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Effects of Alkyl Substituents in the Chromic Acid Oxidation of Tetralins

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The chromic acid oxidation of a series of mono- and polyalkyl-1,2,3,4-tetrahydronaphthalenes was investigated. Preferential oxidation occurs at the benzylic methylene position para to an alkyl substituent in the aromatic ring. An alkyl group ortho to a benzylic methylene position may enhance or retard oxidation at that position, depending upon the degree of steric crowding by the alkyl group. 2-Alkyltetralins also undergo preferential oxidation in that 3-alkyl-1-tetralones predominate in the product mixture.

Chromic acid oxidation of hydrocarbons has been intensively studied. In general, for aliphatic hydrocarbons, the relative rates of oxidation in primary, secondary, and tertiary CH positions are 1:110:7000.[2] Although considerable data exist concerning the oxidation of aromatic–aliphatic systems,[3] very little information is available on oxidation of hydrocarbons containing nonequivalent benzylic positions capable of competing for the oxidizing agent. Linstead[4a] and Ghosal[4b] showed that a pronounced electronic effect is operative in the oxidation of 6-methoxytetralin to 6-methoxy-1-tetralone.

The mechanism of chromic acid oxidation of hydrocarbons has been extensively investigated.[2,3,4b,4c] A current rationalization utilizes an initial hydrogen abstraction to give a resonance hybrid of (a) an alkyl radical–Cr(V) complex and (b) a carbonium ion–Cr(IV) complex.[5,6] Since the rates of oxidation of hydrocarbons have been shown to parallel those for solvolysis of the corresponding tosylates, a carbonium ion intermediate is further implicated.[7a] It has been concluded that steric hindrance is not important in chromic acid oxidation of alkylcyclohexanes.[7b]

This study of the chromic acid oxidation of tetralins was prompted by an earlier observation that some alkyltetralins may be converted to 1-tetralones in high yield with considerable selectivity and thereby provide otherwise less accessible ketones.[8a] We previously utilized chromic acid in the conversion of indans to indanones in high yields.[8b]

The data presented in Table I provide ample evidence that an electronic effect is operative in the oxidation of tetralins substituted with alkyl groups in the aromatic ring. This is apparent from the ratio of product tetralones **3b**:**3c** (1.0:1.3) and **4b**:**4c** (2.7:1.0). Comparison of the latter ratio to those of **7b**:**7c** (2.9:1.0) and **10b**:**10c** (2.4:1.0) shows that the methyl, ethyl, and *tert*-butyl group have about the same electronic effect. The electronic effect responsible for the ratio of products obtained from **3a** and **4a** is manifest throughout the series in Table I. Steric effects result from alkyl groups at the peri position of the aromatic ring or from an alkyl group adjacent to a potential carbonyl site (C-2) in the saturated ring. The latter effect is illustrated by the products from **2a**, **5a**, and **8a** (methyl, ethyl, *tert*-butyl). The most obvious effect, steric and electronic, is shown by the products obtained in the oxidation of **6a** and **9a** compared to the products from **3a** (effects of peri alkyl groups) as well as by a comparison of the oxidation of **12a** and **13a** *vs.* **14a** and **15a** (methyl *vs.* *tert*-butyl groups). The ratio of products **16b**:**16c** (1.0:24) from **16a** suggests that the effects of 2-alkyl and peri alkyl groups are synergistic.

A diminution, owing to steric influence of methyl at C-2, appears in the ratio of products obtained from oxidation of **4a** and **12a**, the ratio decreasing from 2.7:1.0 to 2.0:1.0. Comparison of the ratios of 1-tetralones obtained from **10a**, **14a**, and **15a** indicate a very pronounced alkyl (*tert*-butyl) steric effect at the C-2 position. As expected, this effect decreases in changing from *tert*-butyl to methyl for **4a**, **12a**, and **13a**.

The alkyl groups in the aromatic ring may have a pronounced electronic influence on the ratio of 1-tetralones, as evidenced by comparison of the products from **3a**, **11a**, and **17a**, in which **3c**, **11c**, and **17c** predominate over **3b**, **11b**, and **17b** despite possible steric interference of the methyl group at the peri position. However, this effect is reversed for **6a** and **9a** (as expected) owing to the increased bulk of the ethyl and the *tert*-butyl group, and the ratio becomes 1.2:1.0 (for **6b**:**6c**) and 2.9:1.0 (for **9b**:**9c**) as compared to 1.0:1.3 (for **3b**:**3c**).

The ratio of 1-tetralones formed from tetralins by chromic acid oxidation may become established at either the initial hydrogen abstraction or a subsequent stage during the conversion of alcohol or related species to ketone.[4c] We believe that the former is more likely, since in the oxidation of **15a**, no **15b** is formed. We argue that differences in rate of oxidation of alcohols can have no influence if one of the alcohols is not formed.

The ratios of 1-tetralones presented in Table I were obtained by glc studies.[9a,c] The identification of 1-tetralones responsible for individual peaks was made possible in the case of **5b**:**5c** (1.0:2.1) and **7b**:**7c** (2.9:1.0) through preparative glc separation,[9i] which yielded samples adequate for mass spectrometry but not for other analyses. The isomers **5b** and **5c** were distinguished by comparing relative peak intensity values at *m/e* 174 (M^+) and 146. The relative intensities of these peaks were 5.8 and 100 for **5b**, and 48 and 42 for **5c**, respectively. These peak positions and their relative intensities show that **5b** is capable of γ-hydrogen transfer whereas **5c** does not undergo this mode of fragmentation.[10b] Consequently, **5b** yields the smaller relative amount of M^+ and greater relative intensity at *m/e* 146. It should be noted that the relative intensity values for **8b** and **8c** were 2 and 24 at *m/e* 202 (M^+).

An authentic sample of **7c** was available with which to identify its glc peak. Mass spectrometry of samples of **7b** and **7c** isolated by preparative glc[9i] showed that these 1-tetralones are isomers.

The 1-tetralones from tetralins **12a**, **13a**, **14a**, and **17a** could not be separated. However, their identities and product ratios were readily established by ratios of pmr peaks observed for alkyl substituents at C-2 and C-3. It should be noted that the ratios obtained through glc studies agreed with those obtained from pmr spectra.

All of the remaining 1-tetralones in Table I were isolated in adequate quantities as pure compounds from reaction mixtures, and identification of compounds and determination of product ratios were precise and conclusive.

Experimental Section[9]

Preparation of Tetralins. The tetralins used in this study were obtained either from our API hydrocarbon synthesis project or as a gift.[10a] These tetralins were synthesized as outlined below and their purities were established by glc and spectral data.[9]

Tetralins 2a, 4a, 11a, and 16a were prepared *via* a previously described general Friedel-Crafts synthesis[11a] using benzene and methylsuccinic anhydride for **2b**, toluene and succinic anhydride for **4c**, *m*-xylene and succinic anhydride for **11b**, and *p*-xylene and methylsuccinic anhydride for **16b** and **16c**. Hydrogenolysis[11a] was used to convert **2b**, **4c**, **11b**, and **16b** or **16c** to **2a**,[11b] **4a**,[11b] **11a**,[11b] and **16a**,[11a] respectively.

Tetralin 5a was prepared by Pd/C-catalyzed hydrogenation of 2-ethylnaphthalene to a 1:1 mixture of **5a** and **7a**. This mixture was subjected to alkylation[12a] with *tert*-butyl chloride and $AlCl_3$. Distillation afforded a mixture of *tert*-butylated **5a** (52%) from which **5a**[12b] was obtained in 65% yield by de-*tert*-butylation[8a] with $AlCl_3$ in benzene, bp 62–63° (0.4 mm).

Tetralin 6a was prepared by Pd/C-catalyzed hydrogenation of 1-ethylnaphthalene to a mixture (1.0:1.3) of 1-ethyl-1,2,3,4-tetrahydronaphthalene and **6a**. These were separated by distillation[9g] to give pure **6a**,[12c] bp 94° (0.4 mm).

Tetralin 7a[12e] was prepared by hydrogenolysis[12d] of the semicarbazone of 5,6,7,8-tetrahydro-2-acetonaphthone, mp 236°.[12f]

Tetralin 8a was prepared by hydrogenation of 2-*tert*-butylnaphthalene and dealkylation of the resulting mixture of tetralins as previously described.[8a]

Tetralin 9a was prepared as previously described from ethyl 5,6,7,8-tetrahydro-1-naphthoate.[12g]

Tetralin 10a was prepared by *tert*-butylation of tetralin.[12a]

Tetralins 12a, 13a, 14a, and 15a were prepared by Pd/C-catalyzed hydrogenation of the corresponding naphthalenes in acetic acid. The purification of the gift[13a] dimethylnaphthalenes was accomplished *via* their picrates.[13b]

tert-Butylation[12a] of naphthalene provided a mixture of 2,6- and 2,7-di-*tert*-butylnaphthalene, which was separated by a combination of fractional crystallization of the arenes and selective formation of the thiourea clathrate of 2,6-di-*tert*-butylnaphthalene.[14]

Tetralin 17a. Hydrogenolysis[11a] of commercially available **17c** was used to prepare **17a**.

General Procedure for Chromic Acid Oxidations. To a magnetically stirred solution of 0.04 mol of hydrocarbon in 1 l. of acetic acid was added dropwise 170 ml of 10% aqueous CrO_3 acetic acid solution[15] over a period of 30 min. The reaction temperature was maintained between 17 and 21° with an ice bath. The reaction was allowed to proceed to completion (*ca.* 2 hr) as evidenced by glc.[9a] The reaction mixture was then diluted with 6 l. of distilled water and extracted with ether (2 × 1.5 l.). The combined ether extract was washed with water and saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated. The resulting crude products were distilled and analyzed as outlined below.

Yield Maximization of 1-Tetralone (1b) from Tetralin (1a). A series of five experiments in which the molar ratio of CrO_3:**1a** ranged from 7.4:1 to 3.1:1 were carried out to determine optimum conditions. The maximum yield of **1f** (55%) was obtained with the ratio 5:1 as described above. In addition, three experiments varying the volume of acetic acid indicated that dilution over the amount specified in the procedure lowers the yield and allows survival of tetralin.

Tetralone 2b had bp 76–78° (0.3 mm) [lit.[16,17a] bp 127–131° (12 mm)]; ir[9f] (neat) 1681 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 160 (47), 131 (17), 118 (100), 90 (61), 89 (21), 28 (26); pmr[9e] ($CDCl_3$) δ 8.03–7.79 (m, 1, ArH peri to carbonyl), 7.94–6.94 (m, 3, ArH), 3.05–2.72 (m, 2, $ArCH_2$), 2.67–1.29 (m, 3, $ArCH_2CH_2CH$), 1.16 (d, 3, $ArCOCCH_3$).

Tetralone 2c had bp 78° (0.5 mm) [lit.[17d] bp 132° (14 mm)]; mass spectrum (70 eV) *m/e* (rel intensity) 160 (53), 145 (39), 118 (100), 115 (15), 91 (15), 90 (42); pmr[9e] ($CDCl_3$) δ 8.00–7.75 (m, 1, ArH peri to carbonyl), 7.52–6.92 (m, 3, ArH), 2.91–1.79 (envelope, 5, $ArCH_2CHCH_2$), 1.07 (d, 3, $ArCH_2CHCH_3$).

Tetralone 3b had mp 48–50°; mass spectrum (70 eV) *m/e* (rel intensity) 160 (63), 132 (100), 104 (56), 103 (22), 78 (23), 51 (22); pmr[9e] (CCl_4) δ 7.73 (d, 1, ArH peri to carbonyl), 7.33–6.90 (m, 2, ArH), 2.78 (t, 2, $ArCH_2$), 2.27 (s, 3, $ArCH_3$), 2.60–1.84 (m, 7, $ArCOCH_2CH_2$ and $ArCH_3$).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.58; H, 7.59.

Tetralone 3b had mp 48–50°; mass spectrum (70 eV) *m/e* (rel *m/e* (rel intensity) 160 (48), 132 (100), 104 (35), 103 (17), 78 (19), 51 (16); pmr[9e] (CCl_4) δ 7.30–6.76 (m, 3, ArH), 2.86 (t, 2, $ArCH_2$), 2.56 (s, 3, $ArCH_3$), 2.72–2.42 (m, 5, $ArCOCH_2$ and $ArCH_3$), 1.98 (m, 2, $ArCOCH_2CH_2$).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.39; H, 7.55.

Tetralone 4b had bp 75–77° (0.2 mm); mass spectrum (70 eV) *m/e* (rel intensity) 160 (51), 145 (18), 132 (100), 104 (40), 78 (19), 51 (18); pmr[9e] (CCl_4) δ 7.76 (d, 1, ArH peri to carbonyl), 7.06–6.84 (m, 2, ArH), 2.81 (t, 2, $ArCH_2$), 2.19 (s, 3, $ArCH_3$), 2.56–1.86 (m, 4, $ArCOCH_2CH_2$).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.60; H, 7.55.

Tetralone 4c[17a,b] had mp 32–34° (lit.[17a,b] mp 35–36°); ir (neat)[9f] 1680 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 160 (73), 132 (100), 104 (75), 103 (23), 28 (21); pmr[9e] (CCl_4) δ 7.67 (s, 1, ArH peri to carbonyl) 7.08 (m, 2, ArH), 2.83 (t, 2, $ArCH_2$), 2.55–1.91 (m, 4, $ArCH_2CH_2CH_2$), 2.30 (s, 3, $ArCH_3$).

Tetralones 5b and 5c. These 1-tetralones were separated by glc,[9i] the minor component, **5b**, being eluted first, mass spectrum (70 eV) *m/e* (rel intensity) 174 (5.8), 146 (100), 145 (18), 118 (41), 115 (15), 90 (36). The major component, **5c**, had mass spectrum (70 eV) *m/e* (rel intensity) 174 (48), 146 (42), 145 (36), 118 (100), 115 (29), 90 (51). We were unable to obtain adequate samples for other analyses.

Tetralone 6b had bp 82° (0.1 mm); ir[9f] (neat) 1680 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 174 (89), 159 (32), 146 (100), 118 (56), 117 (62), 115 (39); pmr[9e] (CCl_4) δ 7.98–7.79 (m, 1, ArH peri to carbonyl), 7.38–7.08 (m, 2, ArH), 2.08–2.45 (overlapping m, 4, $ArCH_2CH_2CH_2$), 2.60 (q, 2, $ArCH_2CH_3$, $J = 8$ Hz), 2.36–1.98 (m, 2, $ArCH_2CH_2$), 1.24 (t, 3, $ArCH_2CH_3$, $J = 8$ Hz).

Table I
Chromic Acid Oxidation Products of Tetralins

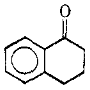
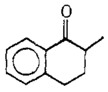
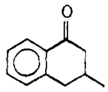
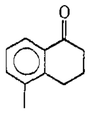
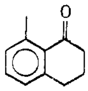
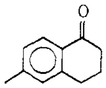
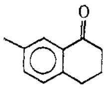
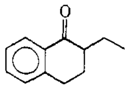
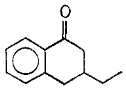
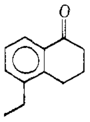
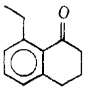
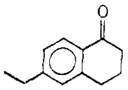
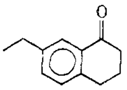
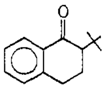
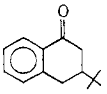
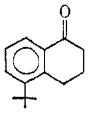
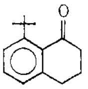
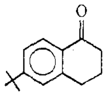
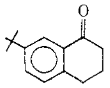
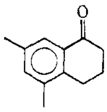
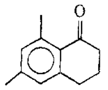
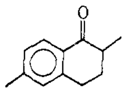
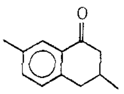
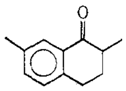
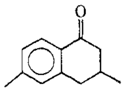
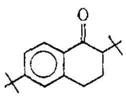
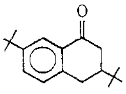
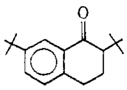
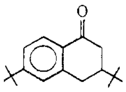
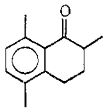
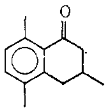
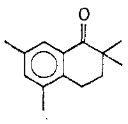
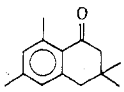
Tetralins[a]	1-Tetralones produced				Ratio b:c	Yield of combined 1-tetralones, %
1a	1b					55
2a	2b		2c		1.0:2.1[b,c]	72
3a	3b		3c		1.0:1.3[b]	60
4a	4b		4c		2.7:1.0[b,c]	72
5a	5b		5c		1.0:2.1[b]	83
6a	6b		6c		1.2:1.0[b,d,e]	71
7a	7b		7c		2.9:1.0[b,c,e]	63
8a	8b		8c		1.0:5.8[b,c]	70
9a	9b		9c		2.9:1.0[b]	62
10a	10b		10c		2.4:1.0[b]	58
11a	11b		11c		1.0:4.4[c,f]	62
12a	12b		12c		2.0:1.0[d,f]	65
13a	13b		13c		1.0:8.0[d,f]	66
14a	14b		14c		1.0:3.0[d,f]	75
15a	15b		15c		0.0:1.0[d,f]	71
16a	16b		16c		1.0:24[c,f]	74
17a	17b		17c		1.0:6.1[c,d,f]	57

Table I (*footnotes*)

[a] Corresponding to 1-tetralones of this table. [b] Ratio determined and separation achieved by glc.[9a,b,c,h,i] [c] Authentic samples of **2b**, **2c**, **4c**, **7c**, **8b**, **8c**, **11b**, **11c**, **16b**, **16c**, and **17c** were available (*cf.* Experimental Section). [d] Ratio determined by pmr analysis based upon the differences in chemical shifts produced by alkyl substituents at C-2 and C-3. Pmr spectra of **8b** and **8c** show that the C-2 alkyl is deshielded relative to the C-3 alkyl group (*cf.* pmr spectra of **2b** and **2c** in Experimental Section).[8a] [e] Tetralins **6a** and **7a** were oxidized in part to the acetyl derivatives, which comprised 3 and 7% of the respective product mixtures. [f] Ratio verified by glc analysis.[9a,c]

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82,60; H, 8.09.

The red-orange 2,4-DNP melted at 188–190°.

Anal. Calcd for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12. Found: C, 60.93; H, 5.24.

Tetralone 6c had bp 85° (0.2 mm); ir[9f] (neat) 1680 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 174 (50), 146 (100), 117 (33), 115 (21), 91 (14), 39 (13); pmr[9e] (CCl_4) δ 7.34–6.91 (m, 3, ArH), 3.16–2.79 (overlapping m, 2, Ar$\mathbf{CH_2}$), 3.01 (q, 2, Ar$\mathbf{CH_2}$$CH_3$, J = 7 Hz), 2.67–2.47 (m, 2, ArCO$\mathbf{CH_2}$), 2.20–1.90 (m, 2, ArCH$_2$$\mathbf{CH_2}$), 1.17 (t, 3, ArCH$_2$$\mathbf{CH_3}$, J = 7 Hz).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.50; H, 8.05.

The dark red 2,4-DNP melted at 211–213°.

Anal. Calcd for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12. Found: C, 60.80; H, 5.24

Tetralones 7b and 7c. These 1-tetralones showed the glc[9c,i] ratio 2.9:1.0 for **7b:7c,** and they were separated[9i] in quantity adequate for mass spectrometry. The isomer **7c** preceded **7b** on the glc column.[9c,i] Isomer **7b** had mass spectrum (70 eV) *m/e* (rel intensity) 174 (46), 159 (19), 146 (100), 118 (19), 117 (19), 115 (17). Isomer **7c** had mass spectrum (70 eV) *m/e* (rel intensity) 174 (74), 159 (35), 146 (100), 118 (66), 117 (31), 115 (27). The glc[9c] of this mixture showed **7c**:**7b**:5,6,7,8-tetrahydro-2-acetonaphthone (**18**)[18] in the ratio 2.6:7.6:1.0 and that order of emergence from the column. Although **18** was present in the sample of **7b** used for mass spectral measurement and contributed to the spectrum, this contribution did not interfer with identification of **7b**. The mass spectrum of **7c** agreed with that of a commercial sample.[19]

Tetralones 8b and 8c. *Cf.* ref 8a.

Tetralone 9b had bp 96–98° (0.4 mm); ir[9f] (CCl_4) 1675 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 202, M$^+$ (28), 188 (15), 187 (100), 117 (13), 115 (19), 41 (11); pmr[9e] (CCl_4) δ 7.90, 7.82 (d of d, 1, ArH peri to carbonyl), 7.50, 7.42 (d of d, 1, ArH), 7.13 (t, 1, ArH), 3.14 (t, 2, Ar$\mathbf{CH_2}$), 2.54 (t, 2, ArCH$_2$CH$_2$$\mathbf{CH_2}$), 2.06 (p, 2, ArCH$_2$$\mathbf{CH_2}$), 1.42 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.07; H, 8.87.

Tetralone 9c had bp 93–95° (0.2 mm); ir[9f] (CCl_4) 1700 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 202, M$^+$ (85), 187 (94), 174 (100), 159 (96), 115 (49), 43 (35); pmr[9e] (CCl_4) δ 7.40–6.86 (m, 3, ArH), 2.84–2.54 (overlapping m, 4, Ar$\mathbf{CH_2}$CH$_2$$\mathbf{CH_2}$), 2.17–1.90 (p, 2, ArCH$_2$$\mathbf{CH_2}$), 1.38 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.03; H, 9.09.

Tetralone 10b had bp 102° (0.2 mm); ir[9f] (neat) 1680 cm^{-1} (C=O); mass spectrum (70 eV) *m/e* (rel intensity) 202 (24), 187 (100), 131 (18), 115 (13), 91 (9), 41 (11); pmr[9e] (CCl_4) δ 7.83 (d, 1, ArH peri to carbonyl), 7.30–7.10 (m, 2, ArH), 2.88 (t, 2, Ar$\mathbf{CH_2}$), 2.49 (t, 2, ArCO$\mathbf{CH_2}$), 2.04 (p, 2, ArCH$_2$$\mathbf{CH_2}$), 1.30 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.99; H, 8.94.

The red 2,4-DNP melted at 241–243°.

Anal. Calcd for $C_{20}H_{22}N_4O_4$: C, 62.81; H, 5.80. Found: C, 62.74; H, 5.85.

Tetralone 10c had mp 99–100° (lit.[17c] mp 101–102.5°); mass spectrum (70 eV) *m/e* (rel intensity) 202 (19), 188 (15), 187 (100), 156 (6), 131 (11), 115 (9); pmr[9e] (CCl_4) δ 7.94 (d, 1, ArH peri to carbonyl), 7.46–6.98 (m, 2, ArH), 2.88 (t, 2, Ar$\mathbf{CH_2}$), 2.53 (t, 2, ArCO$\mathbf{CH_2}$), 2.08 (p, 2, ArCH$_2$$\mathbf{CH_2}$), 1.33 (s, 9, *tert*-butyl).

Tetralones 11b and 11c. *Cf.* ref 11a.

Tetralones 12b and 12c had bp of 2.1:1.0 mixture 83–85° (0.2 mm). The ratio of isomers in this mixture was established by glc[9a] and by the ratio of two pmr[9e] (CCl_4) doublets centered at δ 1.14 and 1.04, respectively: mass spectrum of **9b:9c** (2.1:1.0) (70 eV) *m/e* (rel intensity) parent ion 174, M$^+$ (50).

Tetralones 13b and 13c had bp of 1.0:8.0 mixture 93–95° (0.3 mm). The ratio of isomers in this mixture was established by glc[9a] and by the ratio or two pmr[9e] (CCl_4) doublets centered at δ 1.13 and 1.00: mass spectrum of **10b:10c** (1.0:8.0) (70 eV) *m/e* (rel intensity) parent ion 174, M$^+$ (49).

Tetralones 14b and 14c had bp of 1.0:3.0 mixture 128–131° (0.2 mm). *Cf.* ref 8a.

Tetralones 15c. *Cf.* ref 8a.

Tetralones 16b and 16c. *Cf.* ref 11a.

Tetralones 17b and 17c had bp of 1.0:6.1 mixture 96–99° (0.3 mm). The ratio of isomers in this mixture was established by glc[9c] and by the ratio of two pmr[9e] (CCl_4) singlets at δ 1.09 and 0.98: mass spectrum of **14b:14c** (1.0:6.1) (70 eV) *m/e* (rel intensity) parent ion 202, M$^+$ (36). Tetralone **17c** was obtained from Aldrich Chemical Co.

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Registry No.—**1a**, 119-64-2; **2a**, 3877-19-8; **2b**, 1590-08-5; **2c**, 14944-23-1; **3a**, 2809-64-5; **3b**, 6939-35-1; **3c**, 51015-28-2; **4a**, 1680-51-9; **4b**, 51015-29-3; **4c**, 22009-37-6; **5a**, 32367-54-7; **5b**, 21568-62-7; **5c**, 51015-30-6; **6a**, 42775-75-7; **6b**, 51015-31-7; **6b** 2,4-DNP, 51015-32-8; **6c**, 51015-33-9; **6c** 2,4-DNP, 51015-34-0; **7a**, 22531-20-0; **7b**, 22577-91-9; **7c**, 22531-06-2; **8a**, 42044-22-4; **9a**, 42044-24-6; **9b**, 51015-35-1; **9c**, 51015-36-2; **10a**, 42044-26-8; **10b**, 51015-37-3; **10b** 2,4-DNP, 51015-38-4; **10c**, 22583-68-2; **11a**, 21693-54-9; **12a**, 7524-63-2; **12b**, 51015-39-5; **12c**, 51015-40-8; **13a**, 13065-07-1; **13b**, 51015-41-9; **13c**, 51015-42-0; **14a**, 42981-76-0; **15a**, 43012-91-5; **16a**, 30316-17-7; **17a**, 23342-25-8; **17b**, 51015-43-1; **17c**, 5409-55-2; CrO_3, 1333-82-0.

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(1) (a) American Petroleum Institute Graduate Research Assistant, 1969–1973; Continental Oil Company Fellow, 1973; (b) National Science Foundation, Science Faculty Fellowship, 1970–1971, Grant 60052; API GRA 1971–1972.

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(9) (a) 10 ft × 0.25 in. 25% Carbowax 20M on acid-washed Chromosorb W. (b) Preparative separations were made on a Carbowax 20M column, 10 ft × 0.375 in. (c) 11 ft × 0.25 in. 5% Silicone rubber UC W-98 on acid-washed, DMCS-treated Chromosorb W. (d) Petroleum ether, bp 60–68°. (e) Pmr spectra were determined on Varian HA-100 and A-60 spectrometers; mass spectra were obtained with a Consolidated Electrodynamics Corp. Model 21-103C mass spectrometer. (f) Ir spectra were obtained with a Beckman IR5A spectrometer; (g) Nester/Faust autoannular spinning band distillation system, Model NFA-200. (h) Ratios of 1-tetralone products were determined by triangulation of peaks in glc tracings. (i) 10 ft × 0.25 in. 15% FFAP on Anachrom ABS 70–80 mesh.

(10) (a) We thank Ashland Oil and Chemical Co. for hydrocarbon sample from which **3a** was obtained by preparative glc;[9b] (b) M. C. Hamming and N. G. Foster, "Interpretation of Mass Spectra of Organic Compounds," Academic Press, New York, N. Y., 1972.

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(13) (a) We thank Drs. J. A. Hedge, Sun Oil Co., and E. K. Fields, Amoco Chemicals Corp., for generous samples of 2,6- and 2,7-dimethylnaphthalenes; (b) E. J. Eisenbraun, T. E. Webb, J. W. Burnham, and L. E. Harris, *Org. Prep. Proced. Int.*, **3**, 249 (1971).

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(18) An authentic sample of **18** was available.

(19) Eastman Organic Chemicals No. 7381.

Formation and Characterization of 1,2-Diiodoferrocene and Related Derivatives[1]

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Iodoferrocene was mercurated and the 2-mercurated isomer, isolated as bis(2-iodoferrocenyl)mercury, was chemically characterized by conversion to the intramolecular anhydride, 1,2-ferrocenedicarboxylic anhydride. Iodination of bis(2-iodoferrocenyl)mercury gave 1,2-diiodoferrocene in essentially quantitative yield. Treatment of bis(2-iodoferrocenyl)mercury with deuterium chloride gave iodoferrocene-2-d_1. Mercuration of ferrocene was shown to produce 1,2-bischloromercuriferrocene in addition to the two major products, chloromercuriferrocene and 1,1′-bischloromercuriferrocene.

Although many 1,2-disubstituted ferrocenes are now known,[2] only 1,2-dichloroferrocene has been synthesized and reported in the 1,2-dihaloferrocene series.[3] This synthesis was accomplished by metalating chloroferrocene with *n*-butyllithium and then treating the intermediate with tri-*n*-butyl borate at −70°. After hydrolysis, the resulting boronic acid upon treatment with cupric chloride yielded 1,2-dichloroferrocene. Hedberg and Rosenberg[4] have very recently also reported that the lithiation of chloroferrocene, followed by reaction with hexachloroethane, affords 1,2-dichloroferrocene. Earlier, Huffman, Keith, and Ashbury[5] showed that lithiation of chloroferrocene followed by carbonation gave, by analogy with similar known substitutions of halobenzenes, 2-chloroferrocenecarboxylic acid. Unequivocal demonstration that the lithiation of chloroferrocene occurs in the 2 position has been recently provided by the studies of Slocum, *et al.*[6] On the other hand, bromoferrocene[7] and iodoferrocene[8] cannot be metalated as can chloroferrocene, since treatment with *n*-butyllithium gives the halogen–lithium interchange product, ferrocenyllithium.

Nefedov[9] has reported that the mercuration of haloferrocenes produces 1,3- and 1,1′-disubstituted ferrocenes. For example, mercuration of iodoferrocene (1) was indicated to produce 3-chloromercuriiodoferrocene (2) and 1-chloromercuri-1′-iodoferrocene (3). Iodination of the mercurials 2 and 3 then presumably produced 1,3-diiodoferrocene and 1,1′-diiodoferrocene, respectively.

A number of investigators[10-12] have shown that the mercuration of ferrocene produces chloromercuriferrocene, 1,1′-bischloromercuriferrocene, and other unidentified mercurials. Nefedov[9,13] suggested that the mercuration of ferrocene with mercuric acetate followed by treatment with potassium bromide produced, besides bromomercuriferrocene and 1,1′-bisbromomercuriferrocene, 1,3-bisbromomercuriferrocene.

Results and Discussion

In an attempt to prepare 1,3-diiodoferrocene for some additional studies, Nefedov's work was repeated. However, his structural assignment has been found to be in error. Contrary to a previous report[14] that 2-chloromercuriiodobenzene symmetrized on alumina, Nefedov assigned the mercuration product that symmetrized on chromatography on alumina as 3-chloromercuriiodoferrocene (2).[9,15] Nefedov then iodinated the symmetrized product and obtained a material which he assigned as 1,3-diiodoferrocene. The structure of the product was supposedly proved by heating it with cuprous iodide and phenylmagnesium iodide to yield 1,3-diphenylferrocene having a melting point of 107° and exhibiting an infrared absorption at 905 cm^{-1}. The melting point of this derived diphenylferrocene without a mixture melting point determination with authentic 1,3-diphenylferrocene proves nothing, since 1,2-diphenylferrocene melts at 109–110° [18] and 1,3-diphenylferrocene melts at 107°.[18] Moreover, the fact that the infrared spectrum of the product shows a band at 905 cm^{-1} as does 1,1′,3,3′-tetraphenylferrocene[19] does not in itself prove a 1,3 disposition without a comparison of additional bands.[18]

In our work, iodoferrocene (1) was mercurated in the manner of Nefedov and worked up similarly, except that the alumina for chromatography was of activity 3.[20] As the *x*-chloromercuriiodoferrocenes (2–4) passed through the column, 2-chloromercuriiodoferrocene (4) selectively symmetrized and was eluted as a pale yellow solution of bis(2-iodoferrocenyl)mercury (5, 6).

The melting point of the product obtained was the same as that reported by Nefedov.[9] The calculated nmr spectra (see Table I for chemical shift values of several monosubstituted ferrocenes) for bis(2-iodoferrocenyl)mercury and for bis(3-iodoferrocenyl)mercury indicate that these two possible homoannular positional isomers cannot be readily distinguished by nmr spectroscopy (see Table II). Further, the triplet resonance observed in the spectra of the product falls essentially under the two singlets, and hence no coupling constant values can be obtained which could be used in structural assignments. However, since bis(2-iodoferrocenyl)mercury isolated in this work has been shown to consist of a single positional isomer (*vide infra*), the two singlets observed therefore must represent the two possible stereoisomers—meso compound 6 and *dl* com-