manner, nor the thallous valerate prepared by R. K. Abbott from other valeric acid, had a definite melting point. Accordingly the salt was heated with *p*-bromophenacyl bromide to give the corresponding ester (m. p. 67.5–69.5°), which was identified by comparison with an authentic specimen. The *p*-bromophenacyl ester was prepared in another experiment in which the valeric acid was isolated in a 17.5% yield by way of the silver salt.

Summary

A comparison has been made of some reactions of organocalcium, -strontium, and -barium compounds. The recently available organostrontium and organobarium compounds show reactions with some olefins, benzophenone-anil and azobenzene characteristic of the highly reactive organoalkali compounds.

Unlike *n*-butyllithium which metalates methyl phenyl sulfide laterally, diethylstrontium and -barium effect nuclear metalation. The metalation of dibenzothiophene in the 4-position by diethylcalcium was equally unexpected because the 3-position is involved when phenylcalcium iodide is used.

Water-solubilizing groups can be introduced in tetraphenyllead by means of a halogen–metal interconversion reaction between triphenyl-*p*-bromophenyllead and diethylbarium. This novel reaction is made possible by a highly subordinated metal–metal interconversion reaction.

The anomalous formation of tetraphenyllead from triphenyllead chloride and diethylbarium appears to be due primarily to a metal–metal interconversion reaction between the reactive, intermediately-formed triphenylethyllead and diethylbarium.

AMES, IOWA RECEIVED MARCH 19, 1945

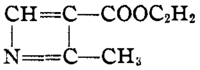
[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORIES OF MONSANTO CHEMICAL COMPANY]

Esters of β-Cyanocrotonic Acid

BY DAVID T. MOWRY AND ALFRED G. ROSSOW

In connection with certain investigations in progress in these Laboratories, authentic samples of some esters of β-cyanocrotonic acid were prepared.

Ethyl β-cyanocrotonate was one of several possible structures proposed by Pinner[1,2] for a compound, m. p. 70–71°, resulting from the action of formamidine on acetoacetic ester. Although at first[1] he reported it to be identical with a compound obtainable from acetoacetic ester and hydrogen cyanide or ammonium cyanide, he later[2] disclosed his inability to obtain the supposed β-cyanocrotonate by this latter method. Later, Shestakove and Kazakov[3] expressed considerable doubt that ethyl β-cyanocrotonate was the correct structure of Pinner's product and favored instead a four-membered ring compound of the possible structure

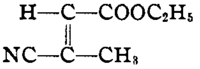


$$\begin{array}{l} \mathrm{CH{=}C{-}COOC_2H_2} \\ \mathrm{|\quad\ \ |} \\ \mathrm{N{=}C{-}CH_3} \end{array}$$

Furthermore, since the ethyl esters of crotonic acid containing either chloro[4] or phenyl[5] substituents in the β-position are mobile liquids at room temperature, it appeared that a melting point of 70–71° was abnormally high for the cyano derivative.

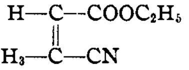
Of several methods attempted, for the preparation of ethyl β-cyanocrotonate, the dehydration of acetoacetic ester cyanohydrin by means of thionyl chloride proved to be the most successful. Two isomers resulted: I, b. p. 94° (24 mm.), f. p. −14°, and II, b. p. 120° (24 mm.), f. p. −40°, having the same composition, $C_7H_9NO_2$. That the compounds were esters of a β-cyano unsaturated acid was shown by the formation of mesaconic acid on long hydrolysis with aqueous alkali.

Three isomers, then, were possible from this dehydration, *viz.*, the *trans* (I)[6] and *cis* (II) ethyl β-cyanocrotonates and, less probably, ethyl β-cyano-β-butenoate (IIa).



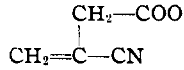
$$\begin{array}{l} \mathrm{H{-}C{-}COOC_2H_5} \\ \quad\ \ \Vert \\ \mathrm{NC{-}C{-}CH_3} \end{array}$$

I



$$\begin{array}{l} \mathrm{H{-}C{-}COOC_2H_5} \\ \quad\ \ \Vert \\ \mathrm{CH_3{-}C{-}CN} \end{array}$$

II



$$\begin{array}{l} \mathrm{CH_2{-}COOC_2H_5} \\ \quad | \\ \mathrm{CH_2{=}C{-}CN} \end{array}$$

IIa

A compound possessing the latter methylene structure (IIa) would be an α-substituted acrylonitrile and should polymerize readily. Neither isomer developed any trace of polymer on standing for one week at 65° in the presence of 0.1% of benzoyl peroxide, whereas both acrylonitrile and methacrylonitrile polymerized completely in a few hours under similar conditions.

A comparison (see Table I) of the boiling points, densities, refractive indices and molecular refractions of the two isomers with the corresponding known values of analogous compounds, involving the same kinds of isomerism, indicated that the

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[1] Pinner, *Ber.*, **18**, 2846 (1885).

[2] Pinner, "Die Imidoaether und ihre Derivate," Robert Oppenheim (Gustav Schmidt), Berlin, 1892, pp. 105–107.

[3] Shestakove and Kazakov, *J. Russ. Phys.-Chem. Soc.*, **44**, 1312–20 (1912).

[4] Autenrieth, *Ber.*, **29**, 1655 (1896).

[5] Schroeter and Wulfing, *ibid.*, **40**, 1593 (1907).

[6] It should be noted that this structure has been called *trans* because it is a derivative of mesaconic acid although it is at the same time a derivative of iso-crotonic acid, the *cis* acid. This election was made because it was felt that the cyano group was of greater import than the methyl group.

TABLE I

Compound	B. p., °C.	B. p., Mm.	Density (20°)	Refractive index (20°)	Molecular refraction
I	94	24	1.015[a]	1.4494[a]	39.43
II	120	24	1.040[a]	1.4518[a]	38.66
Ethyl fumarate	100	13	1.052	1.4410	43.22
Ethyl maleate	104	13	1.067	1.4416	42.67
Ethyl mesaconate	105	15	1.047	1.4494	47.74
Ethyl citraconate	116	15	1.062	1.4458	46.83
Ethyl itaconate	116	15	1.045	1.4388	46.85
Methyl *trans*-β-cyanoacrylate	115–116	100			
Methyl *cis*-β-cyanoacrylate	143–145	100			

[a] At 25°.

lower boiling isomer was the *trans* form. However, these data do not distinguish between the *cis* and the methylene (ethyl β-cyano-β-butenoate) structures. Additional evidence that neither isomer was the methylene compound was afforded by the close similarity of their ultraviolet absorption spectra[7] (see Fig. 1) to that of methyl *trans* β-cyanoacrylate, prepared by the method of Crawford, McLeish and Wood.[8] Considerably weaker absorption in this range would have been exhibited by ethyl β-cyano-β-butenoate, in which the double bond is in conjugation with only the cyano group and not with both the cyano and carboethoxy groups.

As would be expected, the absorption spectra of the β-cyanocrotonates were found to be closely analogous to that of methyl mesaconate as determined by Ruppol,[9] the intensity being intermediate between that of methyl mesaconate and that of mesacononitrile.

On dehydration by the same method with thionyl chloride the cyanohydrin of methyl acetoacetate also gave two isomers, boiling at 82° (22 mm.) and 112° (22 mm.). From *n*-butyl acetoacetate cyanohydrin were obtained two isomers, boiling at 66–67° (1 mm.), and 80–81° (1 mm.). By analogy these were assigned the *trans* and *cis* structures, respectively.

Experimental

Acetoacetic Ester Cyanohydrin.—A modification of the method of Bucherer and Grolee[10] involving the action of sodium cyanide on the sodium bisulfite addition compound of ethyl acetoacetate gave consistently better results than the direct action of aqueous hydrogen cyanide. The addition of an excess of sulfuric acid before vacuum distillation,[11] was found to be essential to prevent excessive decomposition and regeneration of hydrogen cyanide.

To 780 g. (6 moles) of acetoacetic ester was added with stirring and cooling a concentrated aqueous solution of 624 g. of sodium bisulfite. A solution of 326 g. (6 moles) of 95% sodium cyanide was then added in small portions with stirring and cooling over a period of one hour. The supernatant oil was washed with 200 cc. of 1:3 sulfuric acid and 5 cc. of concentrated sulfuric acid was added before distilling under vacuum. The fraction boiling at 132–134° (25 mm.) was 655 g. (70%).

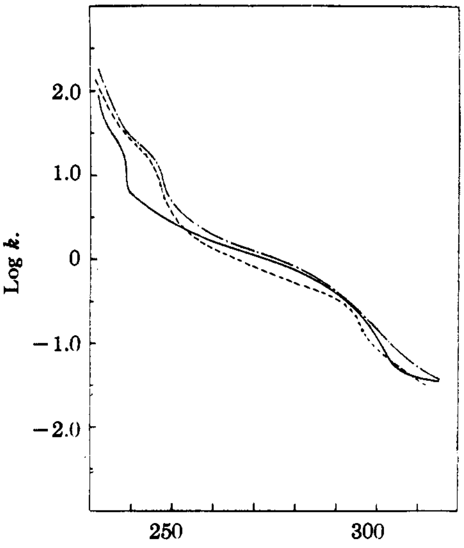

Fig. 1.—Absorption spectra in absolute methanol of ethyl *trans*-β-cyanocrotonate (I), ——·——·; ethyl *cis*-β-cyanocrotonate (II), ----; methyl *trans*-β-cyanoacrylate, ——.

Better yields were obtained when anhydrous liquid hydrogen cyanide was used. To 585 g. (4.5 moles) of ethyl acetoacetate containing 4 g. of sodium cyanide, was added 122 g. (4.5 moles) of liquid hydrogen cyanide from an ice-cooled buret. The solution was stirred and cooled, keeping the temperature at 20–25° during the addition. Five cc. of concentrated sulfuric was then added and the product distilled giving 598 g. (85%) of ethyl acetoacetate cyanohydrin, b. p. 120–124° (13 mm.), n^{25}_D 1.4298.

The acetate was prepared to verify the identity of this compound. The cyanohydrin (55 g., 0.35 mole), acetic anhydride (47 g., 0.46 mole) and two drops of sulfuric acid were refluxed gently for six hours. Distillation from a Claisen flask at 15 mm. gave 44 g. of a fraction boiling at 135–146°. Rectification gave 30 g. of ethyl β-cyano-β-acetoxybutyrate, b. p. 145–146° (15 mm.), n^{25}_D 1.4354.

Anal. Calcd. for $C_9H_{13}O_4N$: C, 54.3; H, 6.57; N, 7.03. Found: C, 54.62; H, 6.57; N, 7.10.

***cis*- and *trans*-Ethyl β-Cyanocrotonates.**—One thousand eighty grams (6.9 moles) of the cyanohydrin in a two-liter flask was heated in an oil-bath maintained at 110°. To this was added 720 cc. (10 moles) of thionyl chloride during a three-hour period. After two days at the same temperature the evolution of hydrogen chloride and sulfur dioxide had virtually ceased. The product was washed with water, distilled under vacuum and the portion boiling at 85–130° (30 mm.) collected. This fraction was washed successively with dilute aqueous solutions of sodium bisulfite, sodium carbonate and hydrochloric acid. Careful fractionation gave the two isomers: I, b. p. 93–94° (24 mm.), f. p. −14°, 294 g., n^{25}_D 1.4494, d^{25}_{25} 1.015; and II, b. p. 119–120° (24 mm.), f. p. −40°, 324 g., n^{25}_D 1.4518, d^{25}_{25} 1.040 together with 50 g. of an intermediate fraction. This represented a combined yield of 69% for the dehydration. The isomers differ greatly with regard to their solubility in petroleum ether, the *trans* isomer (I) being miscible and the *cis* isomer (II) but only slightly soluble.

Anal. Calcd. for $C_7H_9O_2N$: C, 60.4; H, 6.52; N, 10.03. Found for I: C, 60.58; H, 6.65; N, 9.85. Found for II: C, 60.15; H, 6.52; N, 9.93.

Hydrolysis of Ethyl β-Cyanocrotonates.—A 7-g. sample of each isomer was refluxed with 8 g. of sodium hydroxide

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[7] The authors are indebted to Dr. Daniel Norman, of the New England Spectrochemical Laboratories, for obtaining the absorption spectra of these samples.

[8] Crawford, McLeish and Wood, U. S. Patent 2,293,969.

[9] Ruppol, *Bull. Sci. acad. Royal Belg.*, **21**, 236–246 (1935).

[10] Bucherer and Grolee, *Ber.*, **39**, 1227 (1906).

[11] Ultee, *ibid.*, **39**, 1858 (1906).

in 50 cc. of water until no more ammonia was evolved (*ca.* two days). Acidification with hydrochloric acid and evaporation to dryness gave white powders which were ground in a mortar and exhaustively extracted with dry ether. Recrystallization of the ether extracts from hot water gave mesaconic acid in both cases, m. p. 197–198° (uncor.), neutral equivalent, 65.8 (theory, 65.0). Citraconic anhydride, when subjected to the same treatment, also gave only mesaconic acid, which did not depress the melting point of the above hydrolysis products.

cis- **and** *trans*-**Methyl β-Cyanocrotonates.**—By an analogous procedure, 400 g. of methyl acetoacetate yielded 371 g. (75%) of its cyanohydrin, b. p. 116–118° (11 mm.), n^{25}_D 1.4332. Dehydration of 270 g. with 216 cc. of thionyl chloride gave the two isomers of methyl β-cyanocrotonates: III, b. p. 82–83° (22 mm.), f. p. 22.5°, n^{25}_D 1.4543, and IV, b. p. 112–113° (22 mm.), f. p. 24.5°, n^{25}_D 1.4566. The yield of both isomers was 74%.

Anal. Calcd. for $C_6H_7O_2N$: C, 57.6; H, 5.64; N, 11.20. Found for III: C, 57.53; H, 5.75; N, 11.18. Found for IV: C, 57.32; H, 5.81; N, 11.08.

cis- **and** *trans*-*n*-**Butyl β-Cyanocrotonates.**—In a similar fashion, 475 g. of *n*-butyl acetoacetate yielded 391 g. (70%) of *n*-butyl acetoacetate cyanohydrin, b. p. 138–142° (17 mm.), n^{25}_D 1.4318. Dehydration gave a 68% yield of the two isomers of *n*-butyl β-cyanocrotonate: V, b. p. 66–67° (1 mm.), f. p. −36°, n^{25}_D 1.4515 and VI, b. p. 80–81° (1 mm.), f. p. below −78°, n^{25}_D 1.4519.

Anal. Calcd. for $C_9H_{13}O_2N$: C, 64.65; H, 7.84; N, 8.38. Found for V: C, 64.26; H, 8.07; N, 8.21. Found for VI: C, 63.25; H, 8.02; N, 8.55.

Summary

The methyl, ethyl, and butyl esters of *cis* and *trans* β-cyanocrotonic acid have been synthesized and their structures and configurations elucidated.

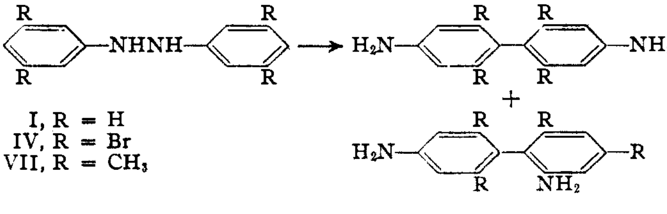
DAYTON, OHIO RECEIVED FEBRUARY 23, 1945

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Rearrangement of 3,3′,5,5′-Tetramethylhydrazobenzene

BY ROBERT B. CARLIN

The acid-catalyzed rearrangement of hydrazobenzene (I) to benzidine (II) was first recognized by Hofmann.[1] Schmidt and Schultz[2] showed that benzidine was accompanied in the rearrangement products by a small amount of an isomeric base, diphenyline (III). The rearrangements of many substituted hydrazobenzenes have since been studied and the experimental results generalized.[3] Although Robinson[4] has proposed an electronic interpretation of the benzidine rearrangement, he was unable to consider the effects of steric factors upon the course of the reaction because of the scarcity of available evidence bearing upon this phase of the problem. A study of the rearrangements of 3,3′,5,5′-tetrasubstituted hydrazobenzenes, in which the substituents are bulky atoms or groups, should serve to furnish some of the required information. The investigation which forms the subject of this report was undertaken in order to determine the effect of the methyl groups in 3,3′,5,5′-tetramethylhydrazobenzene (VII) upon the course of its rearrangement. Particular care was taken to observe any of the four manifestations of the hindering effect of the methyl groups which might occur.

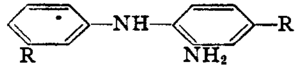


I, R = H
IV, R = Br
VII, R = CH_3

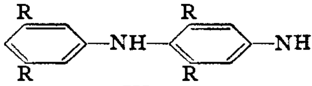
II, R = H
V, R = Br
VIII, R = CH_3

III, R = H
VI, R = Br
IX, R = CH_3

It might be expected that the rearrangement of any such substituted hydrazobenzene to the corresponding 2,2′,6,6′-tetrasubstituted benzidine should be hindered to a certain extent by the presence of the bulky groups occupying all ring positions *ortho* to the carbon atoms engaged in the formation of the new carbon-to-carbon bond. This hindrance, if sufficient to modify the normal electronic effects, might manifest itself by: (1) an increase in the amount of diphenyline, which should be less highly hindered, at the expense of the benzidine; (2) formation of semidines (*e. g.*, X and XI); (3) increased disproportionation of the hydrazobenzene 2ArNHNHAr → ArN=NAr + 2ArNH$_2$; (4) more drastic conditions required to bring about reaction. Numerous attempts have been made to isolate semidines from the rearrangement products of *p*-unsubstituted hydrazobenzenes, but only one has been reported to be successful. Nölting and Werner[5] indicated that traces of *o*-semidine (X, R = H) were formed along with benzidine and diphenyline, by the rearrangement of hydrazobenzene in benzene solu-



X



XI

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[1] Hofmann, *Proc. Roy. Soc.* (London), **12**, 576 (1863).

[2] Schmidt and Schultz, *Ber.*, **11**, 1754 (1878).

[3] Jacobson, *Ann.*, **428**, 76 (1922).

[4] Robinson, *J. Chem. Soc.*, 220 (1941).

[5] Nölting and Werner, *Chem. Ztg.*, **18**, 1095 (1894).