3.07 (broad signals, 1 H each, bridgehead protons), 2.9–1.5 (complex pattern, 10 H, methylene protons), and 1.73 and 1.66 (singlets, 3 H each, isopropylidene methyl groups). This ketone was characterized as its semicarbazone, mp 205–207° dec (from methanol).

Anal. Calcd for $C_{13}H_{21}N_3O$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.46; H, 8.98; N, 17.74.

4,4-Dimethyl-4,6,7,7a-tetrahydroindan-5-one (7).—Treatment of 10.0 g of 3,6,7,7a-tetrahydroindan-5-one[22] according to the procedure of Marshall, Andersen, and Johnson[23] gave 5.43 g of a colorless liquid, bp 52–55° (0.5 mm), which contained approximately 77% **7**. Purification was achieved *via* its semicarbazone, mp 209–210.5° dec (from methanol), to give **7**: bp 55.5–56.5° (0.6 mm); n^{25}D 1.4935; $\lambda_{max}^{isooctane}$ 289 mμ (ε 90), 298 (95), 308 (85), and 319 (45); $\delta_{TMS}^{CCl_4}$ 5.34 (doublet of doublets, $J_{3,2}$ = 2 Hz, $J_{3,7a}$ = 2 Hz, 1 H, vinyl proton), 3.0–1.3 (complex pattern, 9 H, methylene protons), and 1.22 and 1.20 (singlets, 3 H each, methyl groups).

8-Isopropylidenebicyclo[3.2.1]octan-2-one (8).—A solution of 1.50 g (9.15 mmol) of **7** in 450 ml of pentane was irradiated for 30 min under the predescribed conditions. Removal of the solvent *in vacuo* at 25° gave 1.49 g of a light yellow oil which was shown by vpc (column A or B,[20] 130°) to be a mixture of unchanged **7** and a single photoproduct **8** in the ratio 7.6:1. Preparative vpc (column B,[20] 130°) of this mixture led to the isolation of 0.874 g (58%) of **7** and 0.130 g (8.7%) of **8**: $\lambda_{max}^{CCl_4}$ 5.83, 6.89, 7.04, 7.28, 7.65, 8.10, 9.74 μ; $\lambda_{max}^{isooctane}$ 288 sh mμ (ε 360), 296 (420), 305 (390), and 317 (225); $\delta_{TMS}^{CCl_4}$ 3.30 and 3.03 (broad signals, 1 H each, bridgehead protons), 2.7–1.75 (complex pattern, 8 H, methylene protons), and 1.75 and 1.62 (singlets, 3 H each, isopropylidene methyl groups). This ketone was characterized as its semicarbazone, mp 205–206° dec (from methanol).

Anal. Calcd for $C_{12}H_{19}N_3O$: C, 65.12; H, 8.65; N, 18.99. Found: C, 65.18; H, 8.64; N, 19.06.

Photoequilibration Experiments.—Solutions (*ca.* 1%) of ketones **3–8** in pentane were placed under a nitrogen atmosphere in quartz test tubes, affixed to the exterior of the quartz well, and irradiated in the manner described above. The progress of the reactions were monitored by vpc analysis on a Varian-Aerograph Hy-Fi Model 600D gas chromatograph. Aliquots were obtained by piercing the septum-sealed test tubes with a syringe of the proper size.

Registry No.—**3,** 4668-61-5; **3** semicarbazone, 18366-32-0; **4,** 18346-76-4; **4** semicarbazone, 18346-77-5; **5,** 2020-07-7; **5** semicarbazone, 5164-39-6; **6,** 18346-78-6; **6** semicarbazone, 18346-79-7; **7,** 18366-35-3; **7** semicarbazone, 18366-36-4; **8,** 18346-80-0; **8** semicarbazone, 18346-81-1.

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[23] J. A. Marshall, N. H. Andersen, and P. C. Johnson, *J. Amer. Chem. Soc.*, **89**, 2748 (1967).

Notes

Ferrocene Studies. II.
The Reaction of Ferrocenyllithium with Aromatic Aldehydes[1]

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Received July 15, 1968

In general, organometallic compounds react with aromatic aldehydes to give secondary alcohols. A recent exception is the reported formation of 2-aroylpyrroles from the reaction of pyrrylsodium with aromatic aldehydes.[2] This reaction was proposed by Raines to proceed through an alkoxide reduction involving a second mole of the aldehyde.

We now wish to report that the reaction of ferrocenyllithium (I) with aromatic aldehydes in tetrahydrofuran gave aryl ferrocenyl ketones (II). Thus *p*-chlorbenzaldehyde, tolualdehyde, anisaldehyde, and ferrocenecarboxaldehyde gave the appropriate aryl ferrocenyl ketone (II) and no secondary alcohol when either a 3:1 or 1:1 *M* ratio of the aldehyde was added to ferrocenyllithium (I) in tetrahydrofuran. The expected alcohol was obtained (together with the ketone) only when benzaldehyde was allowed to react in a 1:1 molar ratio. With an excess of aldehyde, benzaldehyde also gave rise to ketone and no alcohol.

This reaction apparently follows a course similar to that proposed by Raines[2] in the pyrrole series. Thus when phenylferrocenylmethanol (III) was treated with *n*-butyllithium, alkoxide IV was formed as indicated by the formation of the ether V upon the addition of methyl iodide. When benzaldehyde was added to IV benzoylferrocene (II, Ar = C_6H_5) was obtained (Scheme I).

The ferrocenyllithium (FcLi) was prepared from bromoferrocene in tetrahydrofuran.[3] That complete lithiation of the bromoferrocene had occurred was checked by direct carbonation to form ferrocenecarboxylic acid. In all cases liquid aldehydes were purified by distillation under a nitrogen atmosphere before use and the tetrahydrofuran was distilled freshly from lithium aluminum hydride. In all cases a significant amount of ferrocene appears as a product of the reaction. This could arise by a simple proton abstraction from impurities or solvent, as a product from some mechanistic pathway, or more likely as the result of hydrolysis of unused ferrocenyllithium which had not reacted with the aldehyde. The later reasoning would

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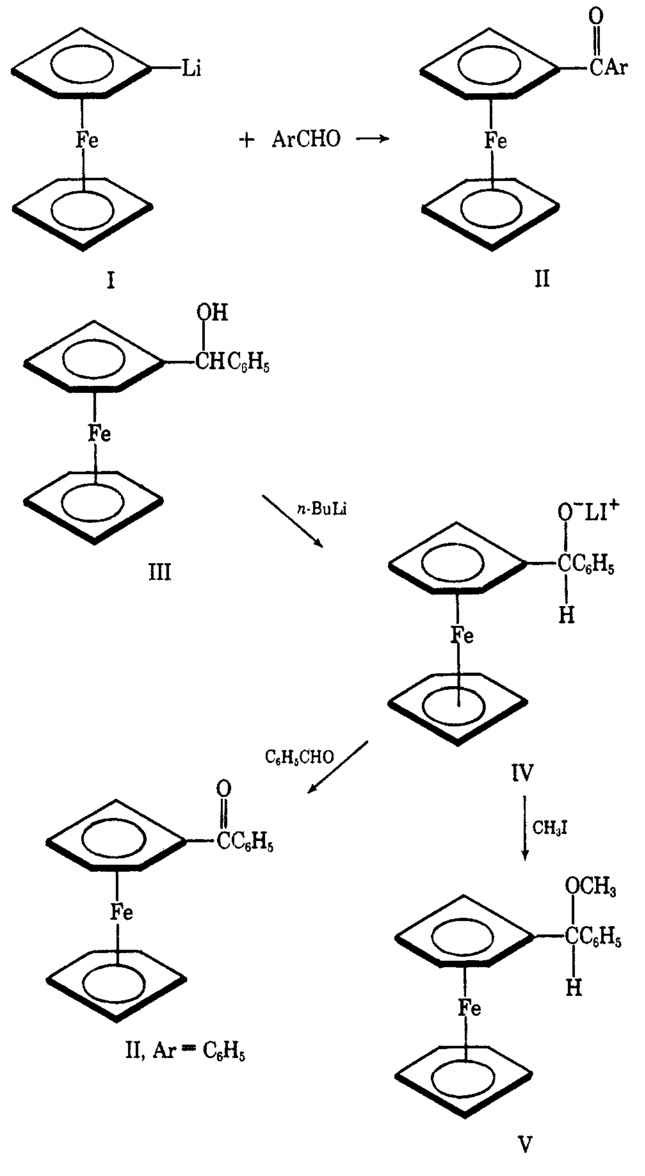
[1] Part I.: F. D. Popp and J. A. Kirby, *J. Chem. Eng. Data*, **8**, 604 (1963). We should like to thank the Norwich Pharmacal Co. for financial support of a portion of this work.

[2] S. Raines, *J. Org. Chem.*, **32**, 227 (1967).

[3] H. Rosenburg, J. M. Barton, and M. M. Hollander, Abstracts of 2nd Annual International Symposia on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965. We should like to thank Dr. Rosenberg for his helpful comments in regard to this preparation.

also explain the formation of triferrocenylmethanol from the reaction of ferrocenyllithium with ferrocenealdehyde. Several unidentified compounds were obtained in a number of reactions. Although no rigorous attempt was made to identify these products, anisaldehyde and tolualdehyde gave products which appear to be diarylferrocenylcarbinols. The possible presence of tertiary carbinols and the isolation of carboxylic acids from two reactions might indicate possible oxidation of aldehyde to acid followed by a Hammick-type reaction with the ketones.

SCHEME I



It is of interest to note that in the case of the 1:1 reaction of benzaldehyde with ferrocenyllithium (where the carbinol was found), the yield of carbinol could be increased by the use of excess n-butyllithium. Finally it should be noted that when phenylferrocenylmethanol was subjected to the separation and purification scheme used in these reactions no evidence of ketone formation could be noted, indicating that the ketone arose from the reaction and not as an artifact from purification.

Experimental Section[4]

Bromoferrocene was synthesized from chloromercuriferrocene[5] by the method of Fish and Rosenblum[5] with the following modifications. The reaction was worked up immediately after the rapid addition of the 10% sodium thiosulfate solution by the addition of 100–125 g of crushed ice followed by extraction with Skellysolve B. The addition of crushed ice was repeated before each extraction. In this manner large runs can be carried out while keeping the volume to a reasonable size. In a typical run 8.4 g of chloromercuriferrocene gave after chromatography and drying 4.6 g (86.5%) of bromoferrocene, mp 30–31°.

Ferrocenyllithium.—The lithiation of bromoferrocene was accomplished according to a procedure followed by Rosenberg and coworkers.[3] In a typical experiment 1.5 ml of 2.51 M (3.77 mmole) n-butyllithium in hexane was added over 10 min to a stirred solution of 1.0 g (3.77 mmol) of bromoferrocene in 35 ml of anhydrous tetrahydrofuran at 0°. After stirring for an additional 30 min at 0° the various aldehydes were added to the solution as described below.

Condensation of Ferrocenyllithium with Benzaldehyde. A. Excess Benzaldehyde.—To a 3.77-mmol solution of ferrocenyllithium as described above was added at 0° over a period of 10 min 4.025 g (37.9 mmol) of benzaldehyde. After stirring for 12 hr at room temperature, 20 ml of distilled water and 40 ml of ether were added and the organic layer was separated. The organic layer was washed successively with two 50-ml portions of a 10% sodium bisulfite solution and two 50-ml portions of distilled water and dried over magnesium sulfate. Concentration gave an oil which on chromatography with Skellysolve B gave 0.25 g (34%) of ferrocene and 0.60 g (55%) (eluted with benzene–ether) of benzoylferrocene. In addition to the usual methods of identification[4] this material was reduced[6] to the expected carbinol.

B. Molar Amounts of Reactants.—In the same manner 3.77 mmol of ferrocenyllithium and 3.77 mmol of benzaldehyde gave the three products as indicated in Table I together with a small amount of unidentified solid, mp 74–77° (not benzylferrocene). *Anal.* Found: C, 74.17; H, 5.62; Fe, 19.43.

TABLE I

FERROCENYLLITHIUM AND AROMATIC ALDEHYDES

Aldehyde	Ratio of FcLi to ArCHO	Ferrocene	Products,[a] % $\mathrm{Fc}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Ar}$	 $\mathrm{Fc}\overset{\mathrm{OH}}{\overset{\vert}{\mathrm{C}}}\mathrm{HAr}$
C_6H_5CHO	1:10	34	55	0
	1:1	50	16	16
	1:1 (x's BuLi)	22	12	42
FcCHO	1:3	36	41	0
	1:1	31	12	0
p-$CH_3OC_6H_4CHO$	1:3	33	66	0
	1:1	21	10	0
p-$CH_3C_6H_4CHO$	1:3	53	12	0
	1:1	54	6	0
p-ClC_6H_4CHO	1:3	50	23	0
	1:1	10	11	0

[a] See Experimental Section for other products in specific reactions.

C. Molar Amounts of Reactants with Excess n-Butyllithium.—In the same manner 3.77 mmol of ferrocenyllithium (from 3.77 mmol of bromoferrocene and 5.42 mmol of n-butyllithium) and 3.77 mmol of benzaldehyde gave the three products as indicated in Table I together with a very small amount of unidentified yellow oil.

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(4) All melting points are corrected and taken in capillaries. Analyses by Spang Microanalytical Laboratory, Ann Arbor, Mich. All aldehydes were purified immediately before use and the tetrahydrofuran was distilled from lithium aluminum hydride before use. The preparation of ferrocenyllithium and all reactions of ferrocenyllithium were carried out under a nitrogen atmosphere. Chromatographic separations were by dry column chromatography [B. Loev and M. M. Goodman, *Chem. Ind.* (London), 2026 (1967)]; we should like to thank Dr. Loev for helpful comments regarding this technique. All known compounds were identified by comparison of melting point and infrared and nmr spectra with authentic samples.

(5) R. W. Fish and M. Rosenblum, *J. Org. Chem.*, **30**, 1253 (1965).

(6) N. Weliky and E. S. Gould, *J. Amer. Chem. Soc.*, **79**, 2742 (1957).

Condensation of Ferrocenyllithium with Other Aldehydes.[7] **Excess Ferrocenecarboxaldehyde.**—Concentration gave diferrocenylketone[8] and an oil (five components by tlc) which on chromatography gave ferrocene, ferrocenecarboxaldehyde and unstable red oils.

Molar Amount of Ferrocenecarboxaldehyde.—Concentration gave 5% of ferrocenecarboxylic acid and an oil which on chromatography gave the products in Table I, 8% of triferrocenylmethanol, and two unidentified solids, mp 120–122 and 142°, in low yield.

Excess and Molar Amount of Tolualdehyde.—Chromatography gave the products in Table I and a solid (16% from excess, 15% from molar), mp 117–118° (from heptane), believed to be ditolylferrocenylcarbinol.

Anal. Calcd for $C_{25}H_{21}FeO$: C, 75.77; H, 6.10; Fe, 14.09. Found: C, 75.34; H, 6.06; Fe, 14.44.

Molar Amount of Anisaldehyde.—Chromatography gave the products in Table I and 9% of a solid, mp 76–78° (from heptane), believed to be dianisylferrocenylcarbinol.

Anal. Calcd for $C_{25}H_{24}FeO_3$: C, 70.10; H, 5.65; Fe, 13.04. Found: C, 70.45; H, 5.82; Fe, 12.82.

Excess and Molar Amount of *p*-Chlorobenzaldehyde.—Concentration gave *p*-chlorobenzoic acid (8% from excess, 49% from molar) and an oil which on chromatography gave the products in Table I. The *p*-chlorobenzoylferrocene had mp 119–120° from heptane.

Anal. Calcd for $C_{17}H_{13}ClFeO$: C, 62.90; H, 4.04; Fe, 17.21. Found: C, 63.06; H, 4.16; Fe, 17.08.

This ketone gave a 2,4-dinitrophenylhydrazone, mp 226°, from methylene chloride–heptane.

Anal. Calcd for $C_{23}H_{17}ClFeN_4O_4$: N, 11.95. Found: N, 11.96.

Reaction of Benzaldehyde with Lithium Phenylferrocenylmethoxide.—To 0.230 g (0.787 mmol) of phenylferrocenylmethanol[9] in 15 ml of anhydrous THF at 0° was added 1 ml of 2.51 *M* *n*-butyllithium in hexane. After 15 min the solution was allowed to warm to room temperature and 1 ml of benzaldehyde was added. The reaction mixture was stirred for 12 hr at room temperature and treated as above to give 0.122 g (50%) of benzoylferrocene.

Reaction of Methyl Iodide with Lithium Phenylferrocenylmethoxide.—In the same manner as above, addition of 1 ml of methyl iodide in place of the benzaldehyde gave a 90% yield of V.

Registry No.—I, 1271-15-4; dianisylferrocenylcarbinol, 12310-26-8; *p*-chlorobenzoylferrocene, 12310-23-5; 2,4-dinitrophenylhydrazone of *p*-chlorobenzoylferrocene, 12310-24-6; ditolylferrocenylcarbinol, 12310-25-7.

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[7] The procedures used are identical with those indicated for benzaldehyde. Major products are indicated in Table I and this section lists minor products isolated.

[8] Samples of diferrocenyl ketone were generously supplied by Drs. M. Rausch and S. Goldberg.

[9] M. Cais and A. Eisenstadt, *J. Org. Chem.*, **30**, 1148 (1965).

Ring Closure of 2,2′-Diiodobiphenyl

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Received August 29, 1968

Collette, *et al.*,[1] have carried out the facile ring closure of the iodoso compounds from 2-iodobiphenyl and its homologs. By this procedure diphenyleniodonium salts have been made in high yield (99%). According to Beringer, *et al.*,[2] the reaction mechanism probably involves electrophilic substitution by the conjugate acid formed by the action of sulfuric acid on the iodoso compound.

In the present work the ring closure of 2,2′-diiodobiphenyl has been carried out to give the bisiodonium salt (**1**). The reaction mixture also affords a small amount of the well-known diphenyleniodonium salt (**3**). The formation of **3** is interesting because it represents electrophilic substitution in which the conjugate acid replaces iodine.

In order to explain the formation of **3** and the nature of the displaced iodine which also must be an electrophile, 2,2′-diiodobiphenyl dissolved in peracetic acid was allowed to stand at *room temperature* for 1 week. During this time 91% of the starting material ring closed to form the iodonium salt and no bisiodonium salt was detected. Diphenyleniodonium iodate **4** (70%) separated as a white solid and there was also isolated the iodonium salt as diphenyleniodonium chloride (21%). A reasonable explanation is that in acetic–peracetic acid solution the iodine present as the iodoso group is displaced and is a better leaving group than hydrogen. In cold concentrated sulfuric acid solution the iodoso group is a better electrophile than it is in the weaker acetic acid. It is also possible that a more favorable structure for hydrogen replacement exists due to a restriction about the biphenyl bond. This may be due to the bulk of the conjugate acid functions and to a repulsion between like charges on the conjugate acid functions. In this connection it is interesting to note that Mascarelli[3] found that when 2,2′-diiodosobiphenyl or the tetrachloride was kept in water for some months the aqueous solution when treated with sulfur dioxide afforded diphenyleneiodonium iodide.

The less drastic conditions for ring closure, described by Collette, *et al.*,[1] are not satisfactory for the formation of **1**. Under these conditions the final reaction mixture contains unreacted 2,2′-diiodobiphenyl, a small amount of **3** and some monoiododiphenyleniodonium salt (**2**) (Scheme I).

The diphenyleniodonium salts and the bisiodonium salts described in the present paper should be useful synthetic reagents. We have found that **3** in water with cuprous chloride and ammonium hydroxide at the refluxing temperature affords carbazole (65%). The pyrolysis of **1** as the diiodide and **2** as the iodide affords, respectively, 2,2′,6,6′-tetraiodobiphenyl and 2,2′,6-triiodobiphenyl.

Experimental Section

2,2′-Diiodobiphenyl was prepared by the pyrolysis of diphenyleniodonium iodide.[1]

Peracetic Acid Oxidation and Cyclization. (*All preparations with organic peracids should be carried out behind a safety shield.*)—2,2′-Diiodobiphenyl (1.7 g) was added to peracetic acid[1] (50 ml) and allowed to stand for 72 hr at room temperature. The reaction mixture which now contained the iodoso compound was cooled in an ice-water bath and added dropwise and with stirring to concentrated sulfuric acid (25 ml) cooled in an ice-water bath. Some white solid separated and the

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[1] J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *J. Amer. Chem. Soc.*, **78**, 3819 (1956).

[2] F. M. Beringer, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *ibid.*, **75**, 2705 (1953).

[3] L. Mascarelli, *Gazz. Chim. Ital.*, **43** (I), 26 (1913).