wise, the recent observation of Laitinen and Shoemaker[4] on the reversible polarographic reduction of the ammonium ion in liquid ammonia to ammonium amalgam indicates a rather high stability of the N–H bonds in this ion. Burg's postulate has, however, been proven to be correct under the experimental conditions employed. The exchange was followed by observing the disappearance of N^{15} in ammonium chloride which originally contained 13.77% N^{15} in the ammonium ion.

Ammonium nitrate containing 14% N^{15} was purchased from Eastman Kodak Co. and was converted to ammonium chloride by allowing ammonia to distil from a sodium hydroxide solution of the salt into hydrochloric acid. After evaporation the ammonium chloride was further dried at 110°. The ammonia was anhydrous commercial grade material and was dried by condensation on sodium metal before use.

The apparatus and procedure for preparing the liquid ammonia solutions were essentially those described by Laitinen and Nyman.[5] In all experiments described here, 0.2 g. of ammonium chloride was dissolved in 10 cc. of liquid ammonia. Approximately six minutes were required to condense the ammonia in the reaction vessel (a plain glass tube) and to get the salt dissolved completely. When the sample had dissolved completely, the ammonia was evaporated as rapidly as possible. The ammonium chloride was converted to nitrogen gas by passing the vapor over hot cupric oxide. The mass spectrographic analysis for N^{15} was carried out by the Mass Spectrometry Section of the National Bureau of Standards.

Two experiments were carried out at −33° (b. p. of ammonia), and seven minutes were required for the removal of the ammonia after the salt was dissolved. The percentage N^{15} decreased from 13.77 to 0.52 in both instances. In an experiment carried out at −60°, the percentage N^{15} decreased from 13.77 to 0.51, twenty-two minutes being required to evaporate off the ammonia. An additional experiment carried out at −40° for two hours showed a decrease in N^{15} concentration in the ammonium ion from 13.77 to 0.52%. Assuming the exchange to be complete in this time, the results indicate complete exchange in the experiments described previously.

The possibility of this reaction being catalyzed by water was considered, and in one reaction, the following precautions were taken to exclude water. An apparatus was constructed which allowed the sample to be dried *in vacuo* over phosphorus pentoxide and in which the ammonia could be condensed without exposing the sample to the atmosphere. The conditions of this experiment were the same as those at −33°, and the results indicated complete exchange as above.

The two possible mechanisms by which the exchange might occur are

$$\overset{*}{N}H_4^+ + NH_3 \rightleftarrows \overset{*}{N}H_3 + NH_4^+ \text{ and} \qquad (I)$$

$$2NH_3 \rightleftarrows NH_4^+ + NH_2^-. \qquad (II)$$

Because of the rapidity of the exchange, it is impossible to determine by our present procedure which of these two mechanisms is correct. An attempt to study this and similar problems in liquid ammonia by use of radioactive hydrogen is in progress. The improved techniques will allow much closer control of the time, concentration and temperature, and, in addition, will allow more complete exclusion of water.

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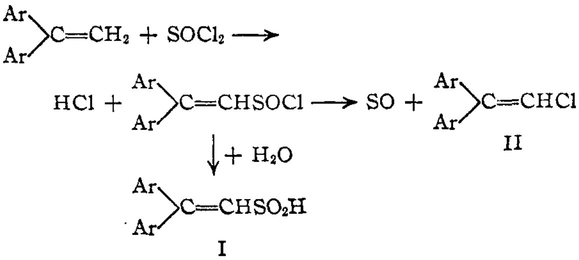
[4] H. A. Laitinen and C. E. Shoemaker, private communication.

[5] H. A. Laitinen and C. J. Nyman, THIS JOURNAL, **70**, 2241 (1948).

On the Reaction of 1,1-Diarylethylenes with Thionyl Chloride

BY SAUL PATAI AND FELIX BERGMANN

1,1-Diarylethylenes are attacked by a number of reagents, which normally do not react with olefinic double bonds, *e. g.*, phosphorus pentachloride[1] and oxalyl chloride.[2] It is a characteristic effect of the strong polarization in 1,1-diarylethylenes that they deform the valency orbitals of the central atom of the above-mentioned reagents towards a cationic state and thus make possible addition to their own negatively charged β-carbon atom. Assuming this to be a general phenomenon, we examined the behavior of diarylethylenes toward other inorganic and organic molecules of similar electronic structure and wish to report here as the first example our results with thionyl chloride. This compound can be considered as a formal analog of phosgene, which has been found previously to react with 1,1-di-(*p*-anisyl)-ethylene.[3] We have been able to isolate from the reaction with 1,1-diphenylethylene the expected 1,1-diphenylethylene-2-sulfinic acid (I) in 17% yield, a reaction which can be represented schematically as



$$Ar_2C{=}CH_2 + SOCl_2 \longrightarrow HCl + Ar_2C{=}CHSOCl \longrightarrow SO + Ar_2C{=}CHCl \;(II)$$

$$Ar_2C{=}CHSOCl \xrightarrow{+H_2O} Ar_2C{=}CHSO_2H \;(I)$$

The structure of the sulfinic acid is deduced from the independent synthesis of I from diphenylvinylmagnesium bromide and sulfur dioxide.

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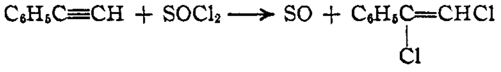
(1) F. Bergmann and Bondi, *Ber.*, **63**, 1158 (1930); **64**, 1455 (1931).

(2) Kharasch, Kane and Brown, THIS JOURNAL, **64**, 333 (1942).

(3) F. Bergmann and co-workers, *ibid.*, **70**, 1612 (1948).

However, in most cases the only compound isolated was the 1,1-diarylvinyl chloride (II), which also represents the main reaction product in the case of 1,1-diphenylethylene. The course of this chlorination is by no means simple. The reaction equation requires the elimination of sulfur monoxide, but so far we have been unable to show its presence among the gaseous reaction products. In some cases higher chlorination products have been found. It is also significant that phenylacetylene (III) is converted into 1,2-dichlorostyrene (IV).



$$C_6H_5C{\equiv}CH + SOCl_2 \longrightarrow SO + C_6H_5\underset{\displaystyle Cl}{\underset{|}{C}}{=}CHCl$$

III IV

In general, the interaction of thionyl chloride with diarylethylenes represents the most convenient method for the preparation of 1,1-diarylvinyl chlorides. In the case of 1,1-di-(*p*-anisyl)-ethylene a nuclear chlorination occurred in addition to the substitution at the *β*-carbon atom. The product contained three chlorine atoms and its structure is now under investigation.

Experimental[4]

Reaction of Thionyl Chloride with 1,1-Diphenylethylene.—A mixture of the chloride (10 cc.) and diphenylethylene (4 g.) in dry ether (10 cc.), when prepared at 0°, showed no sign of reaction until the temperature of the bath was raised to 55°. The reaction vessel was kept at this temperature, until the evolution of gases ceased (about four hours). The mixture was left overnight, then all volatile components were removed *in vacuo* at room temperature and the residue was poured into a mixture of ice and dilute sodium carbonate. The neutral oil that separated, was extracted with ether and the aqueous layer then acidified with ice-cold hydrochloric acid. The white precipitate had a m. p. of 94–95°; yield 0.85 g. (17%). Two crystallizations from dilute ethanol gave white, silky needles of m. p. 97–98°. 1,1-Diphenylethylene-2-sulfinic acid (I) is a strong acid.

Anal. Calcd. for $C_{14}H_{12}O_2S$: C, 68.9; H, 4.9. Found: C, 68.5; H, 5.3.

The ethereal extract gave 2.2 g. (45%) of an oil, boiling at 150° (1.25 mm.). It solidified after prolonged standing and then showed a m. p. of 41°.[5]

Anal. Calcd. for $C_{14}H_{11}Cl$: C, 78.5; H, 5.1. Found: C, 78.3; H, 5.4.

1,1-Diphenylethylene-2-sulfinic acid (I) was synthesized for comparison in the following way: 1,1-diphenylvinylmagnesium bromide was prepared according to Lipp[6] and dry sulfur dioxide bubbled through the solution for ninety minutes. A white precipitate was first formed, but disappeared again and the solution turned dark red-brown. It was washed with ice-water, dilute hydrochloric acid and again water. Then the acid was extracted with 5% sodium carbonate. Acidification gave 1.8 g. (33%) of acid I, m. p. 96°. One recrystallization from dilute ethanol raised the m. p. to 97°, not depressed by admixture of the acid described above.

Reaction of Thionyl Chloride with 1,1-Di-(*p*-bromophenyl)-ethylene.[7]—A mixture of the ethylene (3.4 g.) and thionyl chloride (10 cc.) was kept at room temperature for twenty-four hours and then refluxed on a water-bath for one hour. No acidic product could be isolated from this reaction. The ethereal solution gave 1.5 g. (40%) of 1,1-di-(*p*-bromophenyl)-vinyl chloride; colorless plates from ethanol, m. p. 107–108°.[8]

Anal. Calcd. for $C_{14}H_9ClBr_2$: C, 45.2; H, 2 Found: C, 45.4; H, 2.6.

Reaction of Thionyl Chloride with Di-(*p*-anisyl)-ethylene.—When the ethylene (10 g.) was dissolved in thionyl chloride (30 cc.), a vigorous reaction took place, but the mixture remained cold. It was left at room temperature for six hours and then refluxed for four hours. The excess thionyl chloride was removed *in vacuo*, the residue dissolved in benzene and washed with an ice-cold soda solution. The alkaline extract gave no precipitate upon acidification. The neutral fraction was distilled *in vacuo:* (1) b. p. 130–150° (4 mm.); starting material, about 1 g.; (2) b. p. 170–180° (0.2 mm.). Upon trituration with methanol 4 g. of crystalline material was obtained. From *n*-propanol the product crystallized in long rods of m. p. 155°. Analysis showed it to contain three chlorine atoms.

Anal. Calcd. for $C_{16}H_{13}O_2Cl_3$: C, 56.0; H, 3.8. Found: C, 56.2; H, 3.9.

Reaction of Thionyl Chloride with Phenylacetylene.—Phenylacetylene (5 g.) and thionyl chloride (15 cc.) were mixed at 0° and the mixture left at room temperature for two hours, then refluxed for four hours. Again no acidic product could be isolated. The neutral portion was purified by distillation, b. p. 216° (700 mm.).[9] The yield of 1,2-dichlorostyrene (III) was 1.5 g. (18%). About 2 g. of phenylacetylene was recovered.

Anal. Calcd. for $C_8H_6Cl_2$: C, 55.5; H, 3.5. Found: C, 55.5; H, 3.5.

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[4] All m. p.s are uncorrected.

[5] Buttenberg, *Ann.*, **279**, 325 (1894), gives a b. p. of 189° (39 mm.) and a m. p. of 42° for 1,1-diphenylvinyl chloride.

[6] Lipp, *Ber.*, **56**, 567 (1923).

[7] This reaction is given as an example for the preparation of a diarylvinyl chloride.

[8] Brand and Amelung, *Ber.*, **72**, 1029 (1939), report m. p. 107–108°.

[9] Dyckerhoff, *ibid.*, **10**, 119 (1877), reports a b. p. of 225–231° (760 mm.).

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The Reaction of 1,1-Diarylvinyl Chlorides with Maleic Anhydride

BY FELIX BERGMANN AND JACOB SZMUSZKOWICZ

In an earlier paper[1] we have shown that 1,1-diarylvinyl bromides undergo condensation with maleic anhydride and that the crude intermediate adduct is transformed by heating directly into a fully aromatic derivative of naphthalene-1,2-dicarboxylic acid anhydride (II). In view of the easy preparation of certain 1,1-diarylvinyl chlorides (I) by means of thionyl chloride, described in the foregoing paper,[2] we have investigated the usefulness of such chlorides for the Wagner–Jauregg reaction and observed that the following procedure represents the most convenient route to the anhydrides (II).

The temperature, at which hydrogen chloride is split off is usually 20–30° higher than for the corresponding bromides, but the product is purer and the yield better.

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[1] F. Bergmann and Szmuszkowicz, THIS JOURNAL, **69**, 1777 (1947).

[2] Patai and F. Bergmann, *ibid.*, **72**, 1034 (1950).