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 $C_{25}H_{24}FeO$: 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.

(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

R. B. SANDIN

Department of Chemistry, University of Alberta, Edmonton, Canada

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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]

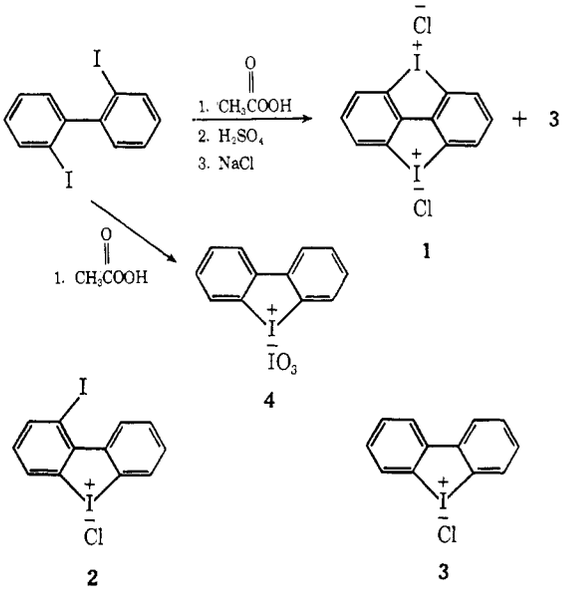
Peracetic Acid Oxidation and Cyclization. (*All preparations with organic peracids should be carried out behind a safety shield.*)—2,2′-Diiodobiphenyl (1.7 g) was added to peracetic acid[1] (50 ml) and allowed to stand for 72 hr at room temperature. The reaction mixture which now contained the iodoso 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

(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).

SCHEME I



mixture was allowed to stand at room temperature for 48 hr. The reaction mixture was poured into ice–water (500 ml) and the solid was collected and washed with water (1.0 l. at 70°). To the combined filtrate was added sodium chloride until precipitation was complete, which afforded III as the chloride.

Anal. Calcd for $C_{12}H_8ICl$: Cl, 11.28. Found: Cl, 10.99.

The residue was dissolved in boiling water (6.0 l.) and filtered while hot. To the hot filtrate was added sodium chloride until precipitation was complete, which afforded I as the dichloride, yield 0.5 g.

Anal. Calcd for $C_{12}H_6I_2Cl_2$ (0.0662- and 0.1310-g samples): AgI + AgCl, 0.1049, 0.2076 g. Found: AgI + AgCl, 0.1048, 0.2106 g.

When the procedure which brings about the facile ring closure of 2-iodobiphenyl[1] (5 g) was followed, the reaction mixture contained unreacted 2,2′-diiodobiphenyl, a small amount of III (0.1 g) and a relatively large amount of pale yellow II (1.1 g) which was isolated as the chloride.

Anal. Calcd for $C_{12}H_7I_2Cl$: Cl, 8.06. Found: Cl, 8.15, 8.39.

The brilliant yellow diiodide of I was prepared by the usual procedure.[1]

Anal. Calcd for $C_{12}H_6I_4$: I, 77.20. Found: I, 76.85.

The diiodide of I (1.5 g) was added to dimethyl sulfoxide (25 ml) and heated to 180° for 0.5 hr or until solution was complete. The solution was poured into 100 ml of ice–water and the solid tetraiodobiphenyl was recovered by filtration and was recrystallized from alcohol–benzene to afford brown crystals (1.0 g), mp 258°. A pale yellow-brown analytical sample melted at 262–263°.

Anal. Calcd for $C_{12}H_6I_4$: I, 77.26. Found: I, 77.22, 77.14.[4]

In a similar manner the iodide of II was prepared.

Anal. Calcd for $C_{12}H_7I_3$: I, 71.61. Found: 71.44.

The iodide was decomposed in hot dimethyl sulfoxide and afforded the triiodobiphenyl (54%). It was recrystallized three times from alcohol to give pale yellow crystals, mp 151–152°.

Anal. Calcd for $C_{12}H_7I_3$: I, 71.61. Found: I, 71.29, 71.38.[4]

A solution of 2,2′-diiodobiphenyl (2.4 g) in peracetic acid (70 ml) was allowed to stand for 1 week at room temperature (30°). White solid diphenyleniodonium iodate (1.9 g) separated and was recrystallized from water.

Anal. Calcd for $C_{12}H_8I_2O_3$: I, 55.94. Found: I, 55.57, 55.94.

An aqueous solution of the iodate was treated with sodium bisulfite and afforded pale yellow diphenyleniodonium iodide.

Anal. Calcd for $C_{12}H_8I_2$: I, 62.56. Found: I, 63.19.

The iodide was decomposed in hot dimethyl sulfoxide to produce 2,2′-diiobiphenyl, mp 109–110°. A mixture melting point with an authentic sample showed no depression.

There was also isolated from the above diphenyleniodonium iodate reaction filtrate the iodonium salt as the chloride (0.4 g).

Anal. Calcd for $C_{12}H_8ICl$: 11.28. Found: Cl, 11.22, 11.41.

Diphenyleniodonium chloride or the sulfate (3 g) was dissolved in boiling water (2 l.) and to the solution was added cuprous chloride (10 g) followed by a *very slow* and *careful* addition of concentrated ammonium hydroxide (100 ml). The mixture was refluxed for 1 hr and carbazole (65%) was recovered by filtration and extraction by the usual procedure.

Registry No.—2,2′-Diiodobiphenyl, 2236-52-4; **1** dichloride, 18399-12-7; **2** chloride, 18399-13-8; 2,2′,6,-6′-tetraiodobiphenyl, 18399-10-5; **2** iodide, 18354-33-1; 2,2′,6-triiodobiphenyl, 18399-11-6; **3** chloride 4673-26-1; **3** iodide, 1010-76-0; **4** 18399-16-1.

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(4) Microanalyses by Micro-Tech Laboratories, Inc., Skokie, Ill.

Reactions of Chloroacetone in Basic Media

H. L. SLATES, S. WEBER, AND N. L. WENDLER

Merck Sharp & Dohme Research Laboratories, Merck & Co., Inc., Rahway, New Jersey

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In the interest of ascertaining the susceptibility of chloroacetone to function as a donor enolate at the chlorine-bearing carbon, the behavior of this ketone to various basic conditions was examined. Initial experiments revealed the essentially titrametric velocity with which chloroacetone reacts with aqueous alkali to afford quantitatively acetol as determined by the blue tetrazolium assay method.[1] Despite this extremely rapid hydrolysis of chloride, however, deuterium exchange and correspondingly formation of the pertinent anion at the chloromethylene center is a more rapid process. Thus when chloroacetone was allowed to react with 0.1 equiv of sodium deuterioxide in D_2O–CH_3OD, the nmr spectrum of the surviving chloroacetone, isolated after a 2-min reaction period, exhibited a 3:1 proton area ratio at τ 7.69 and 5.90 consistent with 1-chloro-1-monodeuterioacetone. In the absence of alkali, chloroacetone did not undergo measurable deuterium exchange after 0.5 hr.

Attempts to mediate condensations of chloroacetone *via* its pyridinium salt (**3**, NR_3 = pyridine)[2] proved ineffective apparently in virtue of the relatively stable character of the latter species. With triethylamine condensation proceeded in two independent directions according to the media employed. In aprotic media such as glyme the two components did not react in a simple manner to give the quaternary salt **3** (R = C_2H_5) but instead gave triethylamine hydrochloride

(1) See Experimental Section; also A. S. Meyer and M. C. Lindberg, *Anal. Chem.*, **27**, 813 (1955), and references therein.

(2) C. Dreser, *Arch. Pharm.*, **236**, 334 (1898).