixture was heated at 160° for 70 hr. Gas chromatography of the product from this treatment indicated again the absence of *trans*-piperylene. The original components remained, with minor amounts of higher boiling compounds present.

Mechanism of the Ullmann Condensation[1]

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The Ullmann condensation was found to be catalyzed by cuprous copper. It was found to be first order in catalyst, first order in halobenzene, and variable order in potassium phenoxide in the media used. A mechanism is proposed.

Preliminary studies[2] on the Ullmann condensation[3] have led to the conclusion that the reaction is most probably a nucleophilic aromatic substitution involving carbon–halogen bond cleavage in the rate step. To follow up this preliminary work a kinetic study was undertaken and is herein reported.

The specific reaction studied was the formation of phenyl ether from bromobenzene and potassium phenoxide in bis(2-methoxyethyl) ether (diglyme) as solvent in the presence of various copper salts at 100°. The reaction was followed by measuring the disappearance of potassium phenoxide by titration.

Early experiments were carried out in Matheson Coleman and Bell's practical diglyme giving smooth, apparently second-order kinetics. However, when the solvent was purified by distillation from LiAlH₄ we found the rate of reaction to be greatly diminished. We soon learned that the impure solvent contained an ingredient which acted in some way to enhance catalytic activity. With the aid of gas chromatographic techniques a fraction containing the active ingredient was isolated. The sample was subjected to infrared, n.m.r., and molecular weight analysis. The structure best representing the data is the diester, $CH_3OCH_2COOCH_2$-CH_2OCHO. We did not demonstrate unequivocally that this compound could cause rate enhancement for at this time we discovered that many esters of ethylene glycol and related glycols gave the same rate enhancement.[4] The readily available ethylene diacetate was then used as a standard additive to the reaction media. The function of the ester is not clearly understood,

but it appears to be related to the solubility of the catalyst. In lithium aluminum hydride purified solvent where little or no reaction takes place large amounts of copper are found in the precipitate.

The most compelling problem of the study involved determining the form of catalytic copper. Literature reports[5] on the subject are meager and inconclusive and we hoped to find a definitive method to distinguish the possibilities. Metallic copper, cuprous oxide, cupric oxide, and cuprous sulfate were inactive as catalysts owing probably to their small solubility in the media. A number of other salts were active including $CuBr_2$, $CuCl_2$, $Cu(OAc)_2\cdot H_2O$, CuI, CuBr, and CuCl. Furthermore, they were interchangeable as catalysts giving equal rates for equal weights of copper. The reason for the insensitivity of the reaction to the ligands on copper was made clear from a study of the catalyst stoichiometry. If $CuBr_2$, for example, is combined with a solution containing an excess of potassium phenoxide in diglyme 2 equiv. of phenoxide are consumed and 2 equiv. of potassium bromide are precipitated. When CuBr is used the changes involve only 1 equiv., suggesting, at least superficially, a simple ligand exchange.

On the other hand, that cuprous and cupric salts should give identical rates was very puzzling. Electron paramagnetic resonance (e.p.r.) and magnetic susceptibility measurements performed on catalytic solutions made from cupric or cuprous salts showed essentially the same result. That is, they both were paramagnetic and gave similar electron paramagnetic signals. These results were interpreted to mean significant amounts of cupric copper were present in the catalytic solutions. However, catalytic solutions prepared under an atmosphere of nitrogen told a rather different story. While the results for cupric salts remained about the same, catalytic solutions prepared from cuprous salts showed a weaker e.p.r. signal and

(1) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, Abstract, p. 16Q.

(2) H. Weingarten, *J. Org. Chem.*, **29**, 977 (1964).

(3) The Ullmann condensation, the copper-catalyzed reaction of aromatic halides with phenol salts (or anilines) to yield aryl ethers (or aryl amines), should be distinguished from the Ullmann coupling reaction used to form biaryls from aromatic halides. (See A. R. Surry, "Name Reactions in Organic Chemistry," Academic Press, Inc., New York, N. Y., 1954.)

(4) Ethylene carbonate, propylene glycol diacetate, propylene glycol α-monoacetate, diacetin, and 1,2-diacetoxycyclohexane are also active. Dimethyl adipate, 1,3-diacetoxypropane, and pinacol diacetate are inactive.

(5) P. W. Weston and H. Adkins, *J. Am. Chem. Soc.*, **50**, 859 (1928); I. Goldberg, *Ber.*, **40**, 4541 (1907).