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Reaction of Iodobiphenyls and Iodonaphthalenes with Concentrated Sulfuric Acid. Attempted Extension of the Jacobsen Reaction to Polycyclic Systems

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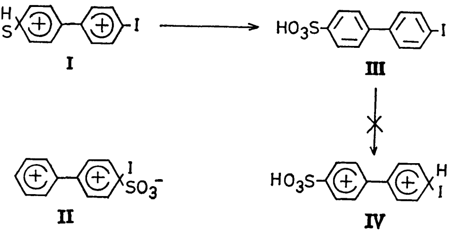
In contact with concentrated sulfuric acid, aromatic iodo compounds undergo disproportionation to give higher iodo derivatives. The reaction has been known as the Jacobsen reaction,[1] but its synthetic possibility has received little attension. In some previous papers,[2] we have reported that such disproportionation of aromatic iodo compounds can be used for one-step preparation of certain polyiodobenzene derivatives, which otherwise require lengthy laborious procedure to obtain. Now the reaction has been attempted to extend to the titled polycyclic iodo compounds with the initial aims to define the scope of its synthetic utility as well as to obtain, if possible, previously unknown higher iodo derivatives. Only several triiodo and tetraiodobiphenyls have so far been recorded in literature.[3] No data have been appeared on the preparation of polyiodonaphthalenes containing more than three iodine atoms, with the exception of a recent note that a trace amount of 1,2,3-triiodo and 1,2,3,4-tetraiodonaphthalene was formed in the photolysis of *o*-bis(iodoethynyl)benzene.[4] No product from the sulfonation of the titled compounds seems to have been adequately characterized before.

Treatment of 1-iodonaphthalene with excess of sulfuric acid at room temperature, followed by dilution with water gave a small amount of reddish-brown pasty solid, chromatography of which on alumina using light petroleum as eluant gave a small amount of 1,4-diiodonaphthalene. Yield was usually below 5% and most part of the starting material went into solution as sulfonic acid. The amount of sulfuric acid relative to iodo compound could be varied over a wide range without any significant improvement on the yield of the diiodo product. The change in temperature from room temperature up to 70°C had no effect on the results. Some elementary iodine was liberated at elevated temperature. From the aqueous part, a sulfonic acid was obtained and identified as 4-iodonaphthalene-1-sulfonic acid by comparison with the authentic specimen. On similar treatment, 2-iodonaphthalene was readily sulfonated to give a mixture of sulfonic acids in which 7-iodonaphthalene-1-sulfonic acid and 6-iodonaphthalene-2-sulfonic acid were the main components, the former being predominant. No disproportionation product could be obtained.

4-Iodobiphenyl reacted with sulfuric acid more readily than did 1-iodonaphthalene, giving some 4,4′-diiodobiphenyl as disproportionation product. Yields varied from nearly zero to 8% depending on the conditions employed. Most part of the starting material was converted to sulfonic acid. Similar treatment of 2- and 3-iodobiphenyls merely gave 4′-sulfonic acids. The orientation of sulfo group in these acids was established through the conversion to iodobiphenylsulfonamides, followed by the reductive removal of iodine atom with aqueous ammonia and zinc dust leading to 4-biphenylsulfonamide. Since iodine atom would deactivate the ring in which it is located, the sulfo group has probably entered at the most reactive 4′-position of another ring.

Although the above results delimit the possible use of the Jacobsen reaction for the preparation of the higher iodo compounds, they still seem to provide some information to understand the process of iodine transfer. A sulfur trioxide will add to the substrate to form either the complex I in which the hydrogen atom at the attacking site may migrate to oxygen to give a sulfonic acid III, or the complex II in which the iodine atom may be transferred to the second molecule *via* S_N2 attack on the iodine atom to yield a higher iodo compound. This interpretation is consistent with the findings that only 1-iodonaphthalene and 4-iodobiphenyl which have the iodine atom at the most favorable position for electrophilic attack under go disproportionation. Since the sulfonic acids derived from these compounds are stable in contact with sulfuric acid, a role of the protonated sulfonic acid IV as a possible iodinating species is less probable. 2-Iodonaphthalene will direct the bulky sulfo group to 6 and 8-positions, while 2- and 3-iodobiphenyls are subject to the preferential attack at 4′-position of the unsubstituted ring. Therefore, the inability of these compounds to undergo rearrangement is attributed to the unfavorable structural condition for electrophilic attack at the position where iodine atom occupies.



As a parallel study to disproportionation, some effort has been made to iodinate iodobiphenyls and iodo-

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[1] H. J. Shine, "Aromatic Rearrangement" Elsevier, London (1967), p. 28; H. Cerfontain, "Mechanistic Aspects in Aromatic Sulfonation and Desulfonation," Interscience, London (1968), p. 221.

[2] H. Suzuki and R. Goto, This Bulletin, **36**, 389 (1963); *Nippon Kagaku Zasshi*, **84**, 167, 284 (1963).

[3] H. Oikawa, *Nippon Kagaku Zasshi*, **84**, 272 (1963); R. B. Sandin, *J. Org. Chem.*, **34**, 456 (1969).

[4] I. D. Cambell and G. Egliton, *J. Chem. Soc.*, *C*, **1968**, 2120.

TABLE 1. PHYSICAL PROPERTIES OF SOME SULFONYL CHLORIDES AND SULFONAMIDES DERIVED FROM IODOBIPHENYLS AND IODONAPHTHALENES

	Mp (°C)	IR spectra[a] (cm^{-1})	Found (%) C	Found (%) H	Calcd (%) C	Calcd (%) H
Sulfonyl Chlorides						
4-Iodonaphthalene-1-sulfonyl chloride	123—124	663, 754, 819, 863, 1131, 1159, 1181, 1199, 1360, 1494, 1550	33.9	1.8	34.0	1.7
6-Iodonaphthalene-2-sulfonyl chloride	138—139	668, 806, 943, 1072, 1165, 1378, 1617	34.2	1.7	34.0	1.7
7-Iodonaphthalene-1-sulfonyl chloride	166—168	680, 744, 813, 832, 1136, 1171, 1176, 1195, 1366, 1492, 1578, 1616	34.1	1.7	34.0	1.7
2-Iodobiphenyl-4-sulfonyl chloride	148—150	686, 769, 808, 1000, 1163, 1373, 1474, 1592	38.1	2.2	38.1	2.1
3-Iodobiphenyl-4-sulfonyl chloride	98—100	687, 786, 835, 1077, 1170, 1367, 1461, 1581	38.2	2.2	38.1	2.1
4-Iodobiphenyl-4-sulfonyl chloride	145—146	770, 809, 1000, 1168, 1373, 1592	38.3	2.2	38.1	2.1
Sulfonamides						
4-Iodonaphthalene-1-sulfonamide	211—213	678, 767, 902, 1138, 1158, 1328, 1501, 1554	36.2	2.6	36.0	2.4
6-Iodonaphthalene-2-sulfonamide	231—232	690—700, 798, 870, 940, 1068, 1124, 1137, 1330, 1562, 1613	35.9	2.4	36.0	2.4
7-Iodonaphthalene-1-sulfonamide	234—237	678, 814, 828, 1080, 1132, 1158, 1327, 1334, 1578, 1621	35.8	2.6	36.0	2.4
2′-Iodobiphenyl-4-sulfonamide	200—204	754, 1096, 1155, 1331, 1460	40.3	2.9	40.1	2.8
3′-Iodobiphenyl-4-sulfonamide	162—163	690, 779, 1096, 1153, 1163, 1330	40.2	3.0	40.1	2.8
4′-Iodobiphenyl-4-sulfonamide	254—256	771, 809, 1000, 1158, 1310, 1337	38.0	2.9	40.1	2.8

a) Principal peaks in 650—2000 cm^{-1} region.

naphthalenes with iodine-periodic acid[5)] in order to obtain the reference compounds as well as to know the substitution pattern in these systems. So far, very little information is available on the direct iodination of these compounds except 4-iodobiphenyl, which has been readily converted to 4,4′-diiodobiphenyl in the presence of iodine and suitable oxidizing agent.[6)]

1-Iodonaphthalene underwent slow iodination to give mainly 1,4-diiodonaphthalene with a little of 1,5-diiodo isomer. 2-Iodonaphthalene reacts quite slowly to give a mixture of diiodonaphthalenes in a low yield, and infrared spectrum of which proved the major component to be 2,6-diiodonaphthalene. Appreciable amounts of amorphous substances are formed as by-product. None of these diiodonaphthalenes could be iodinated further.

The direct iodination of iodobiphenyls took place more readily than did iodonaphthalenes. 2-Iodobiphenyl gave a mixture of diiodobiphenyls, while 3-iodobiphenyl yielded a diiodobiphenyl and a triiodobiphenyl, relative ratio of these products depending on the amounts of the reagent and length of reaction time. Electrophilic substitution in biphenyl has been known to occur mainly at 4 and 4′-positions, since the transition states are stabilized most effectively when attacking species is attached to these positions. Thus, the major products which would result from the iodination of 2-iodobiphenyl are thought to be 2,4′- and 2,4-diiodobiphenyls, while the products from 3-iodobiphenyl can be formulated as 3,4′-diiodobiphenyl and 3,4,4′-triiodobiphenyl, respectively. 4-Iodobiphenyl gave only 4,4′-diiodobiphenyl in high yield. The iodine atom could not be introduced into 2 or 2′-position even with the use of large excess of the reagent under the conditions employed.

Experimental

Authentic iodonaphthalenesulfonic acids and diiodonaphthalenes were mostly obtained by replacement of amino group in aminonaphthalenesulfonic acid or naphthylamine by iodine, respectively. Infrared spectra were measured in KBr disc, unless otherwise stated, with a JASCO DS-402G spectrophotometer.

General Procedure for the Jacobsen Reaction. A typical procedure is as follows: 1-Iodonaphthalene (5 g) and sulfuric acid (10 g) were placed in a small stoppered flask and then stirred magnetically at 20—30°C for 5 hr. The mixture was diluted with water and the oily solid (*ca.* 0.4 g) was extracted with light petroleum and chromatographed on alumina using the same solvent as eluant. Colorless prisms (0.3 g, mp 85—110°C)[7)] were obtained from early eluates and identified as

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5) H. Suzuki, K. Nakamura, and R. Goto, This Bulletin, **39**, 128 (1966). Also *cf.* H. Suzuki, "Organic Syntheses," Vol. 51, in press (1971).

6) A. N. Novikov, *Zh. Obshch. Khim.*, **29**, 58 (1959); H. O. Wirth, O. Königstein, and W. Kern, *Ann. Chem.*, **634**, 84 (1960); T. A. Khalimova and A. N. Novikov, *Probl. Poluch. Poluprod. Prom. Org. Sin.*, *Akad. Nauk SSSR*, *Otd. Obshch. Tekh. Khim.*, **1967**, 82.

7) Some isomeric impurity, possibly 1,5-diiodonaphthalene, might be responsible for the wide melting range of the disproportionation product.

1,4-diiodonaphthalene by infrared spectral comparison with the authentic sample (lit,[8] mp 109—110°C). IR: 743, 775, 808, 942, 1129, 1239, and 1378 cm^{-1}.

Found: I, 67.0%. Calcd for $C_{10}H_6I_2$: I, 66.8%.

The aqueous part was carefully neutrallized with sodium carbonate and the precipitated sodium sulfonate was collected by filtration, dried, and treated with phosphorus pentachloride to give *4-iodonaphthalene-1-sulfonyl chloride*, which was recrystallized from carbon tetrachloride and melted at 123—124°C. On heating with aqueous ammonia, the chloride was converted into *4-iodonaphthalene-1-sulfonamide*, mp 211—213°C.

Physical properties of sulfonyl chlorides and sulfonamides obtained from the reaction of iodonaphthalenes and iodobiphenyls are summarized in Table 1.

Iodination of Iodobiphenyls. Iodine (10.2 g) was added to a mixture of 2-iodobiphenyl (14 g), periodic acid dihydrate (4.56 g), and 80% acetic acid (120 m*l*) containing small amount of sulfuric acid as catalyst, and the mixture was stirred at 70—80°C for 6 hr. Upon cooling, an oily deposit was taken up into light petroleum, washed with aqueous sodium hydrogen sulfate to remove the unchanged iodine, dried, and distilled under reduced pressure to give diiodobiphenyl (19.1 g) as a pale yellow syrup, bp 164—165°C/2 mmHg, which was presumably a mixture of *2,4′- and 2,4-diiodobiphenyls*, the former being predominant. IR: 752, 820, 998, and 1006 cm^{-1}. Found: C, 35.3; H, 2.0%. Calcd for $C_{12}H_8I_2$: C, 35.5; H, 2.0%.

By a similar procedure, 3-iodobiphenyl gave *3,4′-diiodobiphenyl* (mp 75—77°C, IR: 771, 827, and 1003 cm^{-1}. Found: C, 35.4; H, 2.0%. Calcd for $C_{12}H_8I_2$: C, 35.5; H, 2.0%), together with some *3,4,4′-triiodobiphenyl* (mp 114—116°C, IR: 800, and 995 cm^{-1}. Found: C, 27.5; H, 1.6%. Calcd for $C_{12}H_7I_3$: C, 27.1; H, 1.3%). 4-Iodobiphenyl gave *4,4′-diiodobiphenyl* (mp 210—211°C, IR (Nujol), 802, 996, and 1068 cm^{-1}. Found: C, 35.1; H, 1.8%. Calcd for $C_{12}H_8I_2$: C, 35.5; H, 2.0%).

Iodination of Iodonaphthalenes. 2-Iodonaphthalene (5.1 g) mixed with 80% acetic acid (30 m*l*) containing small amount of sulfuric acid as catalyst was treated with iodine (2.6 g) and periodic acid dihydrate (1.14 g) at 70—80°C for 20 hr. The reaction proceeded quite slowly and gave a dark pasty solid, which was taken up into light petroleum-benzene mixture and passed over a column of alumina to yield a low-melting solid substance (*ca.* 3.2 g) from early eluates and fine needles (0.3 g) from later eluates. The former was mainly composed of the unchanged starting material with a little of diiodonaphthalene. The latter product crystallized from ethanol as fine leaflets, mp 210—213°C, had the formula $C_{10}H_6I_2$ and was identified as impure 2,6-diiodonaphthalene on the basis of its high melting point (lit,[9] 203—204°C) and similarity of its infrared spectrum to 2,6-dichloronaphthalene. IR (Nujol): 813, 837, and 888 cm^{-1}. Found: C, 32.9; H, 1.7; I, 66.0%. Calcd for $C_{10}H_6I_2$: C, 31.5; H, 1.6; I, 66.8%.

Similar iodination of 1-iodonaphthalene led mainly to 1,4-diiodonaphthalene with some 1,5-diiodo isomer. The reaction was slow, but polymeric substance was not formed so much.

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[8] R. Meldola, *J. Chem. Soc.*, **47**, 522 (1885).

[9] M. Janczewski and L. Prajer, *Rocz. Chem.*, **28**, 681 (1954).