t-Bu), 5.07 (s, 1, OH), 6.88 (AB q,[24] 2, J = 16.1 Hz, CH=CHPh), and 7.01–7.52 ppm (m, 7, aromatic H); mass spectrum (70 eV) *m/e* 308.2148 (strong; calcd for $C_{22}H_{28}O$, 308.2140).

Anal. Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15. Found: C, 85.71; H, 9.34.

(24) Analysis of this quartet (see J. A. Elvidge in "Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press Inc., New York, N. Y., 1967, p 52) gives δ_A 6.94, δ_B 6.82. For comparison spectra, see H. Güsten and M. Salzwedel, *Tetrahedron*, **23**, 173 (1967).

Registry No.—**1**, 2607-52-5; **3**, 21363-59-7; **11**, 21363-60-0; **20**, 21449-69-4; **23**, 15017-98-8; **24**, 21363-62-2; triethyl phosphite, 122-52-1.

Acknowledgment.—The authors are indebted to Mr. H. J. Tarski for excellent technical assistance and to Drs. F. H. Field and H. G. Schutze for encouragement and administrative support.

Studies of Nitriles. I. Synthesis of Fumaro- and Maleonitrile by a Novel Pyrolytic Coupling Reaction[1]

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Received March 6, 1969

It was found that the pyrolysis of monohalogenoacetonitriles at 800–1000° under reduced pressure resulted in a novel pyrolytic coupling reaction to yield fumaro- and maleonitrile in 50–60% yields. Further refinements of the reaction led to a single-step synthesis of fumaro- and maleonitrile from acetonitrile and chlorine. Similarly, the pyrolysis of di- and trichloroacetonitrile and the mixed pyrolysis of chloroacetonitriles and acetonitrile were studied. Discussions are given on the mechanism of these reactions.

In recent years, three- and four-carbon unsaturated nitriles, prepared mainly by the gas-phase reactions,[2] have attracted much interest as basic building blocks for the production of a number of synthetic polymers. There are also several reports which describe the syntheses of more complicated nitriles, such as malononitrile,[3] cyanoacetylene,[4] dicyanoacetylene,[5] etc., by essentially gas-phase reactions. It should be noted that all these syntheses have been performed on the basis that the nitriles possess considerable stability at high temperatures. Our attention was therefore directed toward synthesizing the nitriles which are difficult to prepare in a liquid phase, by means of a vapor-phase reaction, and utilizing them for the synthesis of various heterocyclic compounds.[6]

To date, several syntheses of fumaronitrile have been reported which involve (a) dehydration of fumaroamide;[7] (b) the reaction of *trans*-diiodoethylene with cuprous cyanide;[8] (c) the reaction between β-chloroacrylonitrile and sodium cyanide;[9] and (d) the reaction of acetonitrile with hydrogen cyanide.[10] However, none of them so far recorded gave a satisfactory yield and all were far from being commercially feasible. Similarly, for the synthesis of maleonitrile, (a) the dehydration of maleoamide;[7] (b) the reaction of *cis*-diiodoethylene with cuprous cyanide;[8] and (c) the isomerization of fumaronitrile in the presence of hydrogen chloride[11] have been reported. A recent patent[12] claims that succinic acid can be converted into a mixture of fumaro- and maleonitrile in a single step over a complex metal oxide catalyst by the reaction with ammonia and oxygen. More recently, after completion of our experiments, another patent[13] appeared which claimed essentially the same reaction as our experiments. They disclosed that the reaction of chlorine with acetonitrile at high temperature afforded a mixture of fumaro- and maleonitrile in less than 20% yield.

We have found that the pyrolysis of monohalogenoacetonitriles at an elevated temperature (800–1000°) and under reduced pressure (5–20 mm) gave a mixture of fumaro- and maleonitrile in 50–60% yield. The pyrolytic coupling of other halogenoacetonitriles have also been investigated under various conditions.

Results

Pyrolysis of Monohalogenoacetonitriles.—The pyrolysis of monochloro- or monobromoacetonitrile was carried out in an unpacked quartz tube at 800–1000°

(1) Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, Japan, April 1968.

(2) Some simple unsaturated nitriles such as acrylonitrile, methacrylonitrile, and benzonitrile are synthesized by the method known as ammoxidation from the corresponding hydrocarbons, *e.g.*, propene, isobutylene, and toluene. They are also made by the oxidation of the corresponding amines. Acrylonitrile has been produced by the addition of hydrogen cyanide to acetylene by a vapor-phase reaction.

(3) J. K. Dixon, U. S. Patent 2,553,406 (1951); *Chem. Abstr.*, **45**, 9081 (1951); U. S. Patent 2,606,917 (1952); *Chem. Abstr.*, **47**, 5964 (1953).

(4) L. J. Krebaum, U. S. Patent 3,079,424 (1963); *Chem. Abstr.*, **59**, 3777 (1963); *J. Org. Chem.*, **31**, 4103 (1966).

(5) E. I. Du Pont de Nemours and Co., Inc., U. S. Patent 3,070,622 (1962); *Chem. Abstr.*, **59**, 454 (1964); E. Ciganek and C. G. Krespan, *J. Org. Chem.*, **33**, 541 (1968).

(6) F. Johnson and R. Madronero, *Advan. Heterocycl. Chem.*, **6**, 95, (1966).

(7) (a) E. H. Keiser and J. J. Kessler, *Am. Chem. J.*, **46**, 523 (1911); (b) L. McMaster and F. B. Langreck, *J. Amer. Chem. Soc.*, **40**, 970 (1918); (c) J. de Wolf and L. van de Straete, *Bull. Classe Sci., Acad. Roy. Belges*, **21**, 216 (1935); *Chem. Abstr.*, **29**, 3985 (1935); (d) D. T. Mowry and J. M. Butler, *Org. Syn.*, **30**, 46 (1950); (e) J. de Wolf and L. van de Straete, *Bull. Soc. Chim. Belges*, **44**, 288 (1935); (f) A. T. Blomquist and E C. Winslow, *J. Org. Chem.*, **10**, 155 (1945); (g) H. A. Pace, U. S. Patent 2,438,019 (1948); *Chem. Abstr.*, **42**, 4606 (1948); (h) U. S. Patent 2,121,551 (1936); *Chem. Abstr.*, **32**, 6259 (1938).

(8) (a) J. Jennen, *Bull. Classe Sci., Acad. Roy. Belges*, **22**, 1169 (1936); *Chem. Abstr.*, **31**, 1010 (1937); (b) J. Jennen, *Bull. Soc. Chim. Belges*, **46**, 199 (1937); (c) C. A. Hochwalt, U. S. Patent 2,399,349 (1946); *Chem. Abstr.*, **40**, 4744 (1946).

(9) D. T. Mowry and W. H. Yanko, U. S. Patent 2,471,767 (1949); *Chem. Abstr.*, **43**, 7498 (1949).

(10) L. J. Krebaum, U. S. Patent 3,055,738 (1962); *Chem. Abstr.*, **58**, 2375 (1963).

(11) H. Mommaerts, *Bull. Soc. Chim. Belges*, **52**, 63 (1943). As for the thermal equilibrium between fumaro- and maleonitriles, see F. M. Lewis and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1533 (1948); and as for ultraviolet light induced isomerization, see J. Jennen, *Bull. Soc. Chim. Belges*, **46**, 258 (1937).

(12) Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler, Netherlands Appl., **6**, 414,353 (1965); *Chem. Abstr.*, **63**, 17915 (1965).

(13) M. Taguchi, M. Aramaki, and T. Fujii, Japanese Patent 42-17965 (1967).

TABLE I

CONDITIONS AND RESULTS OF THE PYROLYSIS OF MONOHALOGENOACETONITRILES

Material	Amt, g	Reaction temp, °C	Other conditions	Reaction time, min	Yield,[a] % II	III	total
$ClCH_2CN$	10	800	Atm press N_2, 40 cc/m	60	13	5	18
$ClCH_2CN$	10	800	Atm press He, 40 cc/m	150	32	16	48
$ClCH_2CN$	10	900	23.5 mm	50	41	16	57
$ClCH_2CN$	5	900	4.5 mm	30	10	4	14
$ClCH_2CN$	5	1000	6.5 mm	35	48	11	59
$BrCH_2CN$	8.7	800	Atm press He, 40 cc/m	90	36	22	58
$BrCH_2CN$	5	800	22.0 mm	41	32	10	42
$BrCH_2CN$	10	900	23.5 mm	50	38	26	64
$BrCH_2CN$	5	1000	6.0 mm	33	36	14	50
ICH_2CN	20	900	21.5 mm	120	11	5	16

[a] Yields were obtained by distillation.

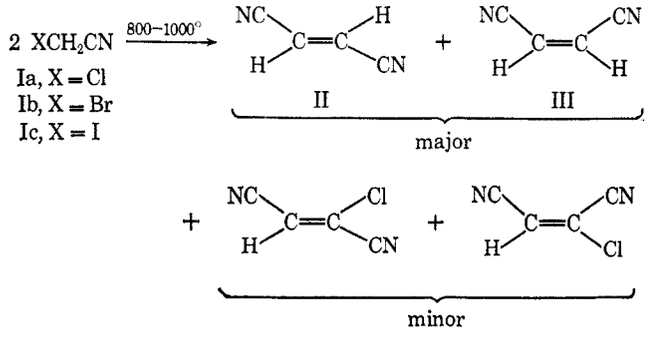
TABLE II

CONDITIONS AND RESULTS OF THE ONE-STEP SYNTHESIS OF FUMARO- AND MALEONITRILE FROM ACETONITRILE AND CHLORINE

CH_3CN Used, g	CH_3CN Consumed, g	CH_3CN/Cl_2 mol ratio	Temp of furnaces, °C II[a]	III[a]	Pressure, mm	Reaction time, min	Total yield[b] of fumaro- and maleonitrile, g (%)	Amt of distillable material,[c] g	Carbon and tar, g	Distillation residue, g
12.3	12.3	3:2	400	800	Atm press	100		1.8		0.6
16.4	16.4	2:1	400	800	Atm press	100		4.6	4.3	0.9
10.6	6.8	1.3:1	500	900	101	100	2.7 (42)	3.9	2.0	0.3
18.5	9.8	3.6:1	500	900	60–80	100	4.7 (50)	6.3	0.8	0.1
8.9	2.7	2.9:1	400	800	60–80	60	1.7 (68)	2.9	0.4	0.03
10.0	5.7	3:1	400	900	64–74	70	2.7 (50)	3.2		0.06
16.0	10.7	3:1	500	900	100	90	4.9 (48)	5.3	1.5	0.2

[a] The length of furnace II was 15 cm, and that of III was 20 cm. [b] Determined by gas chromatography. [c] Distillation was performed at 20-mm pressure.

under reduced pressure. Gas chromatography and physico-chemical measurements of the products clearly demonstrated that the main products were fumaro- and maleonitrile. Each of the products was separated either by a gas chromatographic technique or by a fractional distillation under reduced pressure. The nmr spectrum of fumaronitrile gave a singlet at 6.32 ppm in $CDCl_3$ and maleonitrile gave a singlet at 6.24 ppm. Further scrutiny of the reaction products led to the isolation of two other pure compounds, which were proved to be monochlorofumaro- and monochloromaleonitrile, respectively. Thus, the net reaction of the present pyrolytic coupling is as depicted by the following.



The detailed conditions of the reaction and the yields are summarized in Table I. The results demonstrate that the reaction is feasible at atmospheric pressure, but better yields are accessible under reduced pressure. In case the reaction was carried out under reduced pressure, a higher temperature was required as compared with the reaction at an atmospheric pressure. This would probably be due to the fact that the net contact time is reduced at low pressures. The average contact time in the present experiments was estimated at 3–4 sec at atmospheric pressure and 0.1 sec at a pressure of 25 mm.

Synthesis of Fumaro- and Maleonitrile by Pyrolytic Coupling of Acetonitrile in the Presence of Chlorine.—Our attempt was then directed toward a direct synthesis of fumaro- and maleonitrile from acetonitrile and chlorine because acetonitrile was known to be accessible to chlorination in the vapor phase at 250–550° without catalyst.[14]

The results and the experimental conditions are summarized in Table II. The yields were calculated on the acetonitrile consumed because the exact quantity of chlorine in the experiment was not accurately measurable. When reactions were run at atmospheric pressure, practically no fumaro- and maleonitrile was produced; however, at reduced pressure, the conversion yields reached almost 100% and the selectivity was 60% on the basis of the acetonitrile consumed. By-products in these reactions were isolated by a preparative gas chromatographic technique and were characterized as chlorinated fumaro- and maleonitriles. It should be noted that higher molar ratios of chlorine to acetonitrile and higher reaction temperatures led to higher

(14) Rohm & Haas, U. S. Patent 2,283,237 (1940); *Chem. Abstr.*, **36**, 6171 (1942); J. P. Henry and J. W. Clark, U. S. Patent 3,121,735 (1964).

TABLE III

SINGLE AND MIXED PYROLYSIS OF HALOGENOACETONITRILES. PRODUCTS AND THEIR MOLE PER CENT YIELDS[a]

Material (Amt used, g)	Mol ratio	Temp of furnaces,[b] °C I	II	Pressure, mm	Reaction time, min	Total yield,[c] g	Products and their mol % yields: $Cl_2C{=}CCl_2$	$ClCH_2CN$	$Cl_2C{=}CClCN$	NCClC=CClCN *trans*	NCClC=CClCN *cis*	NCCH=CHCN *trans*	NCCH=CHCN *cis*	$CH_2(CN)_2$
ClH_2CN (10)	Neat	800	900	18	30	4.2								
$Cl_2CHCN + CH_3CN$ (5.5, 2.1)	1:1	800	900	13	53	2.3								
$Cl_2CHCN + CH_3CN$ (5.5, 4.1)	1:2	800	900	15	40	1.8								
Cl_3CCN (10)	Neat	600	800	34	20	3.1	23		55	12	10			
Cl_2CHCN (10)	Neat	600	800	40	28	1.5	1	17	11	28	26	13	4	
$Cl_3CCN + CH_3CN$ (5.0, 1.42)	1:1	720	840	21	20	2.4				4	3	52	29	4	8
$ClCH_2CN + Cl_2CHCN$ (3.75, 5.5)	1:1	700	900	20	30	2.5				8	6	40	25	13	8

[a] Mole per cent yields were calculated on an assumption that the peak area in the gas chromatogram is roughly proportional to the weight of the component; *cf.* D. M. Rosie and R. L. Brob, *Anal. Chem.*, **29**, 1263 (1957); A. E. Messner, E. M. Rosie, and P. A. Argabright, *ibid.*, **31**, 230 (1959). [b] The length of furnace I was 10 cm, and that of II was 20 cm. [c] The total weight of distillable materials.

conversion yields, although the products contained larger amounts of by-products.

Pyrolysis of Di- and Trichloroacetonitrile, and Co-pyrolysis of Di- or Trichloroacetonitrile with Monochloroacetonitrile or Acetonitrile.—Dichloroacetonitrile, trichloroacetonitrile, and mixtures of dichloroacetonitrile and acetonitrile (1:1 and 1:2), dichloroacetonitrile and monochloroacetonitrile (1:1), and trichloroacetonitrile and acetonitrile (1:1) were subjected to pyrolytic coupling at reduced pressure (25 mm) in a quartz tube at temperatures of 800–900°, and the resulting products were analyzed by gas chromatography. Each reaction product revealing several peaks on the gas chromatogram was subjected to isolation by preparative gas chromatography and was characterized by infrared, nmr, and mass spectroscopic data. Table III shows the compounds thus obtained, and the relative yields (mole per cent) of all these products estimated by integrals of the peaks on the chromatogram.

Discussion

The mechanism of the reaction is still highly speculative at present; however, the most plausible one in the case of the pyrolysis of monochloroacetonitrile and a mixture of acetonitrile and chlorine would be represented as shown in eq 1–5.

$$Cl_2 + CH_3CN \longrightarrow ClCH_2CN + HCl \quad (1)$$

$$ClCH_2CN \longrightarrow Cl\cdot + \cdot CH_2CN \quad (2)$$

$$Cl\cdot + ClCH_2CN \longrightarrow ClC\dot{H}CN + HCl \quad (3)$$

$$ClC\dot{H}CN + \cdot CH_2CN \longrightarrow NCCHCH_2CN \quad (4)$$
(Cl)

$$NCCHCH_2CN \longrightarrow NCCH{=}CHCN + HCl \quad (5)$$
(Cl)

It is interesting to note that the pyrolysis of an equimolar mixture of dichloroacetonitrile and acetonitrile led to a product which showed essentially the same gas chromatographic pattern as the one obtained by the pyrolysis of monochloroacetonitrile. Similarly, the pyrolysis of an equimolar mixture of trichloroacetonitrile and acetonitrile furnished a mixture of products which was closely similar to the product from an equimolar mixture of mono- and dichloroacetonitrile. These results would be rationalized on a reasonable assumption that all these chlorinated acetonitriles on pyrolysis gave a similar set of radicals, which recombined to yield a number of products, as shown in Table III.

On this assumption, the formation of fumaro- and maleonitrile from a mixture of dichloroacetonitrile and acetonitrile would be explicable on the following mechanism.

$$Cl_2CHCN \longrightarrow ClC\dot{H}CN + Cl\cdot$$

$$Cl\cdot + CH_3CN \longrightarrow \cdot CH_2CN + HCl$$

$$ClC\dot{H}CN + \cdot CH_2CN \longrightarrow NCCHCH_2CN$$
(Cl)

$$\swarrow$$

$$NCCH{=}CHCN$$

Similarly, the mechanism of the pyrolysis of an equimolar mixture of trichloroacetonitrile and acetonitrile would be given as follows.

$$Cl_3CCN \longrightarrow Cl_2\dot{C}CN + Cl\cdot$$
$$Cl\cdot + CH_3CN \longrightarrow \cdot CH_2CN + HCl$$
$$Cl_2\dot{C}CN + \cdot CH_2CN \longrightarrow NCCCl_2CH_2CN$$
$$\swarrow$$
$$NCCCl{=}CHCN$$

An alternative mechanism, which involves intermediary carbene formation, may also be possible, as can be seen in the pyrolysis of chloroform or methylene chloride.[15] In this connection, the pyrolysis of trichloroacetonitrile appears to provide an interesting speculation for the mechanism. We found that the pyrolysis of trichloroacetonitrile alone resulted in tetrachloroethylene and trichloroacrylonitrile as principal products together with minor quantities of dichlorofumaronitrile. One possible explanation for the mechanism of this reaction would then be depicted as follows.

$$Cl_3CCN \rightarrow :CClCN \xrightarrow{\text{dimerization}} NCClC{=}CClCN$$
$$Cl_3CCN \rightarrow :CClCN \xrightarrow{\text{coupling}} Cl_2C{=}CClCN$$
$$Cl_3CCN \rightarrow :CCl_2 \xrightarrow{\text{dimerization}} Cl_2C{=}CCl_2$$

A similar mechanism appears to be operative for the pyrolysis of monochloroacetonitrile to yield fumaro- and maleonitrile.

$$ClCH_2CN \longrightarrow :CHCN$$
$$2\ :CHCN \longrightarrow NCCH{=}CHCN$$

In fact, we found that the pyrolysis of a mixture of cyclopentadiene (dimer) and monochloroacetonitrile gave benzonitrile in a low yield.

Although the experiment appears to provide evidence for the formation of chlorocyanomethylene carbene as an intermediate of the reaction, this cannot, in our opinion, be unambiguous evidence for the formation of carbene, because benzonitrile may also be formed under such vigorous conditions *via* radical addition of $\cdot CH_2CN$ to cyclopentadiene followed by bond isomerization and dehydrogenation. Further studies should throw light on the mechanism of the present pyrolytic coupling reactions.

Experimental Section

Materials.—Monochloroacetonitrile, monobromoacetonitrile, dichloroacetonitrile, and trichloroacetonitrile were prepared by the dehydration of the corresponding acid amides with phosphorus pentoxide.[16] Monoiodoacetonitrile was prepared by the reaction of monobromoacetonitrile with potassium iodide.[17]

Pyrolysis of Halogenoacetonitriles. A. Examination of the Pyrolytic Behaviors of Halogenoacetonitriles by the "Micro Reactor" Method.—The reaction vessel was a vertical unpacked quartz tube connected to a gas chromatographic column (4 mm × 1 m) packed with 10% tricresylphosphate (TCP) on 60–80 mesh Chromosorb W. The temperature of the column was 150°. The reaction tube was heated to a temperature varying between 600–1000°, while the samples of halogenoacetonitriles (*ca.* 5 mg) were directly injected to the reaction vessel by a microsyringe. The flow rate of helium was *ca.* 40 ml/min and the contact time was *ca.* 10 sec.

B. Pyrolysis of Halogenoacetonitriles by the Flow Method. (1) **Under Atmospheric Pressure.**—A quartz tube (1.2 × 60 cm) was mounted in a horizontally placed cylindrical electric furnace 20 cm long and heated to the desired temperature. The sample to be pyrolyzed was placed in a flask connected to one end of the quartz tube and the flask was heated to *ca.* 100–120° while nitrogen or helium (*ca.* 40 ml/min) was bubbled to carry the reactant into the reaction vessel. A mixed vapor stream of the reactant and the carrier gas was allowed to enter a preheater (15 cm, 250°) and then the reaction tube, which was kept at desired temperatures. The pyrolysis product was collected in two traps in series, the first being cooled with ice–salt and the second with Dry Ice–ethanol. Some of the product, condensed near the outlet of the reaction tube, was washed out with acetone. The combined washing and the reaction products were analyzed by gas chromatography.

(2) **Under Reduced Pressure.**—The reaction was carried out using the same reaction system as used in the experiment under ordinary pressure, with the exception that the gas inlet tube was replaced by a capillary and the end of the trapping system was connected to a vacuum pump. A manometer and a simple pressure controller were inserted. The whole system was evacuated to the required pressure, while the sample was introduced into the reaction tube by distillation under reduced pressure.

Copyrolysis of Acetonitrile and Chlorine. A. Apparatus and Procedure under Atmospheric Pressure.—The reaction equipment was essentially the same as the one described before and consisted of an unpacked quartz tube (6 mm × 60 cm) placed vertically and mounted with three electric furnaces (10, 15, and 20 cm, in this order from the top to the bottom). Acetonitrile was fed to the top of the reaction tube by a stroke pump *via* a vaporizer. The flow rate of chlorine was measured by an orificemeter.

B. Apparatus and Procedures under Reduced Pressure.—The reaction vessel was the same as the one used in the experiment under atmospheric pressure. In order to feed acetonitrile at a given constant rate with an ordinary stroke pump, a vertical mercury column greater than 76 cm in length was placed between the pump and the reaction tube. For the calibration, the flow rate of the chlorine was measured and adjusted, at first under atmospheric pressure by an orificemeter and then under reduced pressure. The crude reaction product, which condensed on the wall of the traps, was collected. Pure samples were isolated by a preparative gas chromatographic technique and identified by their spectral data.

Pyrolysis and Copyrolysis of Polychloroacetonitriles and Acetonitrile. General Procedure.—The reactions were carried out in a 1.2 × 40 cm quartz tube mounted horizontally and heated by two electric furnaces. The whole system was evacuated with an aspirator to *ca.* 20 mm. Samples were leaked into the reaction vessel ("leak method"). The products were collected in a series of traps cooled by Dry Ice–ethanol as described before. The identity of the products thus obtained was established by direct comparison with authentic samples, of which $Cl_2C{=}CClCN$ was produced by the known method.[18]

Copyrolysis of Monochloroacetonitrile and Dicyclopentadiene.—Pyrolysis of a mixture of 7.55 g (0.1 mol) of monochloroacetonitrile and 6.6 g (0.05 mol) of dicyclopentadiene was carried out by the use of the same apparatus and under similar conditions. The pyrolysis took 75 min. The gas chromatography of the reaction product showed three peaks. The second one was identified as benzonitrile from its retention time and the

(15) A. E. Shilov, *Dokl. Akad. Nauk SSSR.*, **98**, 601 (1954).

(16) (a) D. B. Reisner and E. C. Horning, *Org. Syn.*, **30**, 22 (1950); (b) W. Steinkopf, *Ber.*, **41**, 2540 (1908); (c) W. Steinkopf, *ibid.*, **38**, 2694 (1903); (d) H. Bauer, *Ann.*, **229**, 163 (1885).

(17) R. Scholl, *Ber.*, **29**, 2415 (1896).

(18) (a) H. Mommaerts, *Bull. Classe Sci. Acad. Roy. Belges*, **27**, 579 (1941); *Chem. Abstr.*, **38**, 3621 (1944); (b) O. W. Cass, U. S. Patent 2,443,494 (1944); *Chem. Abstr.*, **42**, 7322 (1948); (c) H. Brintzinger, K. Pfannstiel, and H. Koddebusch, *Angew. Chem.*, **60**, 312 (1948).

ir spectrum of the sample isolated by the preparative gas chromatographic technique. The yield of benzonitrile was estimated to be *ca.* 640 mg. Other products were left unidentified.

Registry No.—Fumaronitrile, 764-42-1; maleonitrile, 928-53-0.

Acknowledgment.—The authors are grateful to Dr. S. Tatsuoka, General Manager of the Division, for encouragement throughout this work. Thanks are also due to Mr. K. Shinozaki for measurement of nmr spectra.

Chemistry of Sulfoacetic Acid Derivatives. II.[1a-c] Reactions of Phenyl Esters and Anilides of Sulfoacetic Acid

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Received December 23, 1968

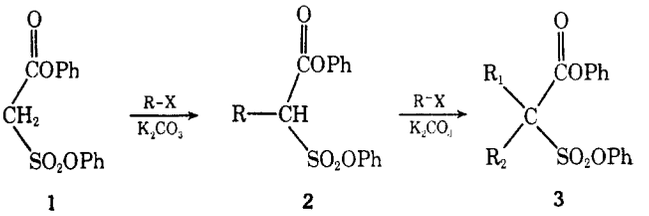
Diphenyl sulfoacetate (1) has been alkylated in an alkaline medium to produce both mono and dialkyl derivatives. 1 was nitrosated in acetic acid–acetic anhydride to form diphenyl acetoximinosulfoacetate (5) and was coupled with benzenediazonium chloride in aqueous alkaline medium to form the phenylhydrazone (6) of diphenyl oxosulfoacetate. Aminolysis of diphenyl sulfoacetate (1) with amines in pyridine medium occurs easily at both the carbonyl and the sulfonyl groups to produce diamides (14, 15, 16, and 17). Phenyl ester and anilide derivatives (1, 14, 18, and 19) of sulfoacetic acid in aqueous acidic medium undergo hydrolysis exclusively at the carbonyl group to form the corresponding carboxylic acids (8 and 23). Under aqueous alkaline conditions, hydrolysis occurs at both the carbonyl and the sulfonyl groups. In constrast, hydrolysis of phenyl ester and anilide derivatives (1, 2, 14, 18, 19, and 21) of sulfoacetic acid in pyridine occurs predominantly at the sulfonyl function, producing the corresponding sulfonic acids, isolated as the pyridinium salts (11, 13, 22, 26, and 28), as the major products. The hydrolysis and aminolysis reactions at the sulfonyl group in pyridine and aqueous alkaline media may occur by the formation of an intermediate sulfene (30), followed by addition of the nucleophilic water or amine to the sulfene.

Derivatives of sulfoacetic acid contain the α-sulfonylacetyl functional grouping, $-SO_2CH_2CO-$. The carbonyl and the sulfonyl groups are both subject to attack by nucleophilic agents, although to distinguishable degrees. The central methylene hydrogen atoms are activated by both the carbonyl group and the sulfonyl group. In summary, derivatives of sulfoacetic acid should show unusual versatility and synthetic utility in the reactions which they undergo and the new products which they form.

The chemistry of sulfoacetic acid and its derivatives has been investigated by Vieillefosse[2] and by Bodendorf and Senger.[3] Derivatives of sulfoacetic acid have been cyclized to form thiadiazines by Hinman[4] and Wawzonek[5] and their coworkers. Loev and coworkers[6] have cyclized N-phenylsulfamylacetic acid to sulfostyril.

Anionic Reactions of Diphenyl Sulfoacetate.—As described earlier,[4c] diphenyl sulfoacetate (1) (Chart I) undergoes reaction with methyl iodide in *t*-butyl alcohol containing *t*-butoxide ion base to form diphenyl α-sulfopropionate (2, R = CH_3) and diphenyl α-sulfoisobutyrate (3, $R_1 = R_2 = CH_3$). Our most recent work has shown that the alkylation of diphenyl sulfoacetate (1) is most conveniently carried out in high yields using refluxing acetone as solvent and anhydrous potassium carbonate as base. Dialkylation of diphenyl sulfoacetate (1) is readily accomplished in high yield by the use of excess alkyl halide and excess potassium carbonate. Monoalkylation, with a minimum of dialkylation, is best achieved by the slow addition of 1 equiv of solid potassium carbonate to an acetone solution of the alkyl halide and diphenyl sulfoacetate (1) (Scheme I).

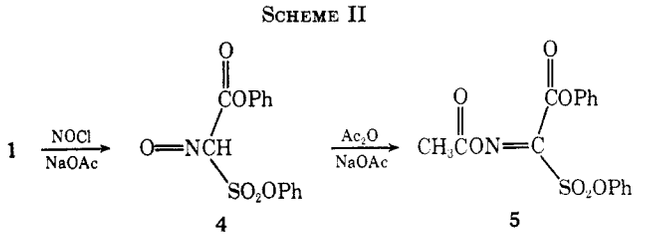
SCHEME I



1 2 3

Diphenyl sulfoacetate (1) undergoes nitrosation at the methylene group on treatment with nitrosyl chloride in an anhydrous mixture of acetic acid, acetic anhydride, and sodium acetate. The nitroso compound (4) initially formed was isolated from the reaction mixture as the oxime acetate (5) (Scheme II).

SCHEME II



4 5

(1) (a) Part I: B. E. Hoogenboom, E. D. Hoganson, and M. S. El-Faghi, *J. Org. Chem.*, **33**, 2113 (1968). (b) Supported by a F. G. Cottrell grant from the Research Corp., Public Health Service Grant GM12153, and National Science Foundation Undergraduate Research Participation, Grant No. GY-3078, GE-1021, GE-2955, and GE-9467. (c) Presented in part before the Organic Division of the American Chemical Society at its 156th National meeting in Atlantic City, N. J., Sept., 1968. (d) To whom all inquiries should be addressed.

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