

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Many-Membered Carbon Rings. VI. Unsaturated Nine-membered Cyclic Hydrocarbons¹BY A. T. BLOMQUIST, LIANG HUANG LIU² AND JAMES C. BOHRER³

RECEIVED JANUARY 21, 1952

The nine-membered cyclic hydrocarbons, cyclononyne, *cis*-cyclononene and *trans*-cyclononene, have been synthesized. The alkali-catalyzed oxidative decomposition of 1,2-cyclononanedione dihydrazone produced cyclononyne. Hydrogenation of cyclononyne over a palladium catalyst led to *cis*-cyclononene while reduction of the acetylene with sodium in liquid ammonia gave *trans*-cyclononene. *trans*-Cyclononene was also formed by the thermal decomposition of cyclononyltrimethylammonium hydroxide. The *trans*-olefin appears to be the labile form and to be strained. It is isomerized thermally, under acidic conditions, to *cis*-cyclononene and is reactive toward phenyl azide. Dehydration of cyclononanol with boiling phthalic anhydride gave a mixture of the *cis*- and *trans*-olefins, indicating that *trans*-cyclononene is probably less strained than *trans*-cyclooctene. The infrared spectra of several of the nine-membered carbocycles are given.

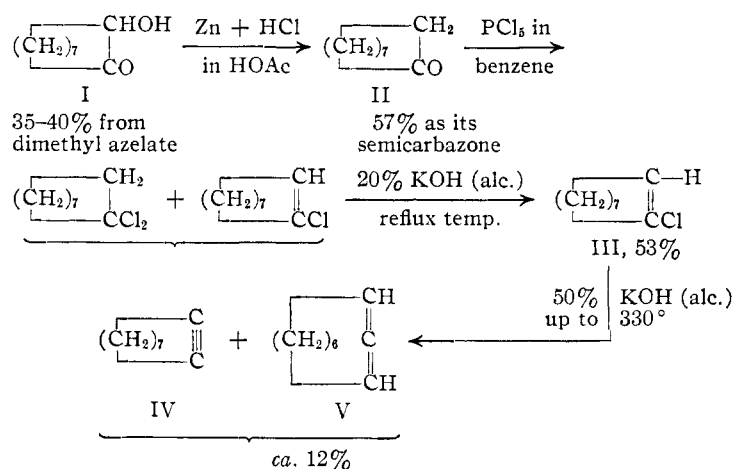
The preparation and properties of some simple unsaturated ten-membered cyclic hydrocarbons were described recently.¹ It was reported that cyclodecyne, free from its isomeric allene, could be obtained only by the oxidative decomposition of 1,2-cyclodecanedione dihydrazone. Also, chemical evidence was presented to support the view that both *cis* and *trans* forms of cyclodecene are probably strainless. This paper describes the synthesis of cyclononyne (IV), *cis*-cyclononene (XI) and *trans*-cyclononene (X). Evidence is also presented indicating that the *trans* form of cyclononene may be strained while the *cis* isomer is probably strainless.

Azeloin (I), obtained in improved yield (35–40%) by the method used to prepare sebacoïn,¹ served as the starting carbocycle for all syntheses. Purification of the various nine-membered unsaturated hydrocarbons was frequently achieved through methods of chromatography while it was most convenient to follow these purifications by measurement of infrared spectra and refractive indices.

Cyclononyne (IV).—The first attempt to obtain this acetylene was by the dehydrohalogenation of 1-chlorocyclononene (III), a procedure applied successfully by Ruzicka, *et al.*, in the synthesis of cyclopentadecyne and cycloheptadecyne.⁴ These experiments are summarized in the diagram which follows.

The product obtained by vigorous treatment of III with strong alcoholic potassium hydroxide solution was a hydrocarbon which absorbed two molar equivalents of hydrogen. That it was a mixture of approximately equal amounts of IV and V was indicated by ozonolysis which afforded roughly equal quantities of azelaic and suberic acids. The infrared spectrum of this product (IV + V) showed very weak absorption in the region charac-

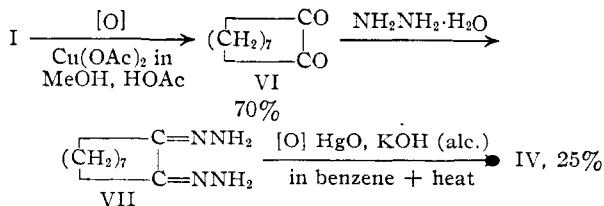
teristic for $\text{—C}\equiv\text{C—}$ (*ca.* 4.5 μ) and stronger absorption around 5 μ , characteristic of $\text{C}=\text{C}=\text{C}$.



The molecular refractivity was found to be intermediate between the values calculated for IV and V.

Fig. 1.—Enantiomorphs of *trans*-cyclononene.

The alkali-catalyzed oxidative decomposition of 1,2-cyclononanedione dihydrazone (VII)⁵ gave IV free from V. Following the route outlined below, pure IV was obtained in 25% yield from VII; final purification of distilled product was achieved by chromatographing through silica gel to constant refractive index (n_D^{20} 1.4890).



Cupric acetate in acetic acid–methanol proved to be superior to the reagent chromium trioxide in acetic acid for the oxidation of I to VI.

(5) (a) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 496; (b) T. Curtius and R. J. Kastner, *J. prakt. Chem.*, [2] **83**, 215 (1913); (c) W. Schlenk and E. Bergmann, *Ann.*, **463**, 71 (1928).

(1) For the preceding paper in this series see A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *THIS JOURNAL*, **74**, 3636 (1952).

(2) Postdoctoral Research Fellow under the du Pont grant-in-aid, 1951–1952.

(3) Part of this paper is abstracted from a dissertation submitted by J. C. Bohrer in February, 1951, to the Graduate Faculty of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) L. Ruzicka, M. Hürbin and H. A. Boekenoogen, *Helv. Chim. Acta*, **16**, 498 (1933).

The infrared spectrum of IV and some of its other properties were reported earlier.⁶ The sample of IV absorbed 102% of two molar equivalents of hydrogen upon quantitative reduction in acetic acid using Adams catalyst. It gave only azelaic acid upon ozonolysis and was converted to II when hydrated.

trans-Cyclononene (X).—This hydrocarbon has been obtained by the thermal decomposition of cyclononyltrimethylammonium hydroxide and by the reduction of IV with sodium in liquid ammonia.

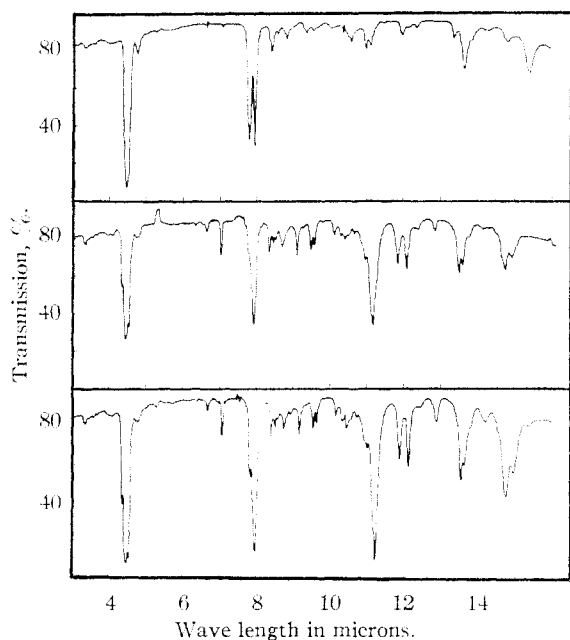


Fig. 2.—Infrared spectra: upper curve, cyclononane; middle curve, X from VIII; lower curve, X from reduction of IV with sodium in liquid ammonia.

The specimens of X obtained by the two methods showed practically the same refractive index, n_D^{20} 1.4799 and 1.4800, respectively. The infrared spectra for the two samples also were in excellent agreement (Fig. 2), both spectra showing very strong absorption at 10.25μ , characteristic of a *trans* C=C.

X absorbed 100.5% of one molar equivalent of hydrogen and gave only azelaic acid upon ozonolysis. When treated with phenyl azide according to Ziegler and Wilms,⁷ X gave a crystalline solid adduct within 2–3 hours. Also following the procedure of Ziegler and Wilms, X was isomerized to XI when heated for 1.5 hours at 150° in the presence of a small amount of β -naphthalene-sulfonic acid. The infrared spectrum and other properties of the hydrocarbon, produced on isomerization, were in excellent agreement with those of XI. The infrared spectrum (Fig. 3) showed strong absorption in the 13.5 – 14.5μ region (*cis* C=C) and no absorption at 10.25μ . When treated with phenyl azide, the isomerized hydrocarbon showed no appreciable reaction after a period of two weeks.

(6) A. T. Blomquist, et al., THIS JOURNAL, **73**, 5510 (1951).

(7) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

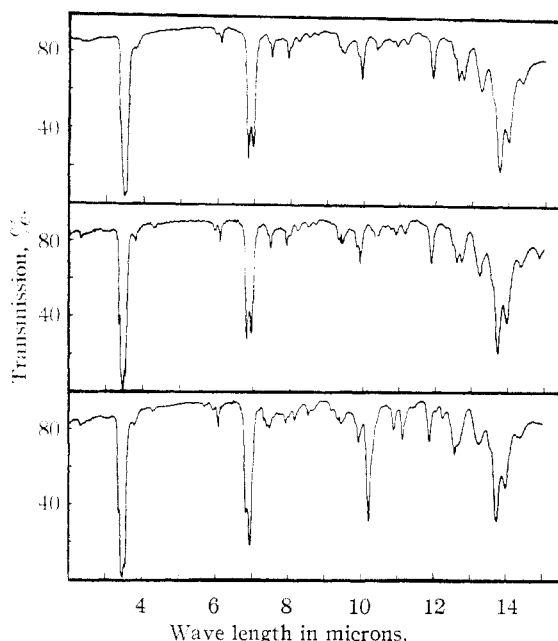
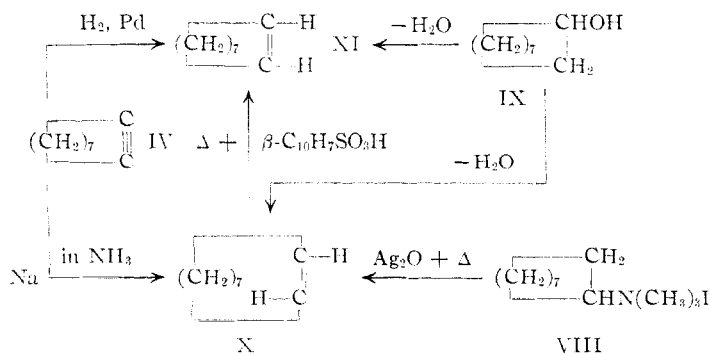


Fig. 3.—Infrared spectra: upper curve, XI from catalytic hydrogenation of IV; middle curve, XI from isomerization of X; lower curve, mixture of X and XI from dehydration of IX.

cis-Cyclononene (XI).—This hydrocarbon was produced by the selective catalytic hydrogenation of IV over a palladium catalyst supported on barium carbonate. The specimen of IV so obtained showed strong general absorption in the 13.5 – 14.5μ region of the infrared and no absorption at 10.25μ (Fig. 3). It absorbed 101% of one molar equivalent of hydrogen and gave only azelaic acid upon ozonolysis. When treated with phenyl azide there was no observable reaction; no crystalline adduct formed over a period of 4 weeks.

As mentioned earlier, XI was also obtained by the acid-catalyzed thermal isomerization of X.

Dehydration of cyclononanol (IX) with boiling phthalic anhydride afforded a mixture of X and XI as indicated by the infrared spectrum (Fig. 3). The interrelationship of the three hydrocarbons IV, X and XI is shown in the diagram below.



Discussion

It is interesting to compare the properties of the *cis*-*trans* isomers of the eight-, nine- and ten-membered cyclic olefins.^{1,7} It has been observed previously¹ that within a related series of hydrocarbons, both cyclic and open-chain, in which all the members are strainless there is a decrease in refrac-

tive index and density in the order: acetylene, *cis* olefin, *trans* olefin, paraffin. With the eight-membered carbocycles, where the *trans*-olefin is a labile strained modification, the positions of *cis*- and *trans*-cyclooctene respecting refractive index and density are reversed. The nine-membered cyclic hydrocarbons appear to occupy a position intermediate between the eight- and ten-membered series. The refractive indices of *cis*- and *trans*-cyclononene are almost the same. Contrary to the statement of Ziegler and Wilms,⁷ the *trans*-olefin is somewhat strained; indicated by its reactivity toward phenyl azide and its thermal isomerization to the *cis* form. The degree of strain is probably not as great as in *trans*-cyclooctene for it is formed, together with the *cis* isomer, in the dehydration of cyclononanol.

The spacial configuration of X is also of interest. An examination of models of this hydrocarbon shows that it is asymmetric and hence it should exist in two enantiomorphous modifications (Fig. 1). There appears to be sufficient restriction in rotation about carbon-carbon bonds to prevent a ready interconversion of the enantiomorphs. In order to confirm isomerism of this type, a study of *trans*-1-cyclononene-6-one, which should be asymmetric and resolvable, is in progress.

The properties of cycloöctyne, as reported by Domnin,⁸ when compared with similar properties of other eight-membered cyclic hydrocarbons and with the nine- and ten-membered cyclic acetylenes seem to be abnormal. The synthesis and properties of this hydrocarbon are being re-examined.

In order to make the infrared data on the nine-membered hydrocarbons more complete the spectrum for cyclononane is given (Fig. 2). The properties of this specimen of cyclononane were in good agreement with those reported previously.

Experimental Part⁹

Azeloin (2-Hydroxycyclononane) (I).—This cyclic acyloin was obtained in 35–40% yield from dimethyl azelate following the procedure described for sebacoin.¹ Preparations were carried out on a 2-molar scale and the product used in subsequent reactions showed b.p. 91–103° (3 mm.), with the main portion distilling at 97–100° (3 mm.).

Cyclononane (II).—The reduction of I to II was carried out as previously described.¹ I was obtained as its crude semicarbazone, m.p. 150–160°, in 57% yield. After recrystallization from 90% methanol the m.p. was raised to 179.5–180.5°.

Regeneration of II from its semicarbazone was done by steam distilling a mixture of 13.1 g. of II semicarbazone, 22 g. of phthalic anhydride and 45 ml. of water. After collecting 300 ml. of distillate the latter was extracted with ether. From the dried ether extracts there was obtained 8.36 g. (90%) of II: b.p. 100–101.5° (15 mm.); n_D^{20} 1.4768.

The oxime of II was obtained by a standard procedure. From 20 g. of II there was obtained 21.5 g. of crude oxime, m.p. 75–77°. After one recrystallization the oxime (16 g., 74%) showed m.p. 76.5–77.5°.¹⁰

1-Chlorocyclononene (III).—To a suspension of 25 g. (0.12 mole) of phosphorus pentachloride in 50 ml. of benzene there was added with cooling 7 g. (0.05 mole) of II.

(8) N. A. Domnin, *J. Gen. Chem. (U. S. S. R.)*, **8**, 851 (1938); *C. A.*, **33**, 1282 (1939).

(9) Melting points are corrected and boiling points are uncorrected except where indicated. The infrared spectra were determined with a Perkin-Elmer Double Beam Infrared Spectrophotometer, Model 21, using a sodium chloride prism. Pure liquid samples, *i. e.*, free of solvents, of varying thickness (up to 0.002 in.) were used in the determinations.

(10) L. Ruzicka, M. Kobelt, O. Häfner and V. Prelog, *Helv. Chim. Acta*, **32**, 544 (1949), report m.p. 79°.

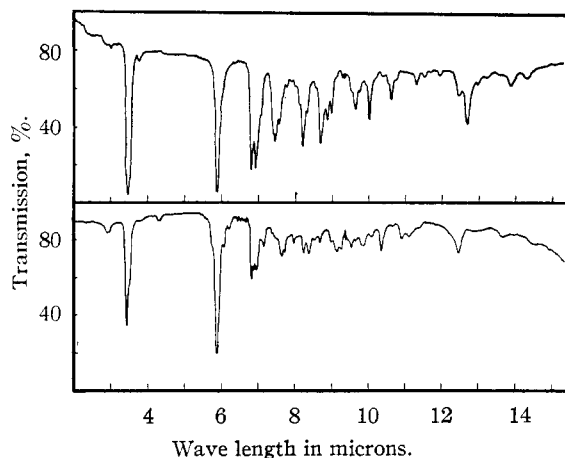


Fig. 4.—Infrared spectra: upper curve, cyclononane; lower curve, 1,2-cyclononanedione.

The mixture was allowed to stand overnight and then worked up in the usual way to remove inorganic compounds. On distillation there was obtained 6.3 g. of a fraction showing b.p. 90–120° (15 mm.) which was largely a mixture of III and 1,1-dichlorocyclononane. This mixture of chloro compounds (6.3 g.) was refluxed for 6 hours with 20 ml. of 20% alcoholic potassium hydroxide. After distilling about 15 ml. of alcohol from the mixture, it was filtered and the filter cake washed with ether. The combined filtrate and ether washings were washed with 30–40% calcium chloride solution, dilute hydrochloric acid and finally with water. Distillation of the dried ether solution gave 2.6 g. (32%) of a pale yellow liquid; b.p. 125–142° (100 mm.). Redistillation of this liquid gave a sample which still possessed a pale yellow color; b.p. 142–144° (100 mm.); n_D^{20} 1.4987; d_4^{20} 1.004.

Anal. Calcd. for $C_9H_{15}Cl$: C, 68.12; H, 9.51. Found: C, 68.11, 68.16; H, 9.54, 9.58.

Dehydrohalogenation of III.—To a distilling flask containing 30 g. (0.65 mole) of potassium hydroxide and 18 ml. of ethanol heated to 125° there was added 14 g. (0.09 mole) of III. Nothing distilled during the addition so the temperature of the mixture was increased gradually to 330°. The cloudy distillate was taken up in 100 ml. of ether and this ether solution washed and dried. After removal of the ether the residue was distilled twice under reduced pressure. Finally there was obtained 1 g. of a colorless liquid which gave a negative Beilstein test for halogen and decolorized potassium permanganate solution and a solution of bromine in carbon tetrachloride: b.p. 105–115° (100 mm.); n_D^{20} 1.4950; d_4^{20} 0.926.

Anal. Calcd. for C_9H_{14} : C, 88.45; H, 11.55. Found: C, 88.30, 88.31; H, 11.60, 11.49.

Quantitative reduction in acetic acid using Adams catalyst required 100.6% of two molar equivalents of hydrogen.

Ozonolysis of the hydrocarbon in ethyl acetate was carried out as previously described.¹ Two solid acidic fractions were obtained: fraction I (less soluble in acetic acid and in water) showed m.p. 129.5–130.5°; fraction II (more soluble in acetic acid and water) showed m.p. 101.0–102.5°. Determination of the m.p. of mixtures of fractions I and II with pimelic, suberic and azelaic acids indicated that fraction I was probably suberic acid. A mixed m.p. of fraction I with an authentic specimen of suberic acid, m.p. 135.6–137.1°, showed 133–138°. The bis-*p*-bromophenacyl ester of fraction I, m.p. 142.8–146.3°, showed m.p. 142.0–143.5°, when mixed with a sample of bis-*p*-bromophenacyl suberate, m.p. 143.9–144.4°. The m.p.'s of mixtures of fraction II with pimelic and azelaic acids did not permit a decision to be made regarding the identity of fraction II. The bis-anilide of fraction II, m.p. 189–190° (micro m.p.), and the bis-*p*-toluidide, m.p. 196–199.5°, demonstrated that II was azelaic acid. This was confirmed by determining the m.p.'s of mixtures of the two derivatives of II with corresponding derivatives of pimelic, suberic and azelaic acids. Approximately equal amounts of fractions I and II were obtained.

1,2-Cyclononanedione (VI).—This α -diketone was obtained by the oxidation of I using three different reagents. Oxidation of 217 g. of I with 89.2 g. of chromium trioxide in 1000 ml. of glacial acetic acid as described by Prelog, *et al.*,¹¹ gave 70 g. (33%) of VI; b.p. 80–85° (3 mm.), n_D^{20} 1.4750. Oxidation of 31 g. of I with 102.5 g. of cupric sulfate dissolved in 100 g. of pyridine and 40 g. of water¹² gave 17 g. (55%) of VI; b.p. 80–82° (3 mm.). Finally, oxidation of 39 g. of I in 20 ml. of methanol using 90 g. of copper acetate dissolved in 200 ml. of 50% acetic acid¹³ gave 25–28 g. (67–72%) of VI; b.p. 80–82° (3 mm.), n_D^{20} 1.4750.

The dihydrazone of VI was prepared following the procedure described for sebacil dihydrazone.¹ From 67.8 g. of diketone there was obtained 64–69 g. (80–84%) of VII; m.p. 104–105° (dec.). On recrystallization from commercial absolute ethanol, keeping the temperature below 60°, there was obtained 51.5 g. (64.5%) of VII; m.p. 106–107° (dec.).

Anal. Calcd. for $C_9H_{16}N_4$: C, 59.30; H, 9.95; N, 30.74. Found: C, 59.24, 59.27; H, 9.85, 10.05; N, 30.84.

Cyclononyne (IV).—The procedure used was a modification of methods previously described.^{1,5} From 52 g. (0.285 mole) of VII there was obtained 15.2 g. (44%) of crude IV on distillation *in vacuo*. Redistillation gave 14 g. (39%) of IV which was still impure; b.p. 67–69° (15 mm.). This impure acetylene was chromatographed through silica gel until fractions of constant refractive index were obtained. The sample of IV thus obtained showed the following properties: b.p. 177–178° (740 mm.) (micro method), n_D^{20} 1.4890, d_4^{20} 0.8972.¹⁴

Anal. Calcd. for C_9H_{14} : C, 88.45; H, 11.55. Found: C, 88.40, 88.32; H, 11.62, 11.40.

The infrared spectrum for IV was given previously.¹

Quantitative reduction in acetic acid using Adams catalyst required 102% of two molar equivalents of hydrogen.

Ozonolysis of 0.9 g. of IV following the procedure used for cyclodecyne¹ gave 0.75 g. of an acidic product, m.p. 101–104°. Upon recrystallization from water the product melted at 102–104°. A mixed m.p. with an authentic specimen of azelaic acid was 103–105°. The bis-*p*-toluidide of the acid was prepared and it proved to be identical with the bis-*p*-toluidide of azelaic acid; m.p. 200–200.5°.

Following the procedure described by Thomas, Campbell and Hennion¹⁵ 0.8 g. of IV was hydrated by treatment with a mixture of 80% acetic acid, sulfuric acid and mercuric sulfate. The resulting crude hydration product was converted to a semicarbazone (m.p. 177–179°) which after recrystallization melted at 180–181°. When this semicarbazone was mixed with an authentic specimen of II semicarbazone the m.p. was not depressed.

Cyclononylamine.—The oxime of II was reduced to cyclononylamine by means of sodium and absolute ethanol according to methods previously described.^{16,17} From 10.2 g. of the oxime there was obtained 7.5 g. (79%) of the amine: b.p. 99–96.5° (12 mm.), n_D^{20} 1.4851.

Cyclononyltrimethylammonium Iodide (VIII).—Using a procedure described by Ziegler and Wilms,⁷ 8.6 g. of cyclononylamine was converted to the quaternary salt VIII. After recrystallization from water there was obtained 17 g. (90%) of crystalline VIII; m.p., on the Dennis bar, 273–273.5° (dec.) (uncor.).

Anal. Calcd. for $C_{12}H_{26}I$: C, 46.29; H, 8.43. Found: C, 46.32, 46.23; H, 8.38, 8.45.

trans-Cyclononene (X) A. From VIII.—A solution of 16 g. of VIII in 100 ml. of water was treated with an excess of freshly precipitated silver oxide. After filtering, the filtrate gave a negative test for silver and iodine ions. This filtrate was concentrated and decomposed at 140–160° at the water-

pump. The distillate was extracted with ether and the ether extracts washed and dried. On distillation there was obtained 4.4 g. (69%) of X: b.p. 73–74° (30 mm.); n_D^{20} 1.4798. The hydrocarbon was then chromatographed through silica gel giving a series of fractions having practically the same refractive index: n_D^{20} 1.4799; d_4^{20} 0.8615.

Anal. Calcd. for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.09, 87.20; H, 12.93, 13.11.

The infrared spectrum of this sample of X (Fig. 2) showed a very strong absorption at 10.25 μ .

Quantitative reduction in acetic acid using Adams catalyst required 100.5% of one molar equivalent of hydrogen.

On ozonolysis only azelaic acid was obtained (66%). The acid was characterized by methods previously described under the ozonolysis of IV.

Treatment of this sample of X (0.5 ml.) with 0.6 ml. of phenyl azide according to the procedure of Ziegler and Wilms⁷ gave a crystalline solid within a few hours. Heat was evolved on mixing the two compounds and the mixture solidified after standing at room temperature for 2 hours and cooling in the refrigerator 30 minutes. The phenyl azide adduct was recrystallized from petroleum ether; m.p. 97.8–98.2°.

Anal. Calcd. for $C_{15}H_{21}N_3$: C, 74.03; H, 8.70; N, 17.27. Found: C, 73.60; H, 8.66; N, 17.17.

B. From IV.¹⁸—To a solution of 1.38 g. (0.06 g. atom) of sodium in 60 ml. of purified liquid ammonia¹⁹ there was added dropwise with stirring 2.44 g. (0.02 mole) of IV (n_D^{20} 1.4890). After stirring for 2 hours excess sodium was decomposed by adding ammonium nitrate to the disappearance of the blue color. Dilute aqueous ammonia (50 ml.) was then carefully added. The reaction mixture was extracted with benzene, the benzene extracts washed with dilute hydrochloric acid, sodium bicarbonate solution, water and dried. After removal of the benzene there was obtained 1.83 g. of a colorless liquid; b.p. 73–74° (30 mm.). This distillate was chromatographed through silica gel and 86% of the material obtained showed n_D^{20} 1.4800. The remaining 14% was identified through its refractive index and infrared absorption as unreduced IV. The infrared curve (Fig. 2) of this reduction product indicated it to be X.

This sample of X formed an adduct with phenyl azide just as rapidly as did the sample described under A; m.p. 97–97.8°. A m.p. determination of a mixture of the two phenyl azide adducts showed no depression.

cis-Cyclononene (XI). From IV.²⁰—Using the procedure described for the selective catalytic hydrogenation of cyclodecyne¹ 3.04 g. of IV in 4 ml. of ethyl acetate gave, after two distillations, 2.47 g. (81%) of XI; b.p. 167–169° (740 mm.). When chromatographed through silica gel all fractions showed the same refractive index; n_D^{20} 1.4805, d_4^{20} 0.8671.

The infrared spectrum of this sample of XI (Fig. 3) showed general absorption in the region 13.5–14.5 μ and no absorption at 10.25 μ .

Anal. Calcd. for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 86.99, 87.03; H, 12.89, 12.90.

Quantitative reduction in acetic acid using Adams catalyst required 101% of one molar equivalent of hydrogen.

On ozonolysis only azelaic acid was obtained (70% as pure acid). The azelaic acid was characterized as previously described under IV.

On treating 0.5 ml. of XI with 0.6 ml. of phenyl azide there was no observable heat of reaction. After the mixture had stood in the refrigerator for 4 weeks there was no separation of a crystalline product.

Isomerization of X.—Following the procedure of Ziegler and Wilms⁷ a mixture of 0.93 g. of X (n_D^{20} 1.4800), 0.018 g. of hydroquinone and 0.018 g. of β -naphthalenesulfonic acid was heated at 150° under nitrogen in a sealed tube for 1.5 hours. After filtering, taking up in benzene, washing the benzene solution and drying there was obtained on distilla-

(11) V. Prelog, L. Frankiel, M. Kobelt and P. Barman, *Helv. Chim. Acta*, **30**, 1741 (1947).

(12) H. Gilman and A. H. Blatt, "Organic Syntheses," Col. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 87.

(13) P. Ruggli and P. Zeller, *Helv. Chim. Acta*, **28**, 741 (1945).

(14) The value d_4^{20} 0.8979 was reported previously. The present figure is considered to be more nearly correct.

(15) R. J. Thomas, K. N. Campbell and G. F. Hennion, *Texas Journal*, **60**, 718 (1938).

(16) A. H. Blatt, "Organic Syntheses," Col. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 318.

(17) V. Prelog, M. F. El-Neweiky and O. Häfliger, *Helv. Chim. Acta*, **33**, 365 (1950).

(18) (a) A. I. Henne and K. W. Greenlee, *THIS JOURNAL*, **65**, 2020 (1943); (b) K. N. Campbell and L. T. Eby, *ibid.*, **63**, 216 (1941); (c) M. C. Hoff, K. W. Greenlee and C. E. Boord, *ibid.*, **73**, 3329 (1951).

(19) The liquid ammonia was purified by adding a small amount of sodium and then distilling the ammonia directly into a well dried reaction vessel.

(20) (a) M. L. Sherrill and E. S. Matlack, *THIS JOURNAL*, **59**, 2134 (1937); (b) P. Piganiol, "Acetylene Homologs and Derivatives," Mapleton House, Brooklyn, N. Y., 1950, p. 128.

tion ca. 0.5 g. of a colorless liquid; b.p. 70° (28 mm.), n_D^{20} 1.4801.

Anal. Calcd. for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.18; H, 12.82.

The infrared spectrum of this product (Fig. 3) showed strong absorption in the region 13.5–14.5 μ and no absorption at 10.25 μ indicating the substance to be XI.

This sample of XI when mixed with phenyl azide showed no observable reaction over a period of 2 weeks.

Cyclononanol (IX).—The reduction of 32.6 g. (0.023 mole) of II with lithium aluminum hydride gave 31 g. (94%) of distilled cyclononanol; b.p. 115–119° (15 mm.), n_D^{20} 1.4903.

Dehydration of IX.—Following a procedure previously described for the dehydration of cyclodecanol¹ 13.1 g. (0.09 mole) of IX was added to 45 g. of boiling phthalic anhydride. Distillation of the reaction product gave 8 g. of a colorless liquid: b.p. 51.3–53° (7 mm.), n_D^{20} 1.4776. This

distillate was then chromatographed through silica gel. About 60% of the fractions thus obtained showed n_D^{20} 1.4792–1.4796. The infrared spectrum of this material (Fig. 3) showed characteristic absorption for both X and XI.

Anal. Calcd. for C_9H_{16} : C, 87.02; H, 12.98. Found: C, 87.05, 87.15; H, 12.83, 12.98.

Quantitative reduction of this mixture of cyclononenes in acetic acid using Adams catalyst required 98.91% of one molar equivalent of hydrogen.

Cyclononane.—The products obtained in the quantitative hydrogenation of the various samples of cyclononene were combined and distilled. The sample of cyclononane thus obtained showed b.p. 171–172.5° (740 mm.) (lit. gives b.p. 170–172° (760 mm.))²¹ and n_D^{20} 1.4663. The infrared spectrum of this sample of cyclononane is shown in Fig. 2.

(21) N. D. Zelinsky, *Ber.*, **40**, 3277 (1907).

ITHACA, N. Y.

[CONTRIBUTION FROM AMERICAN CYANAMID COMPANY, MINERAL DRESSING LABORATORY]

The Reaction of Arylamines with Diethyl Thionothiodiformate

BY RALPH SAYRE

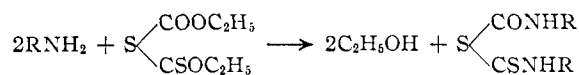
RECEIVED JANUARY 10, 1952

Diethyl thionothiodiformate reacts with arylamines to form ethyl arylthionocarbamates. Earlier investigators had erroneously formulated the products as diarylamides of thionothiodiformic acid.

By treating six aromatic monoamines with diethyl thionothiodiformate,¹ $C_2H_5OC-S-COC_2H_5$,

Guha and Dutta² claimed to have obtained a new series of compounds, to which they assigned the structure $RNHC-S-CNHR$, and which they desig-

nated as "thiodicarbomonothiodiarylamides."³ The reaction was carried out in each case at about 0° by adding the amine gradually to the ester dissolved in alcohol; the mixture was subsequently shaken with dilute hydrochloric acid in order to remove unreacted amine, and the solid product which separated at that point was filtered and crystallized from alcohol. In some instances Guha and Dutta added two moles of amine to one of ester, while in others the ratio was one to one. No information was given as to the yields obtained, nor was the reaction represented by an equation. The article seemed to imply, however, that the ethoxy groups were simply replaced by amine radicals.



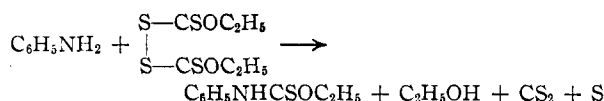
Such behavior with amines is at variance with that of other xanthic acid derivatives structurally

(1) "Ethylxanthogen ethylformate," first made by B. Holmberg, *J. prakt. Chem.*, [2] **71**, 264 (1905). The complex xanthic acid esters referred to in this paper are named as thionothiodiformic acid derivatives in conformity with C. A. nomenclature (Coll. Form. Index, pp. 134 and 135).

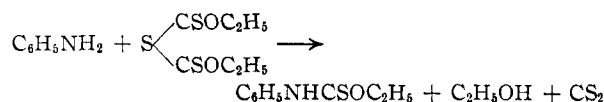
(2) P. C. Guha and D. N. Dutta, *J. Indian Chem. Soc.*, **6**, 65 (1929); abstracted in *Brit. Chem. Abstracts A*, 583 (1929); *Chem. Zentr.*, 100, I, 2779 (1929); *C. A.*, **23**, 2952 (1929).

(3) Beilstein, 2nd Suppl. XII, lists four of the products as arylaminoformylarylaminothioformyl sulfides and two of them as tolylcarbamic acid-tolyldithiocarbamic acid anhydrides.

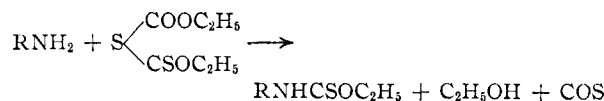
related to diethyl thionothiodiformate. Hofmann⁴ obtained ethyl phenylthionocarbamate as the principal product of the reaction between aniline and diethyl dithiois-(thionothiodiformate)⁵



In 1928 the present writer⁶ similarly treated aniline with the monosulfide, diethyl thiobis-(thionothiodiformate),⁷ and has subsequently used the reaction



for the preparation of the corresponding esters from *o*-toluidine, α -naphthylamine, N-ethylaniline and cyclohexylamine. The reaction of amines with diethyl thionothiodiformate might reasonably be expected to proceed in an analogous manner, forming carbonyl sulfide instead of carbon disulfide as a by-product. It is noteworthy that



Guha and Dutta applied the reaction to phenylhydrazine, which they had expected to yield a "diphenylhydrazide," and obtained instead ethyl 2-phenylthionocarbamate⁸; accordingly they repre-

(4) A. W. Hofmann, *Ber.*, **3**, 774 (1870).

(5) "Dixanthogen" or "bisethylxanthogen," first made by P. Desains, *Ann. chim.*, [3] **20**, 504 (1847).

(6) Unpublished work.

(7) "Ethylxanthic anhydride," first made by H. Welde, *J. prakt. Chem.*, [2] **15**, 45 (1877).

(8) No reference was made to the previous preparation of this compound by H. L. Wheeler and B. Barnes, *Am. Chem. J.*, **24**, 65 (1900).