dropwise to 34 g. of melted *m*-dinitrobenzene. The mixture was refluxed carefully for three hours and then steam distilled to remove unreduced *m*-dinitrobenzene. The residue was extracted with hot benzene. The benzene was evaporated and the residue yielded a red compound. After recrystallization from alcohol and benzene, the compound, m. p. 140°, gave on analysis: C, 52.99; H, 2.92; N, 20.82. Calculated for dinitroazobenzene: C, 52.94; H, 2.94; N, 20.58.

Reduction with Diethanolamine.—Thirty-four grams of *m*-dinitrobenzene and 84 g. of diethanolamine were refluxed as above for three hours. Steam distillation yielded a distillate from which ether extracted a trace of a compound, m. p. 110°, which gave tests for the amino group. This compound is probably *m*-nitroaniline.

The residue from the steam distillation was cooled and filtered from the tarry solids which were then treated with hot benzene. There was finally obtained after recrystallization an orange compound, m. p. 145°, which formed a white hydrochloride charring at 240° and a diacetyl compound melting at 265° corresponding to 3,3′-diaminoazobenzene. A small amount of 3,3′-diaminoazoxybenzene was isolated.

Reduction with Triethanolamine.—One hundred and nineteen grams of triethanolamine and 34 g. of *m*-dinitrobenzene were refluxed for three hours at 160–170°. The mixture was treated with hot water and filtered. The insoluble solids were extracted with benzene, the benzene evaporated and the residue recrystallized from alcohol. There was thus obtained a red compound, m. p. 144°, insoluble in hydrochloric acid, and forming no acetyl derivative. The compound is probably 3,3′-dinitroazoxybenzene reported in the literature as having m. p. 143–146°.

The filtrate was steam distilled and the residue extracted with ether. Evaporation of the ether left an orange residue from which by recrystallization from water there was obtained a yellow compound, m. p. 109°. This compound gave the usual tests for an amino group: N, 21.31; calculated for $2NH_2C_6H_4\cdot N_2OC_6H_4NH_2N(CH_2CH_2OH)_3$, *i. e.*, addition product of the azoxy compound and triethanolamine, N, 20.82. It formed an acetyl derivative corresponding to the aminoazoxy compound.

Reduction with Excess Triethanolamine.—The molar ratio of *m*-dinitrobenzene to triethanolamine was 1 to 6. The mixture was refluxed for three hours over a free flame. treated with hot water and allowed to stand. The water insolubles were filtered off and yielded 3,3′-dinitroazoxybenzene. The filtrate was extracted with ether. The residue obtained after evaporation of the ether was treated with hot water. The water-soluble portion upon cooling deposited the same addition compound as in the previous experiment while the insoluble portion yielded 3,3′-diaminoazobenzene.

Reduction with Monoethanolamine.—To 34 g. of molten *m*-dinitrobenzene was added slowly 48.8 g. of monoethanolamine and refluxed for three hours with a small flame. The mixture was treated with 200 cc. hot water and filtered. The filtrate was cooled and the solid that separated was extracted with benzene. Petroleum ether was added to the benzene extract. A crystalline precipitate of 3,3′-diaminoazobenzene settled out.

Summary

The ethanolamines reduce *m*-dinitrobenzene to the nitroazo, aminoazo, aminoazoxy stages. An addition compound of the aminoazoxy and triethanolamine was isolated.

NEW YORK, N. Y. RECEIVED MARCH 16, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Application of the Cyano Ester Ring Closure to Five- and Six-Membered Rings

BY REYNOLD C. FUSON AND WAYNE COLE

A simple method of closing the cyclobutane ring was discovered by Fuson and Kao,[1] who prepared ethyl 1-cyano-1,2-cyclobutanedicarboxylate (II) by treating ethyl α,α′-dibromoadipate (I) with sodium cyanide.[2] That the reaction may prove to be generally useful in synthesizing cyclobutane derivatives has been indicated by its successful application in the preparation of a methylcyclobutanedicarboxylic acid[3] and norcaryophyllenic acid.[4] Where it is applicable, this synthesis is superior to other methods of closing the cyclobutane ring, because it affords higher yields and involves a comparatively simple procedure.

The present work was undertaken with the object of determining whether this method of ring closure could be extended to the synthesis of rings of other sizes. The attempts have been successful for cyclopentane and cyclohexane rings.

For the synthesis of a five-membered ring, ethyl α,α′-dibromopimelate (III) was employed. Treatment with sodium cyanide in absolute alcohol converted this ester into ethyl 1-cyano-1,2-cyclopentanedicarboxylate (IV) in yields of 80 to 88%. As was to be expected, these are somewhat

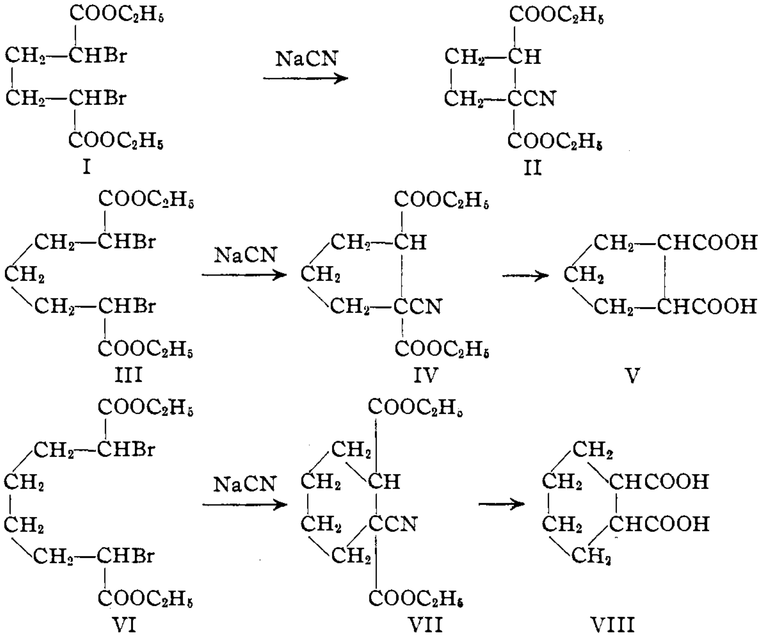
---

[1] Fuson and Kao, THIS JOURNAL, **51**, 1536 (1929).

[2] The method is novel, but the reaction which it involves has long been known to take place with open chain compounds. See, for example, Franchimont, *Ber.*, **5**, 1048 (1872); Zelinsky, *ibid.*, **21**, 3160 (1888); Poppe, *ibid.*, **23**, 113 (1890); Bone and Perkin, *J. Chem. Soc.*, **69**, 253 (1896).

[3] Fuson, Kreimeier and Nimmo, THIS JOURNAL, **52**, 4074 (1930).

[4] Rydon, *J. Chem. Soc.*, 593 (1936).



higher than the yields obtained with the corresponding cyclobutane derivatives, which varied from 70 to 80%.[1]

Hydrolysis followed by decarboxylation served to convert the cyano ester into 1,2-cyclopentanedicarboxylic acid (V), which was obtained in both the *cis* and the *trans* forms. These, as well as the *cis*-anhydride and the *cis*-phenylimide, were found to have the melting points given by Perkin.[5]

For the synthesis of a six-membered ring, ethyl α,α′-dibromosuberate (VI) was used. The corresponding cyano ester (VII) was obtained in yields of 48 to 55%. It was converted into 1,2-cyclohexanedicarboxylic acid (VIII), which was obtained in the *trans* modification, melting at 221° as described by Baeyer.[6]

Experiments with ethyl α,α′-dibromoazelate and ethyl α,α′-dibromosebacate failed to give detectable amounts of the cyclic cyano esters containing seven- or eight-membered rings.

Experimental Part

Ethyl α,α′-dibromopimelate[7] was prepared in 78% yield by brominating pimelyl chloride at 75° and esterifying the product with absolute ethanol. It boils at 193–199° (17 mm.) or 171–178° (5 mm.), and gives the refractive index n^{20}_{D} 1.4880.

Ethyl 1-Cyano-1,2-cyclopentanedicarboxylate.—A mixture of 50 g. of ethyl α,α′-dibromopimelate, 25 g. of powdered sodium cyanide and 30 cc. of absolute ethanol was refluxed over a steam-bath or a low free flame for sixty hours. Sodium bromide and excess sodium cyanide were removed from the cooled mixture by filtration and washed with 10 cc. of ethanol. The filtrate, when distilled *in vacuo*, gave a colorless distillate boiling at 125–130° (2 mm.). Redistillation gave 25 to 29 g. (80 to 88% of the theoretical amount) of liquid boiling at 135–136° (3.5 mm.) or 126–128° (2 mm.); d^{20}_{4} 1.108; n^{20}_{D} 1.4560; M_D calcd. 58.49; M_D found 58.64.

Anal. Calcd. for $C_{12}H_{17}O_4N$: C, 60.25; H, 7.11. Found: C, 60.14, 60.12; H, 7.43, 7.31.

trans-1,2-Cyclopentanedicarboxylic Acid.[5]—Fifteen grams of ethyl 1-cyano-1,2-cyclopentanedicarboxylate was hydrolyzed by refluxing with 75 cc. of concentrated hydrochloric acid for thirty hours. The ester dissolved completely, giving a light brown solution which deposited, on cooling, 5 g. of crude *trans*-1,2-cyclopentanedicarboxylic acid, melting at 155–158°. This was converted into the pure *trans* acid by heating to 160° with 1 cc. of concentrated hydrochloric acid in a sealed tube for one hour. The pure *trans* acid melted at 161°.

cis-1,2-Cyclopentanedicarboxylic Anhydride.[5]—The mother liquors from the crude *trans* acid were evaporated to dryness. The residue (7 g.) was warmed *in vacuo* to expel moisture and ammonium chloride, then mixed with 40 cc. of acetic anhydride and refluxed over a low free flame for ten hours. The mixture was distilled under diminished pressure. The distillate boiling between 95 and 100° at 3.5 mm. solidified to a gelatinous mass weighing 4 g. Recrystallization from low-boiling petroleum ether gave fluffy needles melting at 73.5–74°.

Anal. Calcd. for $C_7H_8O_3$: C, 60.0; H, 5.72. Found: C, 60.1; H, 6.00.

Hydrolysis of 2 g. of the *cis*-anhydride with 10 cc. of 20% potassium hydroxide, and acidification of the resulting solution with hydrochloric acid gave needles of *cis*-1,2-cyclopentanedicarboxylic acid, melting at 139°. Perkin reports this *cis* acid to melt at 140°.[5]

Refluxing for twenty minutes with 8 cc. of aniline converted 1.5 g. of the *cis*-anhydride into 2.3 g. of the phenylimide of *cis*-1,2-cyclopentanedicarboxylic acid, melting at 89°.

Ethyl α,α′-dibromosuberate[7a,8] was prepared by warming a mixture of 1 mole of suberyl chloride and 2 moles of bromine on a water-bath at 60° for six hours, then esterifying the product with excess absolute alcohol. Two distillations gave a 46% yield of the dibromo ester boiling at 165–167° (3 mm.); n^{20}_{D} 1.4873.

Ethyl 1-Cyano-1,2-cyclohexanedicarboxylate.—A mixture of 40 g. of ethyl α,α′-dibromosuberate, 30 cc. of absolute ethanol and 20 g. of powdered sodium cyanide was refluxed over a low free flame for fifty hours. The liquid was cooled and filtered free from sodium bromide and

---

[5] Perkin, *J. Chem. Soc.*, **65**, 572 (1894).

[6] Baeyer, *Ann.*, **258**, 213 (1890).

[7] (a) Willstätter, *Ber.*, **28**, 655 (1895); (b) Hassell and Ingold, *J. Chem. Soc.*, 1465 (1926).

[8] Goss and Ingold, *J. Chem. Soc.*, 1471 (1926).

sodium cyanide. Distillation *in vacuo* gave a colorless distillate boiling at 124–140° (3 mm.). Redistillation gave 10.4 to 13 g. (48 to 55% of the theoretical amount) of product boiling at 129–130° (2 mm.); d^{20}_4 1.082; n^{20}_D 1.4570; M_D calcd. 63.11; M_D found 63.68.

Anal. Calcd. for $C_{13}H_{19}O_4N$: C, 61.65; H, 7.51; N, 5.54. Found: C, 61.50; H, 7.46; N, 5.82.

trans-1,2-Cyclohexanedicarboxylic Acid.—Eight grams of ethyl 1-cyano-1,2-cyclohexanedicarboxylate was refluxed with 40 cc. of 20% hydrochloric acid for thirty hours. The ester dissolved and 5.4 g. of colorless acid, melting at 180–184°, separated from the solution. This crude acid gave a neutral equivalent of 86.5 and therefore appeared to be a mixture of the *cis* (m. p. 190°) and the *trans* (m. p. 221°) forms of 1,2-cyclohexanedicarboxylic acid. Heating the crude acid to 160° with 2 cc. of concentrated hydrochloric acid in a sealed tube for two hours converted it into the pure *trans* acid, melting at 221° as described by Baeyer.[6] A mixture of this acid with an authentic sample of *trans*-hexahydrophthalic acid also melted at 221°.

Summary

The cyano ester ring closure has been extended to five- and six-membered rings.

URBANA, ILLINOIS RECEIVED MARCH 21, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Action of Selenium Tetrachloride on Some Esters of Salicylic Acid[1]

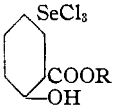
BY R. E. NELSON, ED. F. DEGERING AND JOHN A. BILDERBACK

The action of selenium oxychloride on paraffins, olefins, ethers, ketones, salicylic acid and its esters, amines, and phenols has been described more or less thoroughly in the literature.[2] The question concerning the action of the monochloride and the tetrachloride aroused our interest.

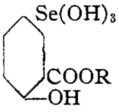
Selenium tetrachloride, according to our study, is a valuable reagent to use in the preparation of organo-selenium compounds. No selenium dioxide or free selenium is produced in this reaction. The use of the oxychloride generally results in the production of selenium dioxide as a by-product. If the monochloride is used, free red selenium is precipitated often in a colloidal state. The presence of either the dioxide or free selenium introduces difficulty in purification of the desired product.

In this investigation, the action of selenium tetrachloride on various esters of salicylic acid was studied. The results obtained indicate that the first reaction taking place between selenium tetrachloride and the esters of salicylic acid gives compounds represented by formula I.

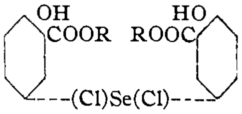
These trichloro derivatives are hydrolyzed very easily. They react slowly, as a matter of fact, with moisture from the air to yield the corresponding hydroxide (formula II),



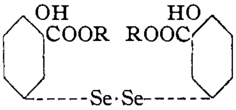
I



II



III



IV

An attempt was made to prove the presence of hydroxyl groups in compounds of formula II by acetylation with acetyl chloride. The addition of acetyl chloride, however, regenerated the trichloride (formula I) and gave acetic acid as the other product. It has been shown by Nelson[3] and co-workers that the hydroxyl group para to selenium is not acetylated.

The trichlorides of this series are yellow, hygroscopic, unstable compounds which change color slowly, and give off hydrogen chloride. The trihydroxides are grayish-white in color and seem to be stable. They are soluble in alcohol, but insoluble in ether and cold water. They react vigorously with acetyl chloride as might be expected, but yield the trichlorides.

If the selenium tetrachloride and ester are heated over a longer period of time the dichloroselenodisalicylates are formed (formula III).

The dichloroselenodisalicylates have been prepared previously by Nelson and co-workers and their properties described. They are usually yellow and quite stable. They are insoluble in ether, alcohol, and chloroform, but are soluble to

---

[1] Abstract of a thesis submitted to the faculty of Purdue University by John A. Bilderback in partial fufilment of the requirements for the degree of master of science, August, 1937. Presented before the Division of Organic Chemistry of the A. C. S. at the Dallas meeting, April, 1938.

[2] Nelson and Alquist, THIS JOURNAL, **53**, 4033 (1931); Nelson and Jones, *ibid.*, **52**, 1588 (1930); Nelson, Bunting and Schroeder, *ibid.*, **55**, 801–803 (1033); Morgan and Burstall, *J. Chem. Soc.*, 3260 (1928); Godchaux, *Ber.*, **24**, 763 (1891); Nelson and Boase, *Proc. Indiana Acad. Sci* **44**. 135–137 (1934).

[3] Nelson and Baker, THIS JOURNAL, **56**, 467 (1934).