addition of an excess of concentrated hydrochloric acid; yield 0.8 g.; mixed m. p. 176–177°.

p-Sulfonamidophenylarsine Oxide. (A).—Three and one-half grams of *p*-sulfonamidophenyldibromoarsine was boiled with 20 cc. of 27% ammonium hydroxide. The mixture was then chilled in ice and the crude oxide removed by filtration; yield, 1.8 g. after recrystallizing from 2% phosphoric acid.

Anal. Calcd. for $C_6H_6O_3NAsS$: As, 30.32; N, 5.67. Found: As, 30.21; N, 5.67.

(B).—Seven grams of crude *p*-chlorosulfonylphenyldichloroarsine was treated with 20 cc. of concentrated ammonium hydroxide. After standing for one hour the mixture was acidified with dilute sulfuric acid and the resulting oxide purified as above; yield 2.2 g.

One-half gram of the oxide was converted to the corresponding dichloroarsine by method (C) outlined under *p*-sulfonamidophenyldichloroarsine; mixed m. p. 176–177°.

p-Chlorosulfonylphenyldichloroarsine.—This substance was prepared by the method of Barber[1] using phosphorus trichloride and phosphorus pentachloride. The yield from 5 g. of sodium *p*-sulfophenylarsonic acid[2] after several recrystallizations from glacial acetic acid was 1 g.; m. p. 84–85°. This substance is soluble in most organic solvents.

Anal. Calcd. for $C_6H_4O_2AsSCl_3$: As, 23.30; Cl, 33.09. Found: As, 23.42; Cl, 32.87.

p-Chlorosulfonylphenylarsonic Acid.—Five grams of *p*-chlorosulfonylphenyldichloroarsine was dissolved in 10 cc. of warm chloroform and saturated with chlorine. The mixture was chilled in ice and the unstable, crystalline *p*-chlorosulfonylphenylarsine tetrachloride removed by filtration. The tetrachloroarsine was hydrolyzed to the corresponding *p*-chlorosulfonylphenylarsonic acid by treating with ice water. The crude acid was dried in vacuum over calcium chloride and recrystallized from ethyl acetate; yield 1.5 g.

Anal. Calcd. for $C_6H_6O_5AsSCl$: As, 24.93. Found: As, 24.89.

p-Sulfonanilidophenylarsonic Acid.—A mixture consisting of 5.3 g. of *p*-chlorosulfonylphenylarsonic acid and 12 cc. of aniline was heated on a water-bath for one-half hour. The resulting mass was treated with 40 cc. of 5% sodium hydroxide. The alkaline layer, which separated on standing, was treated with concentrated hydrochloric acid until acid to congo red paper, whereupon the *p*-sulfonanilidophenylarsonic acid precipitated in a crystalline form; yield, after recrystallization from water, 5 g.

Anal. Calcd. for $C_{12}H_{12}O_5NAsS$: As, 20.97. Found: As, 20.66.

Summary

The preparation and properties of *p*-sulfonamidophenylarsonic acid and a number of its derivatives have been described.

SAN FRANCISCO, CALIF. RECEIVED MAY 31, 1939

---

[1] Barber, *J. Chem. Soc.*, 2047 (1930).

[2] Oneto, THIS JOURNAL, **60**, 2058 (1938).

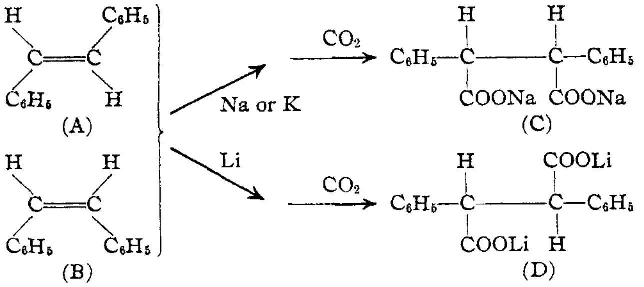
[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Addition of Alkali Metals to the Stilbenes

BY GEORGE F. WRIGHT

Introduction

In 1928 Schlenk and Bergmann[1] presented evidence to show that when alkali metals were added to ethylenes, the configuration of the adduct depended on the metal added and not upon the geometric isomer which was used. Thus, the addition of sodium or potassium to either stilbene (A) or isostilbene (B) gave, after carboxylation, the salt of *meso*-diphenylsuccinic acid (C), whereas addition of lithium to either geoisomer under similar conditions gave the salt of *dl*-diphenylsuccinic acid (D). They further demonstrated that, under conditions not conducive to the addition reaction, isostilbene was isomerized by sodium to stilbene.



While such a directed addition is not impossible from stereochemical considerations, it would seem improbable that two metals as similar as are sodium and lithium should orient themselves so specifically that mixtures of diastereomers would not be formed. The observations of Schlenk and Bergmann have not been questioned; indeed Bachmann and Pence[2] assumed, on the basis of color, that addition of lithium or sodium to 1,2,3,4-dibenzanthracene yielded each a characteristic diastereomer. However Jeanes and Adams[3]

---

[1] Schlenk and Bergmann, *Ann.*, **463**, 98 (1928).

[2] Bachmann and Pence, THIS JOURNAL, **59**, 2339 (1937).

[3] Jeanes and Adams, *ibid.*, **59**, 2608 (1937).

found that sodium, potassium and lithium all added to phenanthrene to give *trans* dimetalated dihydrophenanthrenes. In contrast, therefore, to the findings concerning stilbene, these latter authors find that the configuration of the adduct is independent of the alkali metal used to form it.

Inspection of the experimental data of Schlenk and Bergmann reveals a contradiction concerning their supposed *dl*-diphenylsuccinic acid. This substance was reported by many workers and was finally resolved by Wren and Still.[4] The resolvable acid melts at 183°, resolidifies and again melts at 222°. The melting point of the carboxylated organolithium compound, which Schlenk and Bergmann designated as the *dl*-isomer, was 241°. It will be shown in the present work that the apparent anomaly is eliminated on the basis that Schlenk and Bergmann never obtained any acid other than the *meso*-diphenylsuccinic acid. Although the latter acid ordinarily melts at 229°, it has been found that melting points of 242,[5] 245,[6] and 252°[7] may be obtained. The variation seems to be dependent on the rate of heating. Since a substance having such an indefinite melting point is obviously unsuited for mixed melting point determination, the fact that Schlenk and Bergmann observed a depression on admixture of their two supposed isomers is of little consequence. Likewise their further identification is unconvincing since, of the two methyl esters which they obtained by diazomethane treatment of the acids, the one derived from their supposed *dl*-isomer melted over a 22° range.[8] The extremely questionable evidence upon which these authors base their specific modes of alkali metal addition to ethylenes made it seem advisable to re-investigate the problem.

The addition of the alkali metals to the stilbenes was therefore reëxamined, giving attention to three variables: 1, configuration of the stilbene; 2, choice of metal and 3, choice of solvent. Table I lists the series of experiments carried out to allocate the effect of each of these factors. The resulting organometallic compound was characterized by conversion to the *s*-diphenylsuccinic acids. In no case was a pure diastereomer isolated, although the presence of both isomers could not be demonstrated when the initial yield was low, owing to the difficulty encountered in isolating the *dl*-acid from a mixture with other impurities. Even under favorable circumstances of high yield the reported percentages of *dl*-isomer must be regarded as questionable; on the other hand, the method employed, that of Anschütz and Bendix[6] involving separation by means of barium salt solubilities, gave reliable yields of pure *meso* acid. Both acids, after separation, were identified by conversion to the methyl esters and by mixed melting point determination of the latter with authentic samples.

Reference to Table I shows that *meso*-diphenylsuccinic acid was always obtained regardless of the geometric isomer, or the metal used. This substantiates the claim of Schlenk and Bergmann that *cis*- and *trans*-stilbene give the same product, but disproves their postulate that sodium and lithium orient differently. Although the table shows only the exception (expt. 2) all other experiments yielded impure *trans*-stilbene as recovered ethylene, regardless of the geoisomer originally used. The solvent medium was found to exert a profound effect. In non-coördinating solvents like petroleum ether and benzene, the organometallic compounds were insoluble; the yields were poor. Much better yields were obtained in coördinating solvents like ethyl ether and glycol dimethyl ether in which the organoalkali compounds were soluble. Of greatest significance is the fact that the ratio of diastereomers varies with the solvent used.

Since isostilbene reacted only slightly, and stilbene not at all in 60–70° petroleum ether, even when the reactive sodium–potassium liquid alloy was used, the addition was studied in benzene. Reaction could not be initiated with sodium or lithium unless a small amount of chlorobenzene was added. This unavoidable contaminant may have contributed to the impurity of the carboxylated product; it was found impossible with the methods at hand to isolate *dl*-diphenylsuccinic acid from the poor yield of comparatively low melting crude substance (Table I, expts. 3–8). It can, however, be stated with certainty that the reddish precipitates, obtained with lithium from stilbene or isostilbene, as well as the brownish-black precipitates of disodium compound from

---

[4] Wren and Still, *J. Chem. Soc.*, **107**, 449 (1915).

[5] Sonn and Schellenberg, *Ber.*, **50**, 1517 (1917).

[6] Anschütz and Bendix, *Ann.*, **259**, 91 (1890).

[7] Roser, *ibid.*, **247**, 152 (1888); Ruheman and Naunton, *J. Chem. Soc.*, **101**, 50 (1912).

[8] Although the matter has not been re-investigated in the present study, it should be noted that Schlenk and Bergmann obtained two acids, both melting at 296°, by the action of sodium and lithium on *s*-diphenyldimethylethylene. They claim these acids to be different, but the results obtained in this present work would indicate that the acids are identical.

TABLE I

PREPARATION OF DIPHENYLSUCCINIC ACIDS

								Products						
										Separated diastereomers				
							Time of	Crude		*meso*		*dl*		
Expt.	Stilbene, moles	Isostilbene, moles	Metal atoms Na	K	Li	Solvent	reaction, hrs.	% yield	M. p.,[a] °C.	% of crude	M.p.,[a] °C.	% of crude	M. p.,[a] °C.	Remarks
1	0.1		0.4	0.4		60–70° pet. ether	24	None						
2		0.1	.4	.4		60–70° pet. ether	24	0.4	220–229	90	229	Not found		0.08 mole isostilbene recovered unchanged
3	.01		.02			Benzene	24	.4	200–210					Reaction initiated with 0.05 cc. chlorobenzene
4	.01		.02			Same	144	2.0	205–220					Same
5	.01		.02			Same	312	4.8	200–205	50	223	Not found		Same
6		.01	.02			Same	600	18.0	206–208	>61	229	Not found		Same
7		.01			0.02	Same	800	0.3	200–204					Same
8	.01				.02	Same	2900	.6	223	90	229	Not found		Same
9	.01				.02	Ethyl ether	3	45.0	208	55	229	26	180–200	
10	.01				.02	Same	22	61.0	205–215					
11		.01	.02			Glycol dimethyl ether	1.5	65.0	214–215					
12	.01		.02			Same	2	73.0	213–215	93	224	Not found		
13	.01		.02			Same	1	72.0	214–215	76	229	Not found		Sodium compound treated with dry hydrogen for 1 hr.
14	.01				.02	Same	2	48.0	208–210	78	220	Not found		
15	.01		.02			Same	2	39.0	214–217					Treated with dry hydrogen and Raneynickel for 1 hr.
16	.05		.25			Same	2	74.0	212	94	229	0.3	180–200	

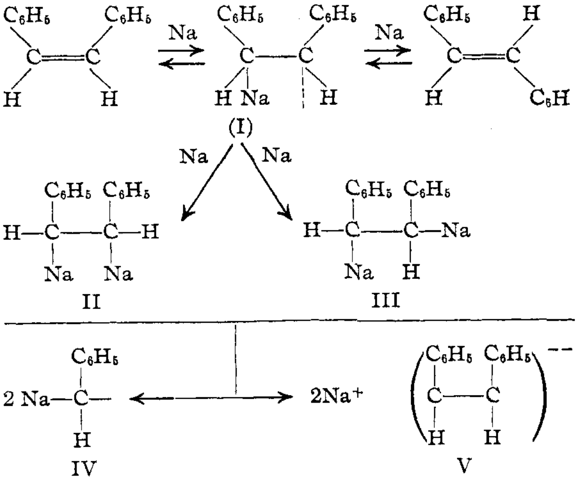
[a] All of these melting points were taken with slow (6°/min.) heating of the bath.

these two geoisomers, all gave *meso*-diphenylsuccinic acid upon treatment with carbon dioxide. Thus in a non-coördinating solvent, from which the organometallic compound precipitates as it is formed, no specific orientation of either sodium or lithium, can be found. Some significance can perhaps be attached to the higher yields from expt. 2 over expt. 1 and expt. 6 over expts. 3, 4 and 5 as indicating that isostilbene is more reactive than stilbene.

Since these results contradicted those of Schlenk and Bergmann, their experiments using lithium and stilbene in diethyl ether were repeated. Instead of an acid melting at 241° as they reported it was found that a mixture of *meso-* and *dl*-diphenylsuccinic acids was obtained when the impure product was subjected to separation through the barium salts. The proportion (55%) of *meso*-diphenylsuccinic acid isolated from the mixture is much more accurate than that of the *dl*-acid. The organometallic compound formed a reddish-brown solution in the ethyl ether. The yield, not reported by Schlenk and Bergmann, was found to be fair, especially over a twenty-four-hour reaction period (expts. 9, 10).

When glycol dimethyl ether[9] was used as a solvent, even better yields were obtained than with ethyl ether, while the reaction period was likewise shorter (expts. 11–16). The solutions of organometallic compounds were so dark that a color difference between organosodium and lithium was difficult to distinguish. The carboxylated product melted higher than that obtained from benzene or ether and, in spite of the careful separation through the barium salts, no *dl*-diphenylsuccinic acid could be isolated until a larger experiment was carried out (expt. 16), wherein 0.3% of the impure *dl*-diphenylsuccinic acid was isolated and identified. The ratio of diastereomers produced is, therefore, found to be different in benzene, ether, and glycol dimethyl ether, although the ratio of isomers is evidently independent of the metal used.

The possible steps in the addition reaction may be outlined according to the following diagram



---

(9) Scott, Walker and Hansley, THIS JOURNAL, **58**, 2442 (1936).

The first step involves random addition of sodium atoms to the ethylene linkage to give I; if this step were reversible the observed isomerization of isostilbene to stilbene would be expected.[10] The further addition of sodium atoms, with or without Walden inversion to give the pair of diastereomers II and III, is remindful of halogen addition to stilbene, if atomic addition is presumed to cause formation of two dibromostilbenes regardless of the isomer used. The possibility that I → II + III is an equilibrium reaction, or that II and III might dissociate to give a free radical of type IV is exceedingly improbable, but may be discounted further by the fact that the reaction mixture was unaffected by hydrogen, with or without a catalyst (Table I, expts. 13, 15). Finally, a dissociation into sodium cation and organic anion, II and III → V, was suggested by Schlenk and Bergmann, and especially favored by Jeanes and Adams,[3] who considered the sodium ion to be solvated. The ionic hypothesis would explain isomerization in the ethers, though not in benzene, but, unless the ether contributed greatly to anion deformation, it is not clear why different ethers should give different ratios of diastereomers. A better explanation might be afforded if it were assumed that the amorphous ion were subjected to the further influence of the reactant used for characterization. This possibility could not be tested heretofore, because all reactants other than carbon dioxide caused a reversion to stilbene.

Schlenk and Bergmann have shown that the vicinal diorganometallic compound when treated with methyl iodide does not react to give the dimethyl derivative but, instead, reverts to the parent ethylene. In the present investigation it has been found that dimethyl sulfate, unlike methyl iodide, reacts as a methylating agent. The ratio of diastereomers thus obtained is quite different from that produced in the same solvent by the carboxylation reaction. The absolute configuration of the 2,3-diphenylbutanes has not yet been established, but about twice as much low melting isomer as high melting isomer was produced. The ratio of diphenylsuccinic acids in the same solvent, glycol dimethyl ether, was about 300:1. On the basis of two reactions of different type (carboxylation and methylation) it can thus be stated that formation of diastereomeric mixtures is a function of the characterizing reactant. The dependence of stereochemical configuration in the adduct upon the nature of the augend to which the organometallic compound has been added has previously been encountered in the case of geoisomeric Grignard reagents.[11]

Experimental Part

Addition of Sodium or Lithium in Benzene.—A solution of 1.80 g. (0.01 mole) of stilbene or isostilbene in 25 cc. of benzene was placed in a nitrogen-filled Schlenk tube together with 0.02 mole of sodium or lithium, cut into about 50 pieces. After two sharp glass rods were added the tubes were sealed and shaken for periods of one to ten days. Since no apparent reaction took place, the tube was opened under nitrogen, and 0.02 g. of chlorobenzene was added. Reaction commenced in several hours. The precipitate was reddish-brown when lithium was used and reddish-black with sodium, the supernatant liquid being colorless. The reaction mixture was carboxylated by opening the tube under nitrogen, then by means of a sharp-pointed nichrome rod inserted through the straight arm of the tube breaking the bottom so that the contents dropped into a sidearm Erlenmeyer flask which was attached to the bole of the Schlenk tube by a rubber stopper. The Erlenmeyer flask contained a large excess of crushed dry-ice, which had been freed of water crystals by violent shaking of the flask under water-pump vacuum, atmospheric pressure being eventually restored by carbon dioxide evolution. The excess of sodium was decomposed by adding water to the carbon dioxide-filled flask. The water layer was separated from the benzene layer containing impure stilbene, and, after shaking with charcoal, was filtered and acidified with 12% hydrochloric acid to yield diphenylsuccinic acid.

Addition of Sodium and Lithium in Ethers.—The technique employed heretofore for preparation of organolithium compounds[12] was utilized, a stopcock having been sealed to the bottom of a three-necked flask. When glycol dimethyl ether[13] was used as solvent a conical flask[11] was found unsatisfactory when sodium was employed because the metal agglomerates to a solid lump after the reaction has started and thus interferes with the stirrer. No such difficulty was encountered with lithium. Reaction started immediately upon addition of the stilbene; protection from the air was afforded by a blanket of nitrogen rather than a stream of this gas over the reaction mixture. Upon completion of the reaction the contents of the flask were drained from unused metal through the stopcock into dry-ice. The carboxylated mixture was freed of the ether by evaporation at 70 mm. pressure and the residue processed as before.

Separation and Identification of the Diastereomeric Diphenylsuccinic Acids.—This method of Anschütz and Bendix was checked using equal mixtures of *meso-* and *dl*-diphenylsuccinic acids, the latter having been prepared by isomerization of the *meso* acid with barium hydroxide at 200°. The *meso* acid was recovered in 85% yield, m. p. 229°, while 70% of the *dl*-acid, m. p. 180–222°, was obtained.

---

[10] Schlenk and Bergmann, *Ann.*, **463**, 1 (1928).

[11] Wright, *J. Org. Chem.*, **1**, 457 (1936).

[12] Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).

[13] Furnished by courtesy of the Roessler and Hasslacher Chemicals Division, E. I. du Pont de Nemours and Company.

In a typical experiment, 1.56 g. of crude diphenylsuccinic acid was dissolved in ammonia, the excess having been boiled off, and treated with 70 cc. of warm barium hydroxide solution saturated at 25°. The solution was then treated with dry-ice until precipitation was complete, the precipitate being then treated with 1:3 hydrochloric acid. The residue, weighing 0.33 g., melted at 160–210°. It was crystallized from hot water to melt at 180–210° (wt. 0.03 g.) and was identified as *dl*-diphenylsuccinic acid by conversion with diazomethane to the dimethyl ester, m. p. 176–177° after two crystallizations from propanol-1. The filtrate from the barium carbonate precipitation was acidified to yield *meso*-diphenylsuccinic acid, m. p. 226°, weight 0.86 g. This was crystallized from acetic acid or propanol-1 to melt at 229–230° (m. p. 238° when placed in bath 10° below this melting point) and was identified by diazomethane treatment in propanol-1 as the dimethyl ester, m. p. 221–222° after crystallization from the same solvent. This ester was hydrolyzed by twelve hours of boiling with a 1:1 mixture of acetic acid and 12% hydrochloric acid. The product, m. p. 232°, was dissolved in ammonia, filtered and re-acidified with hydrochloric acid to melt at 241° (bath initially at 226°). Repeated crystallization failed to raise the melting point. The melting point of the pure *meso*-diphenylsuccinic acid when quickly heated evidently misled Schlenk and Bergmann to assign a diastereomeric configuration to the identical compound.

Methylation of 1,2-Diphenylethanedisodium.—The organodisodium compound prepared over a three-hour period as before from 1.80 g. (0.01 mole) of isostilbene and 0.46 g. (0.02 mole) of sodium in 30 cc. of glycol dimethyl ether was stirred and maintained at 25° while 2.52 g. (0.02 mole) of freshly distilled dimethyl sulfate in 10 cc. of glycol dimethyl ether was added over a twenty-minute period. After the color was completely bleached, the remaining ball of sodium (0.13 g., 0.006 mole) was removed. The reaction mixture was distilled at 40° (10 mm.) to recover the ether; the remainder was mixed with water and the oil which separated was taken up in benzene and treated with an excess of bromine. After evaporation of the benzene at 20 mm., the remainder was steam distilled. The distillate, extracted with ether and the latter evaporated, furnished an oil which was dissolved in hot ethanol. On cooling, 0.46 g. of 2,3-diphenylbutane separated, m. p. 115°. This was identified, after crystallization from 2 cc. of petroleum ether (b. p. 60–70°) m. p. 124°, by mixed melting point with a sample obtained from Dr. C. F. H. Allen and prepared by reduction of 2,3-diphenylbutadiene-1,3.[14] Evaporation of the crystallizing liquors left 0.04 g. more of the solid isomer together with an oil which distilled at 132–134° (6 mm.), wt. 1.14 g. On the basis of the crude products 21% of the solid isomer and 53% of the liquid isomer were obtained.

When the experiment was repeated using stilbene, the yields of solid and liquid diastereomers of 2,3-diphenylbutane were 20 and 45%, respectively.

Nitration of the 2,3-Diphenylbutanes.—A stirred suspension of 0.11 g. (0.0005 mole) of 2,3-diphenylbutane (m. p. 124°) in 3 cc. of acetic anhydride was chilled to 0° while a nitrating mixture of 2 cc. of nitric acid (sp. gr. 1.52) and 2 cc. of acetic anhydride was added over a one-minute period. After fourteen hours the precipitate was filtered off, wt. 0.10 g. (65% of theoretical), m. p. 249°. When crystallized from 7 cc. of benzene this melted at 256°, same on recrystallization from benzene.

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 64.0; H, 5.37; N, 9.33. Found: C, 64.5; H, 5.37; N, 9.50.

The experiment was repeated using the liquid isomer. No precipitate appeared following the nitration, so the reaction mixture was poured into ice and water, and alkali was added to *p*H 6. The precipitate was taken up in ether; after evaporation the latter was crystallized from ethanol to yield a crude dinitrodiphenylbutane, m. p. 121–122° in 40% yield. This was recrystallized from ethanol to melt at 133°. None of the much less soluble high melting diastereomer, which is insoluble in the nitrating mixture, was detected in this latter nitration.

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 64.0; H, 5.37; N, 9.33. Found: C, 64.2; H, 5.31; N, 9.42.

Oxidation of the 2,3-Di-(*p*-nitrophenyl)-butanes.—Both of the dinitro compounds were recovered unchanged after boiling with potassium permanganate in acetic acid, but when 0.05 g. (0.00016 mole) of either dinitro compound was boiled in 1.5 cc. of acetic acid with 0.160 g. of chromic anhydride, a 90% yield of *p*-nitrobenzoic acid, m. p. 238–239°, was obtained and identified by mixed melting point.

Thanks are due Miss Joan Romeyn for carrying out the microanalyses reported here.

Summary

1. It has been found, contrary to previous reports, that the addition of alkali metals to stilbene gives a mixture of diasteromers.

2. When *s*-diphenylethanedisodium is treated with dimethyl sulfate a good yield of 2,3-diphenylbutane may be obtained.

3. The isomerization which results in a mixture of diastereomers is thought to occur chiefly when the organoalkali compound is characterized as the derivative and, therefore, the mixture of isomeric products is not indicative regarding configuration of the organometallic compound.

TORONTO, ONTARIO, CANADA RECEIVED MAY 4, 1939

---

[14] Allen, Eliot and Bell, *Can. J. Research.* **17**, 75 (1939).