alumina. The benzene eluate was washed with 20 ml. of 10% aqueous potassium hydroxide (0.25 g. of isocamphorquinone recovered on acidification), then with water, and dried over sodium sulfate. Evaporation of solvent left a partly crystalline residue which was triturated with light petroleum ether and recrystallized from cyclohexane. The methyl ether was obtained as needle crystals (0.3 g., 19%), m.p. 83–85°; ultraviolet spectrum: λ_{max} 293 mμ (ϵ 16,400) with an inflection at 258 mμ (ϵ 7,500); infrared spectrum, high intensity bands at 6.10 and 6.20μ.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.09; H, 8.95.

5-Ketoheptanoic Acid VIII. (a) **By Alkaline Hydrolysis of Isocamphorquinone.**—A solution of isocamphorquinone (0.50 g.) and potassium hydroxide (5.0 g.) in water (25 ml.) was heated under gentle reflux while the system was swept by a slow stream of nitrogen. The effluent gas was bubbled through an alcoholic solution of 2,4-dinitrophenylhydrazine reagent causing the accumulation, over five hours, of a voluminous yellow-orange precipitate. The solid was collected and, after recrystallization from methanol, had m.p. 123–124° alone or admixed with authentic acetone 2,4-dinitrophenylhydrazone.

The cooled, alkaline reaction solution was washed with ether, concentrated *in vacuo* to 10-ml. volume, cautiously acidified (cooling) to *p*H 3, and extracted with 50 ml. of ether in five portions. After washing with saturated, aqueous sodium chloride, the dried ethereal solution was concentrated *in vacuo* and the residue crystallized from ether-hexane at 0°. The keto acid, 0.203 g. (47%), was thus obtained as fine needle crystals, m.p. 51–52°.

The semicarbazone, crystallized once from ethanol, had m.p. 186–188° alone or admixed with an authentic sample (part c).

The oxime, crystallized once from water, had m.p. 116–118° alone or admixed with an authentic sample (part c).

(b) **By Acidic Hydrolysis of Isocamphorquinone.**—Isocamphorquinone was heated under reflux with dilute sulfuric acid according to the procedure of Manasse and Samuel.[5] The acidic product was directly converted to the semicarbazone and the oxime. Melting point and mixture melting point observations were identical with those recorded above.

(c) **Synthesis from Glutaric Anhydride.**—Ethylmagnesium bromide (0.15 mole) in ether (150 ml.) was treated with cadmium chloride (15.6 g., 0.08 mole) according to de Benneville's procedure[22] for conversion to the dialkyl cadmium reagent. To the resulting ethereal solution was added powdered glutaric anhydride (9.1 g., 0.08 mole) at 0° and with stirring over a period of 15 minutes; reaction was then continued for one hour at reflux temperature. The cooled reaction mixture was treated with 73 ml. of cold 10% hydrochloric acid and the aqueous layer extracted with 150 ml. of ether in three portions. The combined ether solutions were extracted with saturated aqueous sodium bicarbonate; the aqueous layer was separated, carefully acidified, and repeatedly extracted with ether. The combined extracts were washed with water, dried and evaporated at reduced pressure yielding 8.0 g. (69%) of crude, partly oily product which was directly converted to the oxime, m.p. 116–118°, and the semicarbazone, m.p. 186–188°d.

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[22] P. L. deBenneville, *J. Org. Chem.*, **6**, 462 (1941).

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Ring Interconversion by Transacylation in the Benzofluorenone and Benzanthrone Series[1]

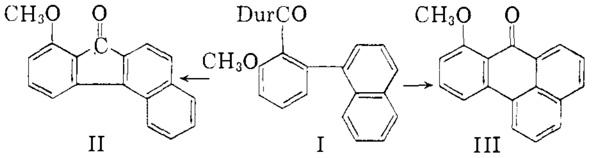
BY REYNOLD C. FUSON, WILLIAM A. HILLS AND BRUNO VITTIMBERGA

RECEIVED SEPTEMBER 8, 1959

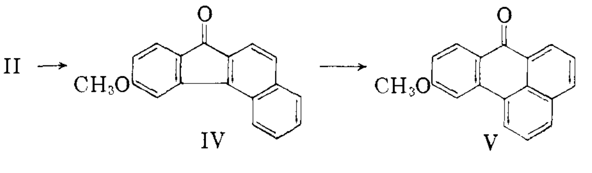
Duryl 6-methoxy-2-(α-naphthyl)-phenyl ketone reacts in the presence of polyphosphoric acid to give 8- and 10-methoxyfluorenones and the corresponding 8- and 10-methoxybenzanthrones. Under mild conditions only the 8-methoxyfluorenone and the 8-methoxybenzanthrone are formed. Drastic conditions afford only the two benzanthrones. When heated with polyphosphoric acid the 8-methoxyfluorenone isomerizes to the 10-methoxy derivative, which in turn forms the 10-methoxybenzanthrone. It appears that the formation of the fluorenones is rate controlled and that that of the benzanthrones is equilibrium controlled.

Acid-catalyzed cleavage of diaryl ketones and subsequent use of the resulting carboxylic acids as acylating agents makes possible transcarbonylation processes, *i.e.*, the formation of one ketone from another.[2] The cleavage, best accomplished with polyphosphoric acid, occurs easily with many ketones having an aryl radical of the hindered type. When the ketone carries in addition a suitable aryl radical in an *o*-position, cyclization may occur to produce a fluorenone.[3]

In the present study this cleavage–cyclization procedure was applied to duryl 6-methoxy-2-(α-naphthyl)-phenyl ketone (I), which offers the interesting possibility of forming a fluorenone or a benzanthrone, depending, respectively, on whether the acylation takes place at the adjacent β-position or in such a manner as to form a *peri*-bridge. Experiment has shown that both types of ring closure occur.



When the ketone was kept for 10 hr. in polyphosphoric acid at room temperature, the fluorenone II was formed in 13.3% yield and the benzanthrone III in a yield of 7.6%, most of the original ketone being recovered. Under more drastic reaction conditions the 10-methoxyfluorenone IV and the 10-methoxybenzanthrone V were produced also. It was observed too that the 8-methoxyfluorenone II, when heated with polyphosphoric acid, rearranged to the 10-methoxy isomer IV and this fluorenone, in turn, was isomerized by similar treatment to the 10-methoxybenzanthrone V.



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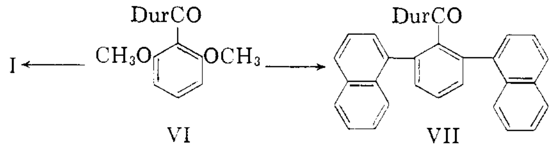
[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

[2] R. C. Fuson, G. R. Bakker and B. Vittimberga, THIS JOURNAL, **81**, 4858 (1959).

[3] R. C. Fuson and J. J. Miller, *ibid.*, **79**, 3477 (1957).

These rearrangements can be explained by assuming cleavage of the fluorenones followed by acylation at a new position. It seems that the formation of the fluorenones is rate controlled whereas that of the benzanthrones is equilibrium controlled. Very drastic treatment of the duryl ketone I produced only the benzanthrones. Moreover, the 8-methoxybenzanthrone was not isomerized by heating with polyphosphoric acid. Heating duryl 4-methoxy-2-(α-naphthyl)-phenyl ketone with polyphosphoric acid gave both the 10-methoxyfluorenone IV and the 10-methoxybenzanthrone V.

Methods were developed for replacing the methoxyl groups of duryl 2,6-dimethoxyphenyl ketone (VI) one at a time and by the same or different aryl radicals. The monomethoxy ketone I was formed by use of 1 mole of α-naphthylmagnesium bromide. Larger amounts of the Grignard reagent produced the di-α-naphthyl ketone VII.



VI VII

Condensation of duryl 6-methoxy-2-(α-naphthyl)-phenyl ketone with phenylmagnesium bromide gave duryl 2-(α-naphthyl)-6-phenylphenyl ketone.

Experimental[4]

Duryl 2,6-Di-(α-naphthyl)-phenyl Ketone (VII).—A solution of 3 g. (0.010 mole) of duryl 2,6-dimethoxyphenyl ketone[5] in 40 ml. of dry benzene was added in a 5-min. interval to a solution of a Grignard reagent made from 8.28 g. (0.04 mole) of α-bromonaphthalene, 0.96 g. (0.04 g. atom) of magnesium and 40 ml. of anhydrous ether. After the mixture had been heated for 8 hr., 100 ml. of a saturated solution of ammonium chloride was added. The crude duryl 2,6-di-(α-naphthyl)-phenyl ketone (3.8 g.) was a slightly yellow solid, m.p. 215–221°. It was washed with ethanol to remove naphthalene and subjected to chromatography. Recrystallization from a chloroform–benzene–ethanol solution followed by sublimation at 0.01 mm. at 224–234° gave the pure ketone, m.p. 232.5–234°. The infrared spectrum[6] has bands at 1666 cm.$^{-1}$, attributed to a conjugated hindered carbonyl group, at 779 and 800 cm.$^{-1}$, attributed to 1,2-disubstitution and 1,2,3-trisubstitution, resepctively, of the benzene ring.

Anal.[7] Calcd. for $C_{37}H_{30}O$: C, 90.57; H, 6.16. Found: C, 90.50; H, 6.31.

Duryl 4-Methoxy-2-(α-naphthyl)-phenyl Ketone.—By a procedure similar to the foregoing, equimolecular amounts of α-naphthylmagnesium bromide and duryl 2,4-dimethoxyphenyl ketone[2] were heated together in a benzene–ether solution for 12 hr. The product, a brown gum, was dissolved in *n*-pentane, and the solution allowed to stand in the refrigerator a month. The methoxy ketone formed light tan crystals (2.035 g.), m.p. 102–108°. Recrystallization from petroleum ether (b.p. 60–90°) gave 2 g. (38%) of colorless crystals, m.p. 152–152.5°. The infrared spectrum has bands at 1665 cm.$^{-1}$ (with a shoulder at 1655 cm.$^{-1}$), corresponding to a conjugated hindered aromatic ketone group, at 1250 cm.$^{-1}$ (with a shoulder at 1240 cm.$^{-1}$), attributable to a methoxyl group and at 810 and 775 cm.$^{-1}$, attributable, respectively, to 1,2,4- and 1,2,3-substitution in the benzene ring.

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64. Found: C, 85.24; H, 6.59.

This compound was made also by condensing anisyl duryl ketone with α-naphthylmagnesium bromide and subjecting the product, presumably a dihydrobenzenoid compound, to dehydrogenation with 30% palladium-on-carbon.

Duryl 6-Methoxy-2-(α-naphthyl)-phenyl Ketone (I).—A solution of α-naphthylmagnesium bromide, made from 0.15 mole of α-bromonaphthalene, was added, over a 0.5-hr. period and at the reflux temperature, to a solution of 4.41 g. (0.15 mole) of duryl 2,6-dimethoxyphenyl ketone in 50 ml. of benzene. The reaction mixture was stirred during the addition and for 8 hr. afterward, being kept at the reflux temperature by heating. The product, isolated by conventional procedures, was a heavy tan oil which crystallized when absolute ethanol was added. Recrystallization from ether–methanol gave 2.23 g. (50%) of the ketone in the form of colorless needles, m.p. 147–148°. The recovered dimethoxy ketone amounted to 15.8%. The infrared spectrum has bands at 1675 cm.$^{-1}$ (with a shoulder at 1635 cm.$^{-1}$) attributed to a hindered aromatic ketone group; at 1265 cm.$^{-1}$, for a methoxy group; and at 800, 765 and 750 cm.$^{-1}$, attributed to various types of aromatic substitution.

Anal. Calcd. for $C_{28}H_{26}O_2$: C, 85.24; H, 6.64. Found: C, 85.44; H, 6.64.

Duryl 2-(α-Naphthyl)-6-phenylphenyl Ketone.—To a solution of Grignard reagent prepared from 1.92 g. (0.0122 mole) of bromobenzene, 0.30 g. (0.0122 g. atom) of magnesium and 25 ml. of ether was added rapidly, with stirring and under reflux, a solution of 1.31 g. (0.0033 mole) of duryl 6-methoxy-2-(α-naphthyl)-phenyl ketone in 40 ml. of dry benzene. A purple suspension formed which after a few hours developed a dark blue color. The ketone, isolated by conventional procedures, was heated to cause the biphenyl to sublime and recrystallized repeatedly from a chloroform–benzene–ethanol mixture. It formed colorless needles (1.195 g., 82.2%), m.p. 181.5–182.5°. The infrared spectrum has bands attributable to a conjugated hindered aromatic carbonyl group (1665 cm.$^{-1}$), to two kinds of vicinal trisubstitution (795 and 770 cm.$^{-1}$) and to monosubstitution (685 and 755 cm.$^{-1}$).

Anal. Calcd. for $C_{33}H_{28}O$: C, 89.96; H, 6.41. Found: C, 89.94; H, 6.32.

Cleavage and Cyclization of Duryl 6-Methoxy-2-(α-naphthyl)-phenyl Ketone (I).—A mixture of 1 g. of the ketone and 25 ml. of polyphosphoric acid[8] was heated gradually to 60° and maintained in the range 60–70° for 4 hr. The red reaction mixture was poured on crushed ice, and concentrated sodium hydroxide solution was added until the mixture was neutral to litmus. The yellow suspension was dissolved in chloroform, and the solution dried over sodium sulfate. Removal of the solvent under diminished pressure left 0.8 g. of crude brown gum. Chromatographic separation on 50 g. of alumina with ether–benzene as the eluent gave three isomeric ketones.

10-Methoxy-7H-benzo[c]fluoren-7-one (IV) crystallized from benzene as golden yellow needles (0.32 g., 48.5%), m.p. 161–161.5°. Bands appear in the infrared spectrum at 1715 cm.$^{-1}$, attributed to a conjugated aromatic ketone group in a five-membered ring; at 1625 cm.$^{-1}$, attributed to a condensed aromatic ring system; at 1600 cm.$^{-1}$, attributed to the C–H stretching on the aromatic ring; and at 1245 cm.$^{-1}$, attributed to a methoxyl group. Bands corresponding to aromatic substitution occur at 775, 740 and 715 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.00; H, 4.68.

The oxime crystallized from absolute ethanol as fine yellow needles which melt at 235–235.5°. The infrared spectrum corresponds to expectations based on the oxime structure.

Anal. Calcd. for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found C, 78.36; H, 4.82; N, 4.95.

10-Hydroxy-7H-benzo[c]fluoren-7-one was made by heating 0.2 g. of the corresponding methoxy compound with 2 ml. of 47% hydriodic acid and 4 ml. of glacial acetic acid on a steam-bath for 18 hr. When recrystallized from isoamyl alcohol, the phenol formed red crystals which decomposed at 275–280°. The infrared spectrum has a broad band (3400–3100 cm.$^{-1}$) and one at 1260 cm.$^{-1}$, attributable to a

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(4) All melting points are corrected.

(5) R. C. Fuson and R. Tull, This Journal, 71, 2543 (1949).

(6) The infrared spectra were determined by Mr. James Brader, Mr. Paul E. McMahon and Miss Mary DeMott.

(7) The microanalyses were performed by Mr. Josef Nemeth, Miss Claire Higham and Miss Jane Liu.

(8) The polyphosphoric acid was obtained from the Victor Chemical Works and was designated as having an ortho equivalent of 115%.

phenolic hydroxyl group and a split band (1682 cm.$^{-1}$), attributable to a conjugated aromatic ketone group. Substitution bands appear at 850, 765, 750 and 705 cm.$^{-1}$. This compound differs from the chelated hydroxy ketones in being readily soluble in base and in failing to yield a copper chelate derivative.

Anal. Calcd. for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09. Found: C, 82.61; H, 4.15.

8-Methoxy-7H-benzo[c]fluoren-7-one (II) was obtained in a yield of 28.8% (0.19 g.). It crystallized from benzene as yellow needles, m.p. 168.5–169°. The infrared spectrum shows bands at 1710 cm.$^{-1}$ (with a small shoulder at 173 cm.$^{-1}$), corresponding to a conjugated aromatic ketone group in a five-membered ring and at 1265 cm.$^{-1}$, corresponding to a methoxyl group. Substitution bands for the benzene ring appear at 800, 740 and 675 cm.$^{-1}$.

Anal. Calcd. for $C_{88}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.00; H, 4.58.

The oxime separated from absolute ethanol as fine yellow needles, m.p. 253.5–254.5°. The infrared spectrum corresponds to the structure assigned.

Anal. Calcd. for $C_{88}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.29; H, 4.75; N, 5.10.

A solution of 0.13 g. of the 8-methoxyfluorenone II, 1 ml. of 47% hydriodic acid and 2 ml. of glacial acetic acid was heated on a steam-cone for 8 hr. The crude **8-hydroxy-7H-benzo[c]fluorenone** was isolated as the copper chelate derivative from which it was recovered by treatment with dilute hydrochloric acid. The infrared spectrum possesses bands at 3350 and 1245 cm.$^{-1}$, attributable to a hydroxyl group and at 1685 cm.$^{-1}$, corresponding to a conjugated chelated ketone group in a five-membered ring.

Anal. Calcd. for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09. Found: C, 82.67; H, 4.01.

8-Methoxy-7H-benz[d,e]anthracen-7-one (III) crystallized from benzene as chartruese needles (0.112 g., 16.9%), m.p. 160.5–161°. The infrared spectrum has bands at 1660° cm.$^{-1}$, attributed to a conjugated aromatic ketone group in a six-membered ring; at 1620 (a small shoulder), attributed to the condensed aromatic ring system; at 1600 cm.$^{-1}$, attributed to the C–H stretching on an aromatic ring; and at 1267 cm.$^{-1}$, attributed to a methoxyl group. Substitution bands appear at 800, 762 and 745 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.86; H, 4.77.

A solution of 0.1 g. of 8-methoxy-7*H*-benz[d,e]anthracen-7-one (III), 1 ml. of 47% hydriodic acid and 3 ml. of glacial acetic acid was heated on a steam-cone for 18 hr. The solution was poured into cold water, and the orange **8-hydroxy-7H-benz[d,e]anthracen-7-one** was recrystallized from isoamyl alcohol. It formed orange-red needles (0.0812 g., 85.7%), m.p. 190.5–191°. The melting point reported in the literature[9] is 187.5–188°. The infrared spectrum has a broad band (from 3032 to 3030 cm.$^{-1}$), attributable to a hydroxyl group that is internally hydrogen bonded and one at 1630 cm.$^{-1}$, attributable to a conjugated aromatic ketone which is strongly hydrogen bonded. Other bands appear at 1250 cm.$^{-1}$, attributable to a phenolic hydroxyl group and at 800 and 750 cm.$^{-1}$, attributed to two kinds of vicinal trisubstitution.

Anal. Calcd. for $C_{17}H_{10}O_2$: C, 82.91; H, 4.09. Found: C, 82.79; H, 4.33.

When treated with cupric acetate in acetone the phenolic ketone formed a chelate derivative which could be reconverted to the hydroxy ketone with dilute hydrochloric acid.

10-Methoxy-7H-benz[d,e]anthracen-7-one (V).—Two grams of duryl 4-methoxy-2-(α-naphthyl)-phenyl ketone was heated with 25 ml. of polyphosphoric acid for 10.5 hr. at 90–100°. Durene was deposited on the sides of the vessel as the reaction progressed. The 8-methoxyfluorenone II, the 10-methoxyfluorenone IV and the 8-methoxybenzanthrone III were isolated in yields of 10.2, 36.6 and 26.6%, respectively.

A fourth isomer, 10-methoxy-7*H*-benz[d,e]anthracen-7-one (V), was isolated in 7.3% yield. It crystallized from chloroform–ethanol as chartruese needles, m.p. 163–163.5°. The infrared spectrum has bands at 1648 cm.$^{-1}$, attributed to a conjugated aromatic ketone group in a six-membered ring; at 1630 cm.$^{-1}$ (a shoulder), attributed to a condensed aromatic ring system; at 1600 cm.$^{-1}$ (strong), attributed to C–H stretching on a benzene ring; at 1250 cm.$^{-1}$ attributed to a methoxyl group; at 843 cm.$^{-1}$, attributed to 1,2,4-substitution on a benzene ring; and at 770 cm.$^{-1}$, attributed to three adjacent hydrogen atoms on a naphthalene ring.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.73; H, 4.64.

The ketone V was made in 60% yield by heating 8-methoxy-7*H*-benzo[c]fluoren-7-one (II) for 24 hr. with polyphosphoric acid at 120–125°. The 10-methoxy-7*H*-benzo[c]-fluoren-7-one (IV) under similar conditions gave the ketone V in a yield of 50%.

A fourth method of synthesis of the 10-methoxybenzanthrone V consisted in heating 1 g. of duryl 4-methoxy-2-(α-naphthyl)-phenyl ketone with 25 ml. of polyphosphoric acid 0.104 g. (16.1%) of 10-methoxy-7*H*-benz[c]fluoren-7-one and 0.065 g. (10%) of 10-methoxy-7*H*-benz[d, e]anthracen-7-one. The latter crystallized from chloroform–ethanol as chartreuse needles, m.p. 163–163.5°. Hydrolysis of the 10-methoxybenzanthrone V gave a compound which was easily soluble in base and which failed to yield a copper chelate derivative.

Treatment of duryl 6-methoxy-2-(α-naphthyl)-phenyl ketone (2 g.) with 25 ml. of polyphosphoric acid, with efficient stirring, for 10 hr. at room temperature gave 0.1723 g. (13.3%) of 8-methoxy-7*H*-benzo[c]fluoren-7-one (II) and 0.0999 g. (7.6%) of 8-methoxy-7*H*-benz[d,e]anthracen-7-one (III). A mixture of 1 g. of the ketone I and 25 ml. of polyphosphoric acid was heated at 120–125° for 20 hr. and then at 170–175° for 2 hr. The crude product, subjected to chromatography, gave 0.1072 g. of 10-methoxy-7*H*-benz-[d,e]anthracen-7-one and 0.062 g. of 10-methoxy-7*H*-benz-[d,e]anthracen-7-one.

URBANA, ILL.

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[9] H. Waldmann, *Chem. Ber.*, **83**, 171 (1950).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Derivatives of 8-Methylhexahydrofluorenone[1a]

BY HERBERT O. HOUSE, VASKEN PARAGAMIAN AND DAVID J. WLUKA[1b]

RECEIVED SEPTEMBER 30, 1959

8-Methyl-*cis*-hexahydrofluorenone and 8-methyl-2,3,4,4a-tetrahydrofluorenone have been prepared and alkylated with ethyl bromoacetate. Comparable alkylation of *cis*-hexahydrofluorene and 2,3,4,4a-tetrahydrofluorenone are described. The structure and stereochemistry of the various alkylation products have been determined.

Our previous studies of 1,1a,2,3,4,4a-hexahydrofluoren-9-one[2] had indicated a suitable synthetic route to the corresponding 8-methyl derivative I which was of interest as an intermediate for the synthesis of certain degradation products of gibberellic acid.[3] In the present work the desired

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(1) (a) This research has been supported in part by National Science Foundation Grant No. G9486; (b) Alfred P. Sloan Postdoctoral Fellow.

(2) H. O. House, V. Paragamian, R. S. Ro and D. J. Wluka, THIS JOURNAL, **82**, 1457 (1960).

(3) For leading references see B. E. Cross, J. F. Grove, J. MacMillan and T. P. C. Mulholland, *Proc. Chem. Soc.*, **221** (1958).