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Dimers of Methacrylic Compounds

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When methyl methacrylate was heated at 225° for 12 hours only one dimer, dimethyl α-methylene-δ-methyladipate, was produced. In contrast three dimers resulted from the thermal dimerization of methacrylonitrile: *trans*-1,2-dimethyl-1,2-dicyanocyclobutane (I), α-methylene-δ-methyladiponitrile (II) and *cis*-1,2-dimethyl-1,2-dicyanocyclobutane (III). At 340° methacrylonitrile was dimerized in 5–10 minutes in about 25% conversion and 50% yield to produce a mixture of dimers in the following proportions: 1 part I, 340 parts II and 1 part III. The dimer fraction obtained by heating at 200° for 12 hours consisted mainly of the dimethyldicyanocyclobutanes. The cyclic dimers were not formed on heating α-methylene-δ-methyladiponitrile. A mechanism for the dimerization is proposed.

Three types of products have been reported from the uncatalyzed thermal dimerization of α,β-unsaturated compounds. Acrolein and methyl vinyl ketone have given the heterocyclic products, 2-formyl-3,4-dihydropyran and 2-acetyl-6-methyl-3,4-dihydropyran, respectively.[1] Acrylonitrile has given 1,2-dicyanocyclobutane.[2] Methyl methacrylate and methacrylonitrile have been reported to give linear unsaturated dimers.[3] This paper reports additional information on the thermal dimerization of methyl methacrylate and methacrylonitrile and on the structures of the dimers obtained.

When methyl methacrylate containing a polymerization inhibitor was heated in a sealed vessel at 225° for 8 hours, material recovered was as follows: 28% unchanged monomer, 39% dimer, 19% trimer and 14% higher boiling residue. Only one dimer was obtained and this was shown by the following experimental evidence to be dimethyl α-methylene-δ-methyladipate. The infrared absorption[4] spectrum of the dimer showed bands characteristic of methylene unsaturation. Ozonization gave formaldehyde and a compound analyzing for dimethyl α-keto-δ-methyladipate. Finally, hydrogenation and saponification of the dimeric ester gave α,δ-dimethyladipic acid. The dimeric ester was shown to be capable of polymerization and copolymerization by free radical initiation.

Crawford[3] has isolated a dimer of methyl methacrylate which was formed in 1% yield as a by-product in the preparation of methyl methacrylate by the acetone cyanohydrin–methacrylamide route. His experiments indicated that the dimer originated as amide by the action of hot sulfuric acid on methacrylamide. Saponification and reduction of the dimeric ester gave α,δ-dimethyladipic acid, and permanganate oxidation of the unsaturated dimeric acid gave methylsuccinic acid. He therefore characterized the unsaturated dimeric acid as α,δ-dimethyl-α-hydromuconic acid. Infrared evidence, discussed below, suggests some double bond migration may occur during acid hydrolysis of dimethyl α-methylene-δ-methyladipate to give α,δ-dimethyl-α-hydromuconic acid. This may explain why Crawford did not obtain a dimer with an α-methylene structure.

Whereas methyl methacrylate yielded only one dimer on thermal treatment in the presence of a polymerization inhibitor, methacrylonitrile gave three dimeric products. As was the case with methyl methacrylate, trimeric and higher boiling materials were also obtained from methacrylonitrile. The relative proportions of the three dimers formed could be varied over a wide range by changing the temperature and time of reaction. For convenience the dimers have been numbered in the order of their appearance on distillation: dimer I, b.p. 120° (25 mm.); dimer II, b.p. 148° (25 mm.); and dimer III, b.p. 170° (25 mm.).

Methacrylonitrile dimers I and III are solids melting at 91 and 108°, respectively, which give no indication of unsaturation. In view of Coyner and Hillman's proof that dimeric acrylonitrile is 1,2-dicyanocyclobutane,[2] it was assumed that methacrylonitrile dimers I and III were dimethyldicyanocyclobutanes. Dehydration of the diacid from dimer III gave an anhydride, whereas similar treatment of the diacid from dimer I failed to give a crystalline product; therefore, dimer I is *trans* and dimer III is *cis*. The infrared absorption spectrum of dimer I corresponded with a 1,2-dicyanocyclobutane sample at 8.3, 10.7, 11.4 and 13.3 μ, indicating equivalent structures. Comparison of the infrared spectra of dimer I and of a 1,2-dimethyl-1,2-dicyanocyclobutane prepared by Byrd and Overberger proved that the two compounds were identical.[5] The spectrum of dimer III showed correspondence with that of dimer I at 8.3, 7.85, 8.1, 10.8 and 11.3 μ, indicating a cyclobutane structure. Dimer I, therefore, is *trans*-1,2-dicyano-1,2-dimethylcyclobutane, and dimer III is *cis*-1,2-dicyano-1,2-dimethylcyclobutane.

Methacrylonitrile dimer II is unsaturated; hydrogenation followed by hydrolysis gave racemic and *meso*-α,δ-dimethyladipic acids. Formaldehyde was identified as an ozonization product, and the infrared absorption spectrum indicated the presence of a $CH_2{=}C{-}CN$ group. Methacrylonitrile dimer II was therefore identified as α-methylene-δ-adiponitrile. Acid hydrolysis gave a mixture of dibasic acids, m.p. 89–90°. The 10.6 μ infrared band, characteristic of α-methylenic substitution, was

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(1) K. Alder, H. Offermans and E. Rueden, *Ber.*, **74B**, 905, (1941); K. Alder and E. Rueden, *ibid.*, **74B**, 920 (1941).

(2) E. C. Coyner and W. S. Hillman, THIS JOURNAL, **71**, 324 (1949).

(3) J. W. C. Crawford, *J. Soc. Chem. Ind.*, **66**, 155 (1947), U. S. Patent 2,244,487 (June 3, 1941); B. W. Howk, U. S. Patent 2,232,785 (February 25, 1941).

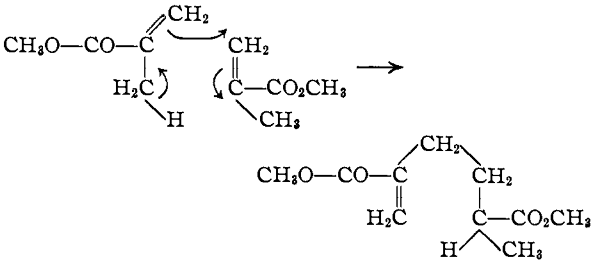
(4) The infrared spectra referred to in this paper have been deposited as Document number 4632 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints, or $1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

(5) Private communication from Dr. N. R. Byrd.

less intense and broader than in the dimers which had not been treated with acid, suggesting that some double bond migration to α,δ-dimethyl-α-hydromuconic acid may have taken place. Similar dibasic acid mixtures were obtained by the acid hydrolysis of dimethyl α-methylene-δ-methyladipate and by thermal dimerization of methacrylic acid.

In the dimerization of methacrylonitrile, the effect of reaction temperature on the composition of the dimer mixture was quite marked. As the temperature was decreased, the ratio of cyclic dimers to linear dimer increased. At 340° methacrylonitrile was dimerized in 7.5 minutes in about 25% conversion to produce a mixture of dimers in the following proportions: 1.3 parts of dimer I, 340 parts of dimer II and 1 part of dimer III. The composition of the methacrylonitrile dimer mixture obtained by thermal dimerization at 240° for 4 hours was about 9 parts dimer I, 15 parts of dimer II and 1 part of dimer III. When the dimerization was carried out by heating methacrylonitrile for 12 hours at 200°, the dimer mixture consisted of 5.5 parts of dimer I, 3.3 parts of dimer II and 1 part of dimer III.

The thermal dimerization conditions are similar to those required for the addition of monoölefins to dienophiles[6] and this suggests that thermal dimerization of methacrylic compounds to α-methylene-δ-methyladipic acid derivatives is a special case of this reaction. Using a transient cycle complex as proposed by Arnold and Dowdall[7] for olefin/maleic anhydride adducts, one might write a mechanism for the dimerization of methyl methacrylate as



As predicted by this mechanism, it was found that methyl methacrylate added to acrylonitrile to yield an unsaturated product, which after hydrogenation and saponification gave α-methyladipic acid. Also, the thermal reaction of methacrylonitrile with diethyl fumarate apparently gave diethyl (β-cyanoallyl)-succinate. Formation of dimer II from methylacrylonitrile can, of course, also be depicted by this mechanism.

The cyclic dimers I and III of methacrylonitrile were not formed on heating dimer II. The latter was recovered unchanged. It is probable therefore that the cyclic products are formed by an independent mechanism, possibly that involving free radicals as suggested by Coyner and Hillman.[2]

As previously indicated, trimeric products were also isolated from the thermal treatment of both methyl methacrylate and methacrylonitrile. By analogy with the structure of the unsaturated dimers and by their infrared absorption spectra, the trimers have been tentatively identified as dimethyl 5-carbomethoxy-8-methyl-2-methylenenonanedioate and 5-cyano-8 methyl-2-methylenenonanedinitrile, respectively.

Experimental

Dimethyl α-Methylene-δ-methyladipate. (a) **Preparation.**—In a typical run 600 g. of methyl methacrylate, 3 g. of picric acid and 3 g. of hydroquinone were charged into a nitrogen-swept one-liter stainless steel autoclave; the vessel was again flushed with nitrogen, closed, and heated under autogenous pressure at 225° for 12 hours. On distillation there was obtained 157 g. of recovered methyl methacrylate, 215 g. of methyl methacrylate dimer (36% conversion), b.p. 107° (7 mm.), $n^{25}D$ 1.4445; 115 g. of methyl methacrylate trimer (17% conversion), b.p. 173° (3 mm.), $n^{25}D$ 1.4588; and 79 g. of higher boiling residue (13% conversion).

(b) **Proof of Structure.**—Careful fractionation indicated that the dimeric component was a single chemical individual regardless of the temperature at which it was prepared. A 25-gram sample of methyl methacrylate dimer in 200 ml. of methanol was ozonized until there was no test for unsaturation. The product was hydrogenated over a palladium-on-charcoal catalyst at 40 lb. pressure for 3 hours at room temperature; water was added and the mixture distilled. Formaldehyde was characterized in the methanol and water distillates by its 2,4-dinitrophenylhydrazone derivative, m.p. 161–165°, mixed m.p. 164–166° with an authentic sample. In addition, there was isolated about 10 g. of material, b.p. 120–125° (4 mm.), which formed a dinitrophenylhydrazone derivative and which analyzed for dimethyl α-keto-6-methyladipate.

Anal. Calcd. for $C_9H_{14}O_5$: C, 53.5; H, 6.9. Found: C, 53.5; H, 7.1.

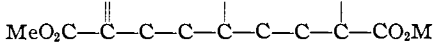
Methyl methacrylate dimer was hydrogenated over palladium-on-charcoal catalyst at 40 lb. pressure at room temperature. The saturated ester, $n^{25}D$ 1.4280, was saponified with excess potassium hydroxide in alcohol and the acidic products were isolated in the usual way. The crude acids, m.p. 120–129°, were separated by seven recrystallizations from boiling water to yield *meso*-α,δ-dimethyladipic acid, m.p. 140–143° (lit.[8] 140–141°); neut. equiv. (calcd.) 87, neut. equiv. (found) 87.2. Recrystallization of the low melting material yielded the racemic acid melting at 71–75° (lit.[8] 74–76°), neut. equiv. (found) 87.3.

(c) **Hydrolysis of Dimethyl α-Methylene-δ-methyladipate.**—A mixture of 50 g. of dimethyl α-methylene-δ-methyladipate, 100 ml. of water and 1 ml. of concentrated sulfuric acid was refluxed under nitrogen, and methanol was removed as formed. Hydrolysis was slow and required five days before no more methanol could be removed. The solution was filtered hot and allowed to cool. The yield of air-dried crystals was 39 g. (91%), m.p. 89–90°; neut. equiv. (calcd.) 86, neut. equiv. (found) 85.4. This acid was probably the same equilibrium mixture of unsaturated diacids as was obtained by acid hydrolysis of α-methylene-δ-methyladiponitrile. The infrared absorption spectrogram showed an absorption peak at 10.6 μ but the intensity and sharpness of the band was not equal to the 10.6 μ bands of spectrograms of dimethyl α-methylene-δ-methyladipate and α-methylene-δ-methyladiponitrile.

Methyl Methacrylate Trimer.—At 225° for 12 hours, about 15% of the methyl methacrylate charged was converted to a trimeric compound boiling at 173° (3 mm.), $n^{25}D$ 1.4588.

Anal. Calcd. for $C_{15}H_{24}O_6$: C, 60.0; H, 8.0; mol. wt., 300. Found: C, 60.1; H, 8.0; mol. wt., 300.

The infrared absorption spectrum showed bands at 12.2, 10.6 and 6.1 μ corresponding to the same type of unsaturation present in methyl methacrylate and dimethyl α-methylene-δ-methyladipate. On this basis the structure tentatively assigned the trimer is dimethyl 5-carbomethoxy-8-methyl-2-methylenenonanedioate.



$$MeO_2C\text{—}\overset{\overset{\displaystyle C}{\|}}{C}\text{—}C\text{—}C\text{—}\overset{\overset{\displaystyle CO_2Me}{|}}{C}\text{—}C\text{—}C\text{—}\overset{\overset{\displaystyle C}{|}}{C}\text{—}CO_2Me$$

Dimethyl α-Methylene-δ-methyladipate Homopolymer.—A 10-g. sample containing 0.5 g. of benzoyl peroxide was heated overnight under a nitrogen atmosphere in a refluxing

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(6) K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76**, 27 (1943).

(7) R. T. Arnold and J. F. Dowdall, THIS JOURNAL, **70**, 2590 (1948).

(8) O. Mohr, *Ber.*, **34**, 807 (1901).

benzene-bath. The product was a clear solid at room temperature, was soluble in acetone and could be pressed to a brittle film at 80°.

Dimethyl α-Methylene-δ-methyladipate/Styrene Copolymer.—A solution of 19 g. of styrene, 37 g. of dimethyl α-methylene-δ-methyladipate and 0.56 g. of α,α′-azodiisobutyronitrile was stirred under nitrogen for 5.5 hours at 60°. The polymer was precipitated and washed with methanol. After vacuum drying there was obtained 4.5 g. (8%) of solid. Analyses for carbon and hydrogen indicated an oxygen content of 20% which corresponds to a copolymer containing 53 mole per cent. of styrene.

Methacrylic Acid Dimer.—A solution of 43 g. of methacrylic acid, 100 ml. of benzene, 0.5 g. of hydroquinone and 0.5 g. of picric acid was heated at 225° for 4 hours. Distillation gave 14.5 g. of an oily solid which, when crystallized from nitromethane, gave white crystals, m.p. 87–89°. A mixed melting point with the unsaturated diacid obtained by hydrolysis of methyl methacrylate dimer, m.p. 89–90°, showed no depression. The significance of the melting points of the mixed acids is questionable.

Dimerization of Methacrylonitrile.—In the thermal treatment of methacrylonitrile, variation of the reaction temperature gave varying proportions of three methacrylonitrile dimers.

(a) **Continuous Dimerization at 340°.**[9]—The continuous unit consisted of a coil of stainless steel tubing having an internal diameter of $^3/_8''$ and a volume of 1555 ml. Stabilized methacrylonitrile, 3580 g./hr., and water, 3000 g./hr., were fed continuously to the reaction coil held at 340° and 200 atm. Under these conditions the contact time of the reaction mixture in the heated zone was about 7.5 minutes. After 22 hours of operation the water layer, 66,300 g., was separated, analyzed and discarded without attempting recovery of 3700 g. of unreacted methacrylonitrile in solution. The organic layer was flash-distilled to recover unreacted methacrylonitrile. The high-boiling materials were washed with alkali, water, dried and fractionated. From 79,120 g. of methacrylonitrile charged there was obtained 47,500 g. of unreacted methacrylonitrile, 51 g. of methacrylonitrile dimer I, b.p. 120° (25 mm.); 13,730 g. of methacrylonitrile dimer II, b.p. 148° (25 mm.); 40 g. of methacrylonitrile dimer III, b.p. 170° (25 mm.); 3875 g. of methacrylonitrile trimer and 1469 g. of high-boiling materials and tars. Considerable methacrylonitrile was lost through the incomplete condensation of the products from the reactor. Based on a minimum figure of 51,200 g. of unconsumed methacrylonitrile, the yield of dimer I was 0.18%, dimer II, 49.2%, dimer III, 0.14%, and trimer, 13.9%. Tars amounted to 1.9% of the methacrylonitrile processed. The ratio of dimers obtained at 340° was 1.3 parts of I, 340 parts of II, 1 part of III.

(b) **Batch Dimerization at 240°.**—In a typical run a one-liter autoclave was swept out with nitrogen and charged with a mixture of 400 g. of methacrylonitrile, 200 g. of butyl acetate and 4 g. of hydroquinone. The reactor was again swept with nitrogen, closed, and heated at 240° for 4 hours. On distillation 228 g. of methacrylonitrile was recovered. The dimer fraction, b.p. 125–160° (20–30 mm.), weighed 89 g. A series of such runs was composited and fractionated into three pure dimer cuts; the three cuts totaled 84% of the weight of the crude dimer charged. From 400 g. of methacrylonitrile charged there was obtained 26 g. (6.5% conversion, 15% yield) of dimer I, 45.5 g. (11.4% conversion, 26.5% yield) of dimer II, and 3 g. (0.75% conversion, 1.7% yield) of dimer III.

(c) **Batch Dimerization at 200°.**—Methacrylonitrile, 200 g., stabilized with 1 g. of hydroquinone and 1 g. of picric acid, was heated at 200° for 12 hours at autogenous pressure in a 500-ml. autoclave. Distillation gave 48 g. of methacrylonitrile, 24.6 g. of dimer I (12.3% conversion, 16% yield), 15 g. of dimer II (7.5% conversion, 10% yield), and 4.5 g. of dimer III (2.3% conversion, 3% yield).

(d) **Separation and Characterization of Methacrylonitrile Dimers.**—Preliminary separation of the dimer mixture was accomplished by distillation. Crystallization of the crude dimer I fraction from ether–hexane gave a solid. Fractionation of this solid, b.p. 120° (25 mm.), and recrystallization from ethyl alcohol gave material having a good freezing point curve at 90.3–89.9°.

Anal. Calcd. for $C_8H_{10}N_2$: C, 71.6; H, 7.5; N, 20.9; mol. wt., 134. Found: C, 71.5; H, 7.6; N, 20.8; mol. wt., 142.

The oil remaining in the mother liquor was combined with the crude dimer II and fractionated and a cut, b.p. 149–150° (27 mm.), $n^{25}D$ 1.4502, was obtained.

Anal. Calcd. for $C_8H_{10}N_2$: C, 71.6; H, 7.5; N, 20.9; mol. wt., 134. Found: C, 71.4; H, 7.3; N, 20.7; mol. wt., 131.

Continued fractionation gave dimer III, b.p. 169–171° (25 mm.). The cooling curve of this solid, saturated material showed no definite break at 96.1 to 83.3°. However, if a sample of the material was crystallized from methanol at −25°, and a melting point taken immediately, the sample melted at 105–108°. On standing at room temperature the crystals soon became soft and no longer melted sharply. Evaporation of an ether solution gave crystals melting sharply at 107–108°, if the melting point was taken immediately.

Anal. Calcd. for $C_8H_{10}N_2$: C, 71.6; H, 7.5; N, 20.9; mol. wt., 134. Found: C, 71.9; H, 7.7; N, 20.7; mol. wt., 136.

t-Butyl amides of the dimers were prepared by reaction with *t*-butyl alcohol in the presence of sulfuric acid.[10] Concentrated sulfuric acid, 5 ml., was dissolved in 10 ml. of glacial acetic acid and cooled. Methacrylonitrile dimer, 3 g., was dissolved in a mixture of 10 ml. of glacial acetic acid and 4.5 ml. of *t*-butyl alcohol. The cold acetic acid solution of sulfuric acid was added to the acetic acid solution of the dimer and *t*-butyl alcohol slowly with swirling so that the temperature did not exceed about 40°. The reaction mixture was allowed to stand 3 hours and then was poured on ice. The crude amides were washed with water and crystallized from a benzene–petroleum ether mixture. Hydrolysis of the dimers yielded diacids having the expected neutral equivalents and the following melting points: I, 237–238°; II, 89–90°; III, 134–135° (anhydride, m.p. 89–90°).

Dinitriles	*t*-Butylamides, m.p., °C.	Nitrogen, %	
		Calcd.	Found
Dimer I	134–136	10.0	10.0
Dimer II	187–188	10.0	9.8
Dimer III	127–129	6.7 (imide)	6.3

(e) **Structures of the Methacrylonitrile Dimers.**—Dinitrile II was hydrolyzed by warm concentrated sulfuric acid. The dibasic acid isolated, m.p. 89–90°, neut. equiv. 86, was identical with an acid formed by the acid hydrolysis of the methyl methacrylate dimer, dimethyl α-methylene-δ-methyladipate. More reliable evidence was obtained by the hydrolysis of the hydrogenated dimer II. The diacids obtained were separated by repeated recrystallizations from boiling water to produce the less soluble acid, *meso*-α,δ-dimethyladipic acid, m.p. 139–142°, and a more soluble acid, m.p. 73–75°, racemic-α,δ-dimethyladipic acid.[8]

Methacrylonitrile dimer II, 25 g., was dissolved in 200 ml. of methanol and ozonized until no test for unsaturation was given by the solution. The product was hydrogenated at room temperature over a palladium-on-charcoal catalyst at 40 lb. hydrogen pressure for 3 hours. On opening the bottle a strong odor of hydrogen cyanide was noted. Water was added and the material distilled. The aqueous distillate contained formaldehyde which was identified by preparation of the 2,4-dinitrophenylhydrazone, m.p. 163–164° (not lowered on mixing with an authentic sample, m.p. 164–166°). The other product of the ozonization would be an α-ketonitrile which would react with methanol to give hydrogen cyanide. A product having the approximate analysis for methyl γ-cyanovalerate was isolated. This indicates the structure of methacrylonitrile dimer II to be α-methylene-δ-methyladiponitrile.

Methacrylonitrile dimers δ and III failed to react with aqueous potassium permanganate. These compounds were therefore considered to be cyclic dinitriles, probably cyclobutane derivatives. *cis*- and *trans*-1,2-dicyanocyclobutane were prepared according to Coyner and Hillman.[2] The solid *trans* isomer was freed of hydroquinone by alkali washing, recrystallized and used as the reference compound in a spectroscopic examination of dimers I and III. Methacrylonitrile dimers I and III showed good agreement with

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(9) M. J. Hogsed, U. S. Patent 2,566,203 (August 28, 1951).

(10) F. R. Benson and J. J. Ritter, THIS JOURNAL, **71**, 4128 (1949).

the spectrum of *trans*-1,2-dicyanocyclobutane indicating that I and III were dimethyldicyanocyclobutanes. Comparison of the infrared spectra of dimer I and of a 1,2-dimethyl-1,2-dicyanocyclobutane prepared by Byrd and Overberger[5] proved that the two compounds were identical. Both dimers I and III yield diacids, m.p. 237–238° and 134–135°, respectively, on hydrolysis, but only the diacid from dimer III gave a crystalline anhydride on warming with acetyl chloride. After being crystallized from benzene-petroleum ether, the anhydride of the dimer III diacid melted at 89–90°. In view of its ability to form an anhydride, dimer III diacid was considered to be the *cis* isomer; dimer I diacid was, accordingly, considered to be *trans*.

Methacrylonitrile Trimer.—This trimer was obtained from both batch and continuous operation. Distillation of a sample from a continuous run gave a yellow oil, b.p. 194° (1 mm.), $n^{25}\text{D}$ 1.4720, which solidified just below room temperature. Recrystallization from methanol gave a white solid, m.p. 47–49°.

Anal. Calcd. for $C_{12}H_{15}N_3$: C, 71.6; H, 7.5; N, 20.9. Found: C, 71.4; H, 7.8; N, 21.0.

Infrared examination revealed a band at 10.60 μ characteristic of $CH_2{=}CRCN$ unsaturation as in the spectrum of methacrylonitrile.

Addition of Methacrylonitrile to Diethyl Fumarate.—From 100 g. of methacrylonitrile and 200 g. of diethyl fumarate, after heating at 300° for 15 minutes in a stainless steel autoclave at autogenous pressure, there was obtained 100 g. of recovered reactants, 35 g. of residues and 31 g., b.p. 146–148° (3.5 mm.), $n^{25}\text{D}$ 1.4545.

Anal. Calcd. for $C_{12}H_{17}O_4N$: N, 5.9. Found: N, 5.7.

This adduct was probably diethyl (β-cyanoallyl)-succinate. Similar treatment of diethyl fumarate with acrylonitrile gave no 1:1 adduct.

Addition of Methyl Methacrylate to Acrylonitrile.—A mixture of 106 g. of acrylonitrile, 100 g. of methyl methacrylate and 80 g. of xylene was heated at 240° for 4 hours. The crude product consisted of 113 g. of monomers and xylene and 47 g. of products which included dimethyl α-methylene-δ-methyladipate. By distillation there was obtained 8 g. of methyl α-cyano-δ-methylenevalerate, b.p. 136–137° (25 mm.), $n^{25}\text{D}$ 1.4511.

Anal. Calcd. for $C_8H_{11}O_2N$: N, 9.2. Found: N, 9.5.

Hydrogenation of the product followed by hydrolysis and crystallization of the diacid from hydrochloric acid gave a product melting at 56–59°. Treatment of the diacid with thionyl chloride gave an acid chloride which was treated with aniline to give a dianilide, m.p. 173–174° (lit.[11] 174–175°).

Acknowledgments.—We wish to thank Dr. J. R. Downing for the interpretation of the infrared spectrograms and Dr. W. H. Wood for the design and operation of the continuous equipment. The presence of methacrylonitrile dimer III was first noted by Dr. D. B. Pattison, Jackson Laboratory, Organic Chemicals Department, du Pont Company. Many helpful suggestions were made by Drs. J. E. Kirby and B. W. Howk.

WILMINGTON, DEL.

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[11] L. Bouveault and R. Locquin, *Bull. soc. chim.*, [4], **3**, 449 (1908).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Preparation of and the Spectral Characteristics of Some 2-Substituted *cis*- and *trans*-Stilbenes[1]

BY DELOS F. DETAR AND LOUIS A. CARPINO

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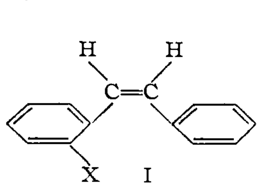
The preparation of a series of *cis*- and *trans*-2-stilbene derivatives is described. The ultraviolet and the infrared absorption spectra of the stereoisomers differ sufficiently so that configurations can be assigned with considerable certainty to stilbenes of unknown configurations.

In continuation of a study concerning the mechanisms of intramolecular free-radical reactions it was desirable to prepare *cis*-stilbene-2-carboxylic acid (I, X = COOH). The decomposition of the corresponding peroxide should give rise to the *cis*-β-styrylphenyl radical (I, X = ·), and would constitute an alternative route to the radical considered to be an intermediate in reactions of diazotized *cis*-2-aminostilbene under alkaline conditions.[2] In order to be certain of the stereochemistry of the various stilbene derivatives, an examination was undertaken of the infrared and the ultraviolet spectra of a number of 2-substituted *cis*- and *trans*-stilbenes.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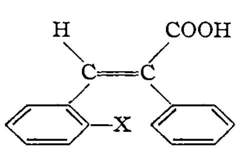
II

Several workers have examined the spectra[3,4] of *trans*-stilbene derivatives, but the corresponding *cis*-isomers have been less extensively investigated.[5] Very few 2-substituted stilbenes have been studied.

The preparation of *cis*-stilbene derivatives usually involves either decarboxylation of the corresponding cinnamic acids[6] or photochemical isomerization[7] of the *trans* compounds. The first method is more convenient for large-scale work. A previous attempt[8] to prepare *cis*-stilbene-2-carboxylic acid by treatment of *cis*-2-chlorostilbene with lithium followed by carbonation led to small amounts of the *trans*-acid together with some *trans*-stilbene.

In the present work *cis*-2-bromostilbene was prepared by condensation of 2-bromobenzaldehyde with phenylacetic acid to give *trans*-α-phenyl-2-bromocinnamic acid (II, X = Br; phenyl groups

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[1] This research was supported by National Science Foundation grant NSF G439.

[2] D. F. DeTar and Y. W. Chu, THIS JOURNAL, **76**, 1686 (1954).

[3] E. A. Braude, *J. Chem. Soc.*, 1902 (1949); R. H. Beale and E. M. F. Roe, THIS JOURNAL, **74**, 2302 (1952).

[4] H. W. Thompson, E. E. Vago, M. C. Corfield and S. F. D. Orr, *J. Chem. Soc.*, 214 (1950).

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