

arylation of the analogous ethyl aryl sulfones by substitution of ethyl sulfate, however, were less well rewarded. Despite a number of variations in the alkylation of sodium benzenesulfinate by ethyl sulfate, the yields could not be increased beyond about 34–48%; sodium *p*-toluenesulfinate gave ethyl *p*-tolyl sulfone in 45% yield. The route of choice for ethyl aryl sulfones, therefore, probably is ethylation of the sulfinate with an ethyl halide.

#### EXPERIMENTAL<sup>8</sup>

*Methyl phenyl sulfone* (I). The reduction was based on that of Oxley *et al.*<sup>4</sup> A mixture of 600 g. of anhydrous sodium sulfite, 420 g. of sodium bicarbonate, and 2.4 l. of water was heated on a hot plate at 70–80°. This temperature was maintained by switching off the hot plate occasionally, while 447 g. (325 ml.) of benzenesulfonyl chloride<sup>9</sup> was added with stirring during 3 hr. Heating and stirring were then continued until the volume did not exceed 2.4 l. (but at least for 1 hr.). The mixture was then allowed to stand overnight at room temperature, and the solid was collected by filtration. The filter cake was then used without further treatment in the alkylation step; moisture in the cake is unimportant, and salts other than the sulfinate probably have a desirable effect in reducing the rate of hydrolysis of methyl sulfate.<sup>9</sup>

In the alkylation procedure, suggested by that of Baldwin and Robinson,<sup>5</sup> the filter cake was mixed with 400 g. of sodium bicarbonate and 490 g. (370 ml.) of methyl sulfate<sup>9,10</sup> in a 3-necked flask provided with a stirrer, condenser, and dropping funnel containing 925 ml. of water. Enough of the water was added to permit stirring (*ca.* 100 ml.), and the remainder then added during 3 hr. with stirring. The mixture was then heated under reflux with stirring for 20 hr. It was then cooled to about 75°, and 200 ml. of benzene was added and the mixture was stirred briefly. All liquid was then decanted from solid into a separatory funnel. The aqueous layer was separated, extracted with 200 ml. more of benzene, and returned to the funnel. Solid remaining in the flask was washed into the separatory funnel with *ca.* 2 l. of water, after which the mixture was shaken with 200-ml. portions of benzene until all solid had been dissolved (three portions usually sufficed).

After the combined benzene extracts had been dried over calcium chloride, the benzene was removed by distillation under reduced pressure. (If the temperature was kept below 50°, well formed crystals were obtained.) The yield of colorless nicely crystalline I was 260 g. (66%), m.p. and mixture<sup>11</sup> m.p. 86–88°. Use of 134 g. of benzenesulfonyl chloride gave I in 69% yield, m.p. 86.5–87°.

The procedure of Baldwin and Robinson,<sup>5</sup> and our own experience on a small scale, suggests that if the I is not to be used in organometallic reactions, where the advantage of thorough drying of the extract is important, it can be isolated simply by allowing it to crystallize from the reaction mixture and washing with water. Carbon tetrachloride and

1:3 ethanol-water are convenient for recrystallization (or water<sup>5</sup> on a small scale), if this should be desired. The only limiting factor toward considerable increases in scale seems to be the extraction.

In exploring alkylation under other conditions, methyl sulfate<sup>9,10</sup> in a molar ratio of 1.7:1 was usually added over 1–2 hr. After the reaction, the excess was hydrolyzed and the I recrystallized. Benzenesulfinic acid in ether (reflux, 14 hr.) gave no crystalline product. Its salt (3 g.) in methyl sulfate<sup>9,10</sup> alone (5 ml.; 85°, 22 hr.) gave I in 24% yield, m.p. *ca.* 86°. Its salt in acetone (55°, 2.5–26 hr.) gave I with ranges in yield of 38–12% and in m.p. of 80–87°; in *t*-butyl alcohol containing 5% of water (reflux, 4.5 hr.), the salt gave I in 19% yield, m.p. 86–87.5°.

*Methyl p-tolyl sulfone* (II). The procedure given for I was followed exactly except that 484 g. of *p*-toluenesulfonyl chloride<sup>9</sup> was substituted for benzenesulfonyl chloride. In four experiments,<sup>12</sup> the II ranged in yield from 69 to 74%, and in m.p. from 83° to 87.5° (a typical product had m.p. and mixture<sup>13</sup> m.p. 86.5–87.5°).

A 20-hr. reflux period was established as sufficient for II by also effecting the alkylation using a 36-hr. period; the yield was 76% m.p. 86.5–87.5°.

*Ethyl phenyl sulfone*. A mixture of 20.0 g. of sodium benzenesulfinate, 20.1 g. of sodium bicarbonate, and 16.4 ml. of ethyl sulfate was heated at 50° with stirring while 50 ml. of water was added during 2 hr. The mixture was then heated under reflux for 20 hr. and the sulfone extracted with benzene; yield, 8.0 g. (39%), m.p. 41.5–42°; m.p. reported,<sup>14</sup> 41–42°.

Repetition of the procedure resulted in a yield of only 44% with twice the amount of ethyl sulfate and of only 48% with four times the amount both of ethyl sulfate and of sodium bicarbonate. Hydrolysis of the sulfate therefore does not seem to be the limiting factor. Indeed, when the procedure was repeated except that the mixture of the sulfinate and sulfate was heated and stirred alone at 120° for 4 hr. before addition (in one portion) of the sodium bicarbonate and water, only a dark oil, which could not be crystallized, was isolated. No favorable effect resulted either from interchanging the water and the sulfate in the original procedure (34%, m.p. 41.5–42°), from doubling the time of reflux (38%, m.p. 41.5–42°), or from other variations.

*Ethyl p-tolyl sulfone*. The procedure used for ethyl phenyl sulfone was repeated with 21.7 g. of sodium *p*-toluenesulfinate and 32.8 ml. of ethyl sulfate; yield 10.0 g. (45%), m.p. and mixture<sup>13</sup> m.p., 53–54°.

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VANDERBILT UNIVERSITY  
NASHVILLE, TENN.

(12) We wish to thank O. D. Keaton and W. E. Stamper for two of these.

(13) L. Field and J. W. McFarland, *J. Am. Chem. Soc.*, **75**, 5582 (1953).

(14) R. Otto, *Ber.*, **13**, 1274 (1880).

## Organic Polynitriles. II. 1,1,2,2-Tetracyano-cyclopropanes and Their Conversion to Substituted Itaconic Acids<sup>1</sup>

RAYMOND P. MARIELLA<sup>2</sup> AND ARTHUR J. ROTH, III<sup>3</sup>

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Several alkylidene bismalononitriles were prepared by the reaction of the appropriate aldehyde with malononitrile<sup>4</sup> (Table I).

(8) Melting points are corrected.

(9) Eastman Organic Chemicals, Yellow Label grade.

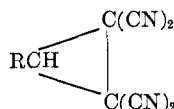
(10) Methyl sulfate is quite toxic and should be used in a hood; see N. I. Sax, *Handbook of Dangerous Materials*, p. 147, Reinhold Publishing Co., New York, N. Y., 1951. Glassware used for transfers may be cleaned with dilute ammonia water, containing detergent. It seems quite unlikely<sup>6</sup> that any methyl sulfate survives the 20-hr. period of reflux during alkylation, and no difficulty whatever has been experienced in handling the mixture after this period without gloves, hood, or other special precautions; nevertheless, the possible presence of methyl sulfate should be borne in mind.

(11) L. Field, *J. Am. Chem. Soc.*, **74**, 3919 (1952).

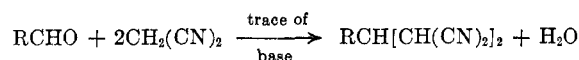
TABLE I  
RCH[CH(CN)<sub>2</sub>]<sub>2</sub>

R	M.P., °C.	Analyses						Yields, %
		Calculated			Found			
		C	H	N	C	H	N	
CH <sub>3</sub>	93	60.75	3.80	35.52	60.68	3.84	35.60	70
CH <sub>2</sub> CH <sub>2</sub>	65	62.79	4.65	32.56	62.98	4.73	32.67	80
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	75	64.52	5.37	30.11	64.58	5.30	30.15	80

TABLE II



R	M.P., °C.	M.W. Calcd.	Found	Analyses				Yields, %
				Calculated		Found		
				C	H	C	H	
CH <sub>3</sub>	192	156	156	61.54	2.56	61.40	2.51	60
CH <sub>2</sub> CH <sub>2</sub>	197	184	170	63.53	3.53	63.64	3.51	90
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	131	197	184	65.21	4.34	65.35	4.69	80



R = CH<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>. The reaction of the alkylidene bismalononitriles with bromine caused the instant discoloration of the bromine, but the products did not contain any halogen. By analogy with somewhat related work<sup>5</sup> it is concluded that cyclopropane derivatives were obtained, a conclusion supported by molecular weights and analyses (Table II). Infrared studies also indicated that cyclopropane structures were obtained<sup>6</sup> (Figure 1). A probable mechanism is

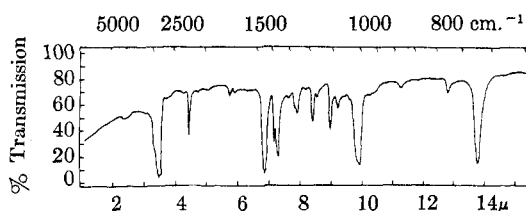
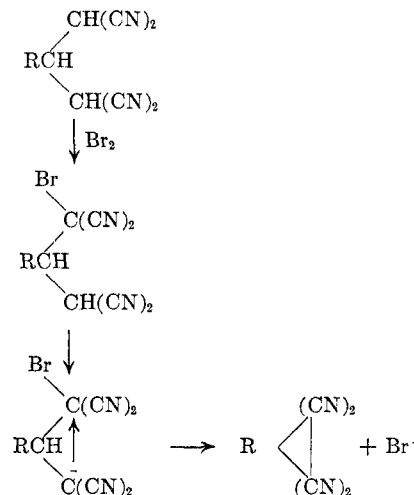


FIG. 1.—1,1,2,2-TETRACYANO-3-METHYLCYCLOPROPANE



Acid hydrolysis of the cyclopropane tetranitriles, for 8 hr., yielded what were probably the cyclo-

(1) This investigation was supported by Research Grant C-1746 (C2) from the National Cancer Institute, of the National Institutes of Health, Public Health Service. For Part I see R. P. Mariella, R. J. Clutter, and H. G. Ebner, *J. Org. Chem.*, **20**, 1702 (1955). This paper was presented April 13, 1956, before the Organic Division at the Dallas meeting of the American Chemical Society.

(2) To whom inquiries should be addressed.

(3) Taken in part from the M.S. thesis of Arthur J. Roth, III.

(4) (a) Diels, Gartner, and Kaack [*Ber.*, **55**, 3444 (1922)] originally reported the reaction of formaldehyde and acetaldehyde with malononitrile and (b) Gal, Fung, and Greenberg [*Cancer Research*, **12**, 565 (1952)] duplicated part of this. (c) Westfahl and Gresham [*J. Org. Chem.*, **21**, 319 (1956)] reported the reaction of formaldehyde and malononitrile. Whereas formaldehyde and acetaldehyde react with malononitrile to give products in addition to the alkylidene bismalononitriles, propionaldehyde and butyraldehyde react smoothly to give the bismalononitrile in very good yields, no other products being isolated.

(5) Wideqvist, *Arkiv. Kemi, Mineral. Geol.*, **B20**, No. 4 (1945); *Chem. Abstr.* **41**, 1621 (1947), reports that the reaction of acetaldehyde, bromomalononitrile and potassium iodide gave 1,1,2,2-tetracyano-3-methylcyclopropane, m.p. 192°. Our sample did not depress the melting point of a sample prepared by the method of Wideqvist.

(6) Hart and Curtis, Jr. [*J. Am. Chem. Soc.*, **78**, 112 (1956)] report that two bands are particularly characteristic of the cyclopropane ring, one at 3100 and the other at approximately 1020 cm<sup>-1</sup>. The three cyclopropanes in this work all showed bands around 3050 and strong bands at 1005 or 1035 cm<sup>-1</sup>. The three cyclopropanes prepared have almost identical spectra, and only one is used as an illustration.

propane tetra-acids. However, acid hydrolysis of the tetranitriles for 36 hr. did not yield the expected cyclopropane-1,2-diacids. The compounds so obtained were unsaturated as indicated by reaction with bromine and potassium permanganate, and their infrared spectra showed almost identical absorption with that of itaconic acid<sup>7</sup> (Figure 2).

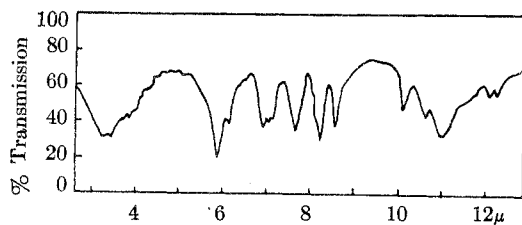


FIG. 2.—ITACONIC ACID

The spectra of our  $\gamma$ -methylitaconic acid was identical with that of an independent sample<sup>8</sup> and a mixture melting point was undepressed. Since the three substituted itaconic acids have almost identical spectra, only one is used as an illustration (Figure 3). The melting point of the three  $\gamma$ -substituted

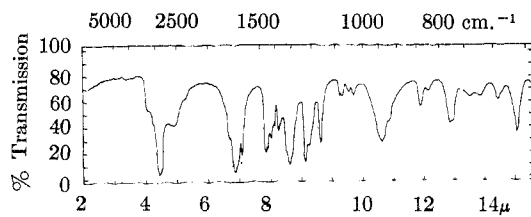


FIG. 3.— $\gamma$ -ETHYLITACONIC ACID

itaconic acids agreed closely with those reported in the literature (Table III) and the amounts of C

TABLE III  
MELTING POINTS OF  $\gamma$ -SUBSTITUTED ITACONIC ACIDS

R	M.P., °C.	Literature <sup>a</sup>	Yields, %
CH <sub>3</sub> <sup>b</sup>	170	167°	20
CH <sub>3</sub> CH <sub>2</sub>	169	165°	35
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	163	159°	40

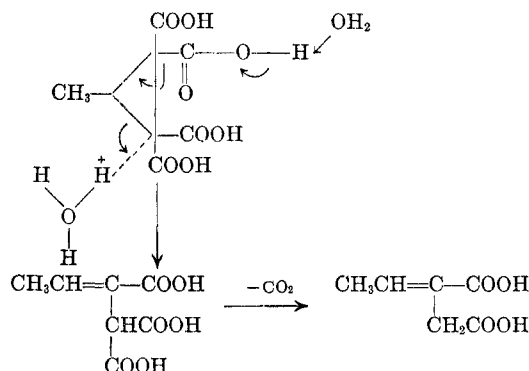
<sup>a</sup> Fittig, *Annalen*, **255**, 39 (1889); **304**, 181 (1899). Compounds prepared by the reaction of appropriate aldehyde with succinic anhydride followed by isomerization by distillation or treatment of the esters with ethoxide. <sup>b</sup> Independent sample<sup>8</sup> had m.p. 169–170°.

(7) In a somewhat analogous reaction, the acid hydrolysis of 3-methylcyclopropane-1,1,2-tricarboxylic ester yielded 3-methylparaconic acid, Harper and Reed, *J. Chem. Soc.*, 779 (1955).

(8) Kindly supplied by M. C. Ettlinger, Rice Institute, Houston, Tex., and prepared by the method of Kloetzel, *J. Am. Chem. Soc.*, **70**, 3571 (1948).

and H found in analysis agreed within 0.25% with the theoretical.<sup>9</sup>

A likely concerted mechanism is:



#### EXPERIMENTAL<sup>11</sup>

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. The Rast method for molecular weights was used. The infrared curves were determined by means of a Perkin-Elmer Model 21, double beam spectrophotometer. All the samples were run in a Nujol suspension.

**Ethylidene bismalononitrile.** To a chilled solution of 6.6 g. of malononitrile and 4.5 g. of acetaldehyde, one drop of modified catalyst ( $\frac{1}{3}$  piperidine and  $\frac{2}{3}$  dioxane) was added. This was kept at 5° overnight. Crystallization may be hastened by scratching the sides of the flask. After 12 hr., the reaction mixture contained a crystalline mass and some sirupy liquid. The acetaldehyde may be allowed to evaporate off at room temperature without heating, leaving a solid mass, or the crystals may be filtered from the mother liquor directly. The crystals were then washed thoroughly with a small portion of ethyl ether and dried in air. Recrystallization from 95% ethanol gave clean, white crystals, which melted sharply at 92–93°. When acetaldehyde was replaced by propionaldehyde or butyraldehyde, the corresponding alkylidene bismalononitriles were obtained (see Table I).

**1,1,2,2-Tetracyano-3-alkylcyclopropanes.** Two grams of alkylidene bismalononitrile were dissolved in 10 ml. of 95% ethanol. The mixture was warmed gently until the solid dissolved. The solution was cooled slightly and 22–23 drops of bromine, or enough to retain the bromine color, were added slowly. (Vigorous agitation is necessary as this reaction is highly exothermic.) The cyclopropane compound crystallized out immediately.

The solution was well chilled and the crystals filtered off and recrystallized from absolute ethanol. (See Table II).

**3-Ethylcyclopropane-1,1,2,2-tetracarboxylic acid.** Ten grams of the 1,2,2-tetracyano-3-ethylcyclopropane were refluxed with 50 ml. of concentrated HCl for 8 hr. Upon cooling, the clear mixture yielded a large mass of crystals. These crystals

(9) Ramberg and Wideqvist, *Arkiv. Kemi, Mineral. Geol.*, **14B**, No. 37 (1941). *Chem. Abstr.*, **36**, 79 (1942) reported that the hydrolysis of 1,1,2,2-tetracyano-3,3-dimethylcyclopropane in base gave a diacid C<sub>7</sub>H<sub>10</sub>O<sub>4</sub>, m.p. 165°, of unknown structure. From our work, it would seem that the diacid actually is  $\gamma$ ,  $\gamma$ -dimethylitaconic acid, whose m.p. is reported as 164° by Stobbe [*Ber.*, **36**, 197, (1903)] who prepared it by the reaction of acetone on diethyl succinate.

(11) Micro-analyses by Micro-Tech Laboratories, Skokie, Ill.

(12) Diels, Ref. 4a, reported a melting point of 113°. Numerous attempts to raise the melting point of our analytical sample were uniformly unsuccessful.

were washed with a small amount of ice water and the tetra acid separated from the remaining ammonium chloride by extraction with absolute ethanol. Evaporation of the ethanol yielded a crude product which was then recrystallized from acetic acid, (25% yield), m.p. 286° (dec.), mol. wt. (Calcd.) 246; mol. wt. (found) 234. The results of a C—H analysis were found to differ from the theoretical by about 1.3% and so are not included here.

The sample did not decolorize a bromine solution. In a similar manner a small amount of the 3-*n*-propylcyclopropane-1,1,2,2-tetracarboxylic acid was obtained, m.p. 271° (dec.). Similar attempts to isolate the 3-methyl isomer were unsuccessful. The tetra acids were difficult to obtain and purify and no further attempts were made to isolate them.

*γ-Alkyl itaconic acids.* 10 grams of 1,1,2,2-tetracyano-3-alkylcyclopropane were refluxed with 50 ml. of concentrated HCl for 36 hr. Upon cooling a large mass of crystals was formed. The solid was filtered off and washed with a small amount of ice water. The acid was separated from the remaining ammonium chloride by extracting with boiling anhydrous benzene. After the benzene solution cooled, a small amount of petroleum ether was added and the crude product slowly came out of solution. This product was recrystallized from anhydrous benzene. (See Table III).

DEPARTMENT OF CHEMISTRY  
LOYOLA UNIVERSITY  
CHICAGO 26, ILL.