The experimental observations appear to be in accord with the following explanation of the changes occurring upon hydrolysis of methyl cellulose. In the initial stage the long chains which may pass through several crystalline and intercrystalline regions are broken and hydrolyzed to the boundaries of the crystalline regions. In the later stage the crystalline regions undergo attack from the surface and those crystallites having short dimensions in the direction of the primary valence bonds are hydrolyzed more rapidly than the longer ones. Through the selective removal of the shorter-chain material the average length of what remains is increased, an increase in viscosity resulting when the material is brought into solution.

It is likely that the introduction of small amounts of methoxyl during the first methylation (batches D and E) disturbed the crystalline pattern of the cellulose more effectively than occurred when essentially all the methoxyl was introduced by the first treatment (batches A and B). Upon hydrolysis the former produced more short-chain crystallites, lower viscosity in chloroform solution, and was more readily attacked by aqueous acid.

An increase in average chain length through selective removal of the shorter material seems to be the most likely explanation of the later-stage viscosity increases. Alternative explanations considered, but regarded as much less satisfactory, include the following: the increases may be due to the partial hydrolysis of methoxyl from the methyl cellulose; or to an altered distribution of the unsubstituted hydroxyl positions as hydrolysis progresses; or to a repolymerization of the hydrolyzed fragments. The first of these explanations seems to be contradicted by analyses indicating no detectable loss of methoxyl due to hydrolysis. The second seems unlikely because the amount of unsubstituted positions is very small. The possibility of repolymerization, the third alternative explanation, seems remote since the only reaction capable of recombining the smaller molecules would involve a reducing end-group forming a glycosidic or acetal structure. In dilute aqueous acid the equilibrium for such a reaction would be expected to favor hydrolysis rather than condensation.

Acknowledgments.—We are indebted to Joseph J. Creely for the X-ray diffraction patterns, and to J. E. Hodge and O. A. Battista for helpful criticism during the preparation of the manuscript.

NEW ORLEANS 19, LOUISIANA

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE HEBREW UNIVERSITY]

The Reaction of 1,1-Diarylethylenes with Thionyl Chloride. II. Preparation of 2,2-Diarylethene-1-sulfinic Acids and Some N-Aryl-2,2-diphenylethene-1-sulfinamides

BY SAUL PATAI AND ABRAHAM PATCHORNIK

RECEIVED MARCH 10, 1952

A number of new 2,2-diarylethene-1-sulfinic acids were prepared by the reaction of 1,1-diarylethylenes with thionyl chloride. The primary product present in the reaction mixture, 2,2-diphenylethene-1-sulfinyl chloride was also used, without isolation, for the preparation of several aryl amides. A polar mechanism is proposed for the reaction. The reaction velocity and the stability of the resulting sulfinyl chlorides and sulfinic acids is shown to be influenced by the various substituents in the para position of the aryl groups.

In a previous communication[1] we reported the preparation of 2,2-diphenylethene-1-sulfinic acid from 1,1-diphenylethylene and thionyl chloride. The main product of this reaction and the only identified product of other 1,1-diarylethylenes with thionyl chloride was the corresponding 1,1-diarylvinyl-2-chloride.

The object of the present work was to elucidate the mechanism of the reaction and to determine whether under more carefully controlled conditions the yield of the 2,2-diphenylethene-1-sulfinic acid could be improved; and on the basis of the information so gained, to prepare other 2,2-diarylethene-1-sulfinic acids and some derivatives of these.

Several experiments were made under different light conditions: in ultraviolet light, in diffuse sunlight and in total darkness, without having any effect on the reaction. The presence of benzoyl chloride in the reaction mixture lowered the yield of the sulfinic acid. Accordingly, the reaction probably proceeds through a polar mechanism, in the manner proposed by Kharasch[2] for the carboxylation of 1,1-diphenylethylene by oxalyl chloride.

Two phases of the reaction could be distinguished by direct observation of the reaction mixture: On addition of thionyl chloride to an ether solution of a diarylethylene, a green color developed immediately, without any other signs of the reaction being perceptible. This color is probably due to the formation of a carbonium ion by the addition of thionyl chloride to the polarized double bond of the ethylene.[3] After a shorter or longer period, depending on the reactants used and on the reaction temperature, the second stage of the reaction becomes evident by the evolution of hydrochloric acid from the reaction mixture, which changes its color from green to yellow or brown. The end of this stage, as indicated by the slowing down of the gas evolution, coincides with the greatest attainable concentration of the 2,2-diarylethene-1-sulfinyl chloride in the reaction mixture. Any further delay in the working up of the reaction

---

(1) S. Patai and F. Bergmann, THIS JOURNAL, **72**, 1034 (1950).

(2) M. S. Kharasch, *et al.*, *ibid.*, **64**, 333 (1942).

(3) A similar green color was observed on the addition of arsenious chloride to 1,1-diphenylethylene (S. Patai, *et al.*, *ibid.*, **72**, 923 (1950)) and also on the addition of stannic chloride to 1,1-diphenylethylene.

mixture diminishes the yield of the sulfinic acids. It was also found that use of a large excess of thionyl chloride catalyzed the decomposition of the sulfinyl chlorides. In this case, or if the reaction was carried out without a solvent, the maximum yield was reached in a shorter time, but was considerably lower than that with a lower concentration of thionyl chloride.

Comparison of the optimum reaction times with different 1,1-diarylethylenes at room temperature shows that substitution of the para hydrogen in the aryl groups by methoxy or methyl greatly increases the reactivity of the ethylene, whereas chlorine or bromine seem to diminish the reactivity.

The stability of the sulfinyl chlorides was also a function of the parent diarylethylene. In general, the quicker a diarylethylene reacted with thionyl chloride, the quicker the corresponding sulfinyl chloride decomposed. The same was also found to be true for the sulfinic acids, which had no true melting points but decomposed at about 100°. The acids derived from the less reactive diarylethylenes were quite stable at room temperature and could be crystallized easily; the 2,2-di-(*p*-anisyl)-ethene-1-sulfinic acid, on the other hand, could not be purified in the free state, as it decomposed even at room temperatures and could be stored only in dilute solutions.

N-Aryl-2,2-diphenylethene-1-sulfinamides were prepared from the ether solution of the sulfinyl chloride, by addition of an ether solution of the aryl amine. In contrast to the acid chlorides and the free acids, these arylamides, as well as the anilinium salts of the sulfinic acids, were quite stable.

Experimental

All melting points are uncorrected.

2,2-Diphenylethene-1-sulfinic Acid. (a) Without Heating.—Four grams of 1,1-diphenylethylene[4] was dissolved in 10 ml. of dry ether or benzene, 10 ml. of purified thionyl chloride[5] was added and the mixture, protected from moisture by a drying tube, was left at room temperature for 48 hours.[6] Worked up as described previously,[1] the acid was obtained in the form of white needles, m.p. 98° (dec.)[1]; yield 30–33%. **(b) With Heating.**—The same reaction mixture as above was heated in a water-bath held at 56–59° for four hours[7] and then worked up as above, yield 28–30%.

2,2-Diphenylethene-1-sulfinyl Chloride.—To a solution of 1 g. of the sulfinic acid in 5 ml. of dry benzene there was added, with cooling in an ice-bath, 0.5 ml. of thionyl chloride. The solution was kept at room temperature for 40 minutes and then the solvent and the excess of thionyl chloride were evaporated *in vacuo*. The sulfinyl chloride was obtained in 90–95% yield, calculated on the basis of different arylamides which were prepared from it.

Preparation of N-Aryl-2,2-diphenylethene-1-sulfinamides.—The arylamides were prepared directly from the reaction mixture of 1,1-diphenylethylene and thionyl chloride, after removal of the excess of thionyl chloride. There was no need to purify the sulfinyl chloride, as all the products of the reaction were ether soluble, and on addition of the arylamine a mixture of the sulfinamide with the hydrochloride of the amine precipitated only. This precipitate was filtered and shaken with water to dissolve the hydrochloride. The water insoluble sulfinamide was dried and crystallized. All the experiments for the preparation of the sulfinamides described below were made with 4 g. of 1,1-diphenylethylene as the starting material. In all cases the yields were about 30%. **N-Phenyl-2,2-diphenylethene-1-sulfinamide** was obtained in the form of white needles from ethanol, m.p. 148–149°. *Anal.* Calcd. for $C_{20}H_{17}NOS$: C, 75.2; H, 5.4; S, 10.0. Found: C, 75.6; H, 5.3; S, 10.4. **The N-*p*-anisyl sulfinamide** was crystallized from ethanol or benzene, m.p. 137–138°. *Anal.* Calcd. for $C_{21}H_{19}NO_2S$: C, 72.2; H, 5.5; N, 4.0; S, 9.2. Found: C, 72.6; H, 5.7; N, 4.0; S, 9.1. **The N-*o*-tolyl** derivative was crystallized from *n*-butanol or dioxane. It retained one molecule of strongly bound water of crystallization, which could not be removed by repeated crystallizations or by drying *in vacuo* at 70°. It melted at 138–142°. *Anal.* Calcd. for $C_{21}H_{21}NO_2S$: C, 71.8; H, 6.0; N, 4.0; S, 9.1. Found: C, 72.2; H, 5.8; N, 4.1; S, 9.1. **The N-1-naphthylsulfinamide** crystallized from ethanol in white needles, containing one molecule of water of crystallization, m.p. 139–140°. *Anal.* Calcd. for $C_{24}H_{21}NO_2S$: C, 74.4; H, 5.5. Found: C, 75.1; H, 5.2.

2,2-Di-(*p*-tolyl)-ethene-1-sulfinic Acid.—To a solution of 2 g. of 1,1-di-(*p*-tolyl)-ethylene[8] in 10 ml. of dry benzene there was added 2 ml. of thionyl chloride and the mixture was heated in a water-bath held at 45° for 45 minutes. The reaction mixture was worked up as above. The sulfinic acid was purified by repeated solution in dilute sodium carbonate and precipitation by hydrochloric acid, and finally by several crystallizations from a mixture of benzene and petroleum ether, taking care not to heat it above 50–55°. It crystallized in long white needles, containing 0.5 mole of benzene. It melted at 78°, resolidified and melted finally at 86° (dec.), yield 30%.

Anal. Calcd. for $C_{19}H_{22}O_2S$: C, 73.3; H, 6.1; S, 10.3. Found: C, 72.7; H, 6.1; S, 10.5.

The anilinium salt of this acid precipitated from the ether solution upon addition of aniline, and was purified by solution in ethanol and precipitation by ether, m.p. 150° (dec.).

Anal. Calcd. for $C_{22}H_{23}NO_2S$: C, 72.3; H, 6.3. Found: C, 72.6; H, 6.3.

2,2-Di-(*p*-anisyl)-ethene-1-sulfinic Acid.—To a solution of 2 g. of 1,1-di-(*p*-anisyl)-ethylene[9] in 60 ml. of dry ether there was added 6 ml. of thionyl chloride. The mixture was heated for 15 minutes in a water-bath at 50° and immediately poured on a large excess of crushed ice and stirred thoroughly. (The usual procedure, *i.e.*, distillation of the solvent and the thionyl chloride *in vacuo*, resulted in this case in largely diminished yields.) The ether layer, containing the free acid, was worked up as usual. The acid, on filtration, turned gummy after a short time and could not be purified. It was again dissolved in ether, dried over potassium sulfate and precipitated in the form of the *anilinium salt*. This was purified by solution in ethanol and precipitation by ether containing aniline, as it was fairly soluble in pure ether. The resulting white crystals melted at 130–135° (dec.), yield 30%.

Anal. Calcd. for $C_{22}H_{23}NO_4S$: C, 66.5; H, 5.8; N, 3.6. Found: C, 66.7; H, 6.2; N, 3.6.

2,2-Di-(*p*-fluorophenyl)-ethene-1-sulfinic Acid.—One gram of 1,1-di-(*p*-fluorophenyl)-ethylene[10] (prepared from the benzophenone[11] and methylmagnesium iodide) was mixed with 1 ml. of thionyl chloride and left at room temperature for 13 hours. Worked up as usual, the acid was obtained in 25% yield. It crystallized from a mixture of benzene and petroleum ether in colorless clusters of needles, m.p. 96–98° (dec.).

Anal. Calcd. for $C_{14}H_{10}F_2O_2S$: C, 60.0; H, 3.6. Found: C, 60.5; H, 3.9.

2,2-Di-(*p*-chlorophenyl)-ethene-1-sulfinic Acid.—A mixture of 2 g. of 1,1-di-(*p*-chlorophenyl)-ethylene[10,12] with 2 ml. of benzene and 2 ml. of thionyl chloride was left at room temperature for 68 hours. Worked up as usual, the acid

---

[4] C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 226.

[5] D. L. Cottle, THIS JOURNAL, **68**, 1380 (1946).

[6] A series of experiments made at room temperature showed that this reaction time gave maximum yields. Longer reaction periods gave diminished yields, and after 260 hours the yield fell to practically nil.

[7] Further heating again diminished the yield.

[8] A. Bistrzycki and E. Reintke, *Ber.*, **38**, 839 (1905).

[9] P. Pfeiffer and R. Wizinger, *Ann.*, **461**, 145 (1928).

[10] G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 567 (1942).

[11] J. P. Picard and C. W. Kearns, *Can. J. Research*, **B28**, 56 (1950).

[12] E. Bergmann and A. Bondi, *Ber.*, **64**, 1468 (1931).

was obtained in 21% yield. It crystallized from a benzene-ligroin mixture in colorless needles, m.p. 98–99° (dec.).

Anal. Calcd. for $C_{14}H_{10}Cl_2O_2S$: C, 53.7; H, 3.3; Cl, 22.6; S, 10.2. Found: C, 53.7; H, 3.2; Cl, 23.0; S, 10.1.

2,2-Di-(*p*-bromophenyl)-ethene-1-sulfinic Acid.—This acid was obtained from 1,1-di-(*p*-bromophenyl)-ethylene[6] as above, but without solvent, after 51 hours at room temperature, in 20% yield, m.p. 102°.

Anal. Calcd. for $C_{14}H_{10}Br_2O_2S$: C, 41.8; H, 2.6; S, 8.0. Found: C, 41.6; H, 2.7; S, 7.8.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, POLYTECHNIC INSTITUTE OF MILAN]

Hydrogen Transfer Reactions Accompanying the Cobalt-catalyzed Addition of Carbon Monoxide to Olefinic Compounds

BY G. NATTA, P. PINO AND R. ERCOLI

RECEIVED FEBRUARY 25, 1952

The cobalt-catalyzed reaction of carbon monoxide and olefins with alcohols and with amines normally yields esters and amides. In some instances, however, products containing added hydrogen are formed. The hydrogen is furnished by the reactants, possibly *via* the formation and decomposition of cobalt hydrocarbonyl.

During the oxo synthesis, some reduction of aldehydes to alcohols occurs and indeed if the reaction temperature is kept at 185–220°, alcohols are formed as principal products. Table I shows that the extent of hydrogenation depends mostly on time and is not greatly influenced by the nature of the solvent.

TABLE I

Cyclohexene, moles	Solvent	Solvent, g.	Time, minutes	Ratio alcohol/alcohol + aldehyde
0.5	None	..	120	0.95
.5	Benzene	50	120	.93
.5	Cyclohexane	50	120	.96
.5	Cyclohexane	50	50	.29
.5	*n*-Hexane	50	50	.38

The one-step synthesis of alcohols, however, does not give as good yields as can be secured by the isolation of the intermediate aldehyde and subsequent hydrogenation.

The hydrogen consumed in the oxo synthesis is unquestionably furnished by the synthesis gas present in the system. In the closely related reactions of olefins and pure carbon monoxide with alcohols and with amines, products containing added hydrogen are isolated. The hydrogen must be furnished by the reactants in some type of transfer process: in fact products from dehydrogenation of reactants are often detected. In all the experiments described below either Raney cobalt or cobalt-on-kieselguhr was employed as catalyst.

Reaction of Carbon Monoxide and Olefins with Alcohols.—The reaction of olefins having *n* carbon atoms with carbon monoxide and alcohols in addition to providing esters, can lead to the formation of aldehydes and alcohols with *n* + 1 carbon atoms and of ketones having 2*n* + 1 carbon atoms. The four possible reactions are illustrated with cyclohexene and isopropyl alcohol as examples

$$C_6H_{10} + CO + CH_3CHOHCH_3 \longrightarrow C_6H_{11}COOCH(CH_3)_2 \quad (1)$$

$$C_6H_{10} + CO + CH_3CHOHCH_3 \longrightarrow C_6H_{11}COC_6H_{11} + CH_3COCH_3 \quad (2)$$

$$C_6H_{10} + CO + CH_3CHOHCH_3 \longrightarrow C_6H_{11}CHO + CH_3COCH_3 \quad (3)$$

$$C_6H_{10} + CO + 2CH_3CHOHCH_3 \longrightarrow C_6H_{11}CH_2OH + 2CH_3COCH_3 \quad (4)$$

It is apparent that the hydrogen required for reactions 2, 3 and 4 is furnished by dehydrogenation of the isopropyl alcohol to acetone. The competition between the various possible reactions is influenced by the ratio of reactants and as shown in Table II the carbinol is found in largest amount when a large excess of hydrogen donor is present.

TABLE II

Ratio alcohol/cyclohexene	Yield, mole %[a]		
	Dicyclohexyl ketone	Cyclohexyl-carbinol	Ester
0.5	12	4	15
1.3	6	14	30
10	Traces	40	31

[a] Based on the initial concentration of cyclohexene.

When methanol is used in the reaction some aldehydes and ketones are produced according to type reactions 2 and 3. It might therefore be expected that formaldehyde would be formed as a result of a hydrogen transfer process but no appreciable quantity was detected. However, dimethyl ether was found in the gaseous reaction products and it is possible that the required hydrogen was formed *via* the reactions

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

$$H_2O + CO \longrightarrow H_2 + CO_2$$

The competition between the various possible type reactions (1–4) when methanol is used is influenced by the olefin. Table III shows that the yield of esters increases and the yield of ketone decreases with increased size of the olefin. When ethylene is the olefinic substrate, diethyl ketone appears to be the principal product regardless of what alcohol is present. Thus, in the presence of butanol-2 and pentanol-3 the yield of diethyl ketone was 64.5 and 60%, respectively, compared to 57% with methanol.

TABLE III

Olefin	Moles, % esters	Moles, % dialkyl ketone	Moles, % aldehyde
Ethylene	21.5	57	5
Propylene	33.2	26	3
Isobutylene	56.0	Traces	3