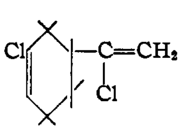
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

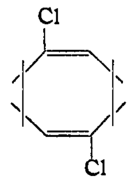
The Dimer of 2-Cyano-1,3-butadiene[1]

BY C. S. MARVEL AND NEAL O. BRACE

Dimerization is a reaction characteristic of 1,3-butadiene and its derivatives. Thus, it was not surprising to find that 2-cyano-1,3-butadiene on standing in an ice-box, even though picric acid was present, gradually changed to a low-melting solid. The closely related 2-chloro-1,3-butadiene has been shown to yield two dimers, the first a cyclohexene derivative (I)[2,3] and the second a cyclooctadiene derivative (II).[3] Hence we have considered similar possibilities for the structure of the dimer of the cyano derivative.

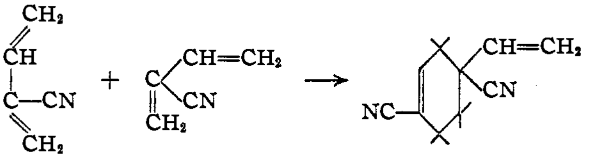


I

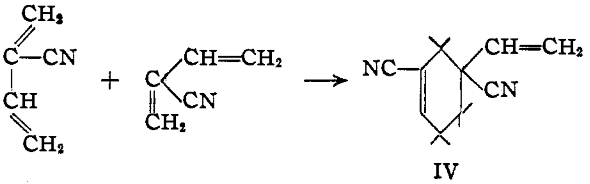


II

Although there are several possible dimers, the Diels–Alder type of dimerization seems somewhat more probable in the case of 2-cyano-1,3-butadiene since there is present a common dieneophilic group. The Diels–Alder type of self-addition could produce either of two isomeric cyclohexene derivatives III or IV depending on the relative positions of the substituents in the final ring.



III

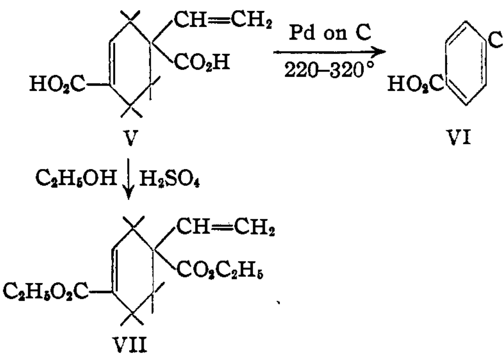


IV

The crude solid obtained from 2-cyano-1,3-butadiene, prepared by cracking the acetate of methyl vinyl ketone cyanohydrin,[4] melted at 30–40°. Purification by evaporation of monomer and crystallization of the solid residue gave long, thin plates which had a melting point of 55°. The melting point was not changed by further purification. Analysis and molecular weight determinations showed this compound was a dimer of the original diene. No other dimer was identified although small amounts may have been present in the residues.

The dimer showed two carbon–carbon double bonds by catalytic hydrogenation. The first mole of hydrogen was absorbed very rapidly and the second mole was added more slowly. Saponification with aqueous alkali gave a single acid (V) with a neutral equivalent of 100.4. This acid also contains two double bonds as shown by catalytic hydrogenation. It gave a diester (VII) with ethyl alcohol. This unsaturated dibasic acid was heated with palladium-on-charcoal containing a little copper chromite catalyst.[5] Carbon dioxide and hydrogen were evolved and a low yield of pure *p*-ethylbenzoic acid (VI) was isolated from the solid residue. No other dehydrogenation product was found.

The isolation of this acid is evidence that the dimer of 2-cyano-1,3-butadiene which we have isolated is best represented by formula III.



VII

Further confirmatory evidence for the structures assigned has been obtained from the infrared spectra[6] of the dimer and of the diester (VII) (see Figs. 1a and b). The infrared absorption curves show two different nitrile absorption maxima, *i. e.*, 2220 (conjugated) and 2243 cm.$^{-1}$ (unconjugated) for the dimer of 2-cyano-1,3-butadiene (III) (curve A), and two different ester carbonyl absorption maxima, 1715 (conjugated) and 1730 cm.$^{-1}$ (unconjugated) for the diester (VII) (curve B) as well as conjugated and unconjugated double bond absorption maxima for both compounds, 1639 and 1649 cm.$^{-1}$ for the dimer (III) and 1636 and 1654 cm.$^{-1}$ for the diester (VII). A structure analogous to either of the 2-chloro-1,3-butadiene dimers (I or II) would have both nitrile groups conjugated with a double bond and would show only one absorption maximum in the nitrile

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[1] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

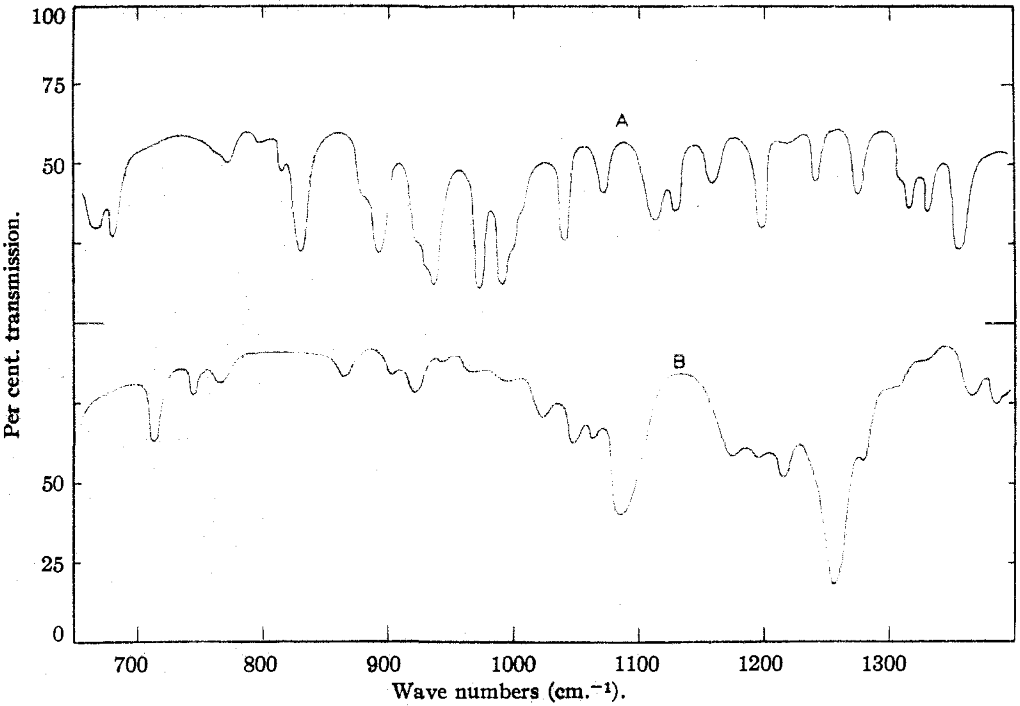
[2] Carothers, Williams, Collins and Kirby, THIS JOURNAL, 53, 4203 (1931); Carothers, Kirby and Collins, *ibid.*, 55, 789 (1933).

[3] Brown, Rose and Simonsen, *J. Chem. Soc.*, 101 (1944).

[4] Marvel and Brace, THIS JOURNAL, 70, 1775 (1948).

[5] Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, Mass., 1941, p. 458.

[6] We are indebted to Dr. Foil A. Miller and Mrs. J. L. Johnson for the infrared absorption curves and for their interpretation.



Infrared absorption spectra: Figs. 1a and b.—Curve A, dimer of 2-cyano-1,3-butadiene (run as crystalline melt between two rocksalt plates); curve B, diester (run as a liquid in an 0.025 mm. rocksalt cell).

frequency band of the infrared absorption spectrum.

The molar refractivity of the diester (VII) as calculated from the physical data is 0.34 higher than the figure obtained using the values given in the tables[7] for atomic refractivities. This exaltation may be attributed to one conjugated ester group but is hardly large enough to indicate two conjugated ester groups.

Experimental

Dimer of 2-Cyano-1,3-butadiene.—A sample of 57 g. of 2-cyano-1,3-butadiene, containing a little picric acid as polymerization inhibitor, when stored at 5° for about three months solidified to the extent of about 75%. When warmed to room temperature the solid dissolved, but after the excess monomer was removed by distillation the residual viscous oil (*ca.* 40 g.) crystallized when cooled, m. p. range 30–40°.

In another instance, the solid residue remaining in a bottle of 2-cyano-1,3-butadiene (containing picric acid as inhibitor) which had been stored in an ice-box for about six months was scraped out and placed in a small ground-glass distilling flask. The dimer was distilled under high vacuum through an 8-in., helix-packed column. There was obtained 4.2 g. of liquid, b. p. 110–112° (1 mm.), which solidified on standing to a white solid, m. p. range 30–40°. A brown, semi-viscous liquid which remained in the flask became spongy when cooled but was interspersed with crystallites. The material darkened on standing. An analysis of the liquid, b. p. 110–112° (1 mm.), was obtained.

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found:[8] C, 74.46; H, 5.94; N, 16.74.

This compound was dissolved in alcohol, treated with Darco, and filtered. The filtrate was evaporated and a few milliliters of water added until the solution began to get cloudy at 50°. When cooled to room temperature, the solution was seeded with a small crystal previously isolated and placed in the ice-box. The mass of crystals which formed was collected on a Buchner funnel, washed with very dilute alcohol, and air-dried, m. p. 54–54.5°. Further similar treatment of the filtrate (omitting the Darco) yielded three more crops of crystals. The third crop, which melted over the range of 44–51°, was contaminated with some residual oil, but the fourth crop was colorless and melted at 54–55°. In another experiment crystals were obtained which melted at 55–56°. Analysis of this crystalline material, in contrast to the compound which had merely been distilled, agreed well with the theoretical for a dimer.

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71; mol. wt., 158.2. Found: C, 75.92; H, 6.53; N, 17.67; mol. wt. (cryoscopic) in acetic acid, 146; in benzene (ebulloscopic), 141.

The dimer is soluble in dioxane, absolute ethanol, acetic acid, acetone, benzene and ether, gives a cloudy solution with methanol, and is insoluble in water, cyclohexane and Skellysolve B. The dimer in acetone solution decolorized dilute potassium permanganate solution rapidly.

Hydrogenation of 2-Cyano-1,3-butadiene Dimer.—In a ground-glass hydrogenation bottle were placed 0.1547 g. of 10% palladium-on-charcoal and 30 cc. of absolute methanol. The bottle was placed in the quantitative hydrogenation apparatus and evacuated and filled twice with hydrogen. Shaking was begun while the volume, temperature and pressure of the hydrogen was noted. The catalyst absorbed 6 cc. of hydrogen at 27° and 742 mm. pressure in seven minutes but absorbed no more hydrogen with shaking an additional twenty minutes.

The reduced catalyst was collected on a Hirsch funnel with suction and washed with 200 cc. of absolute methanol to remove the last traces of chloride ion, keeping the pyrophoric catalyst moist. The catalyst was transferred to the hydrogenation bottle, 0.3635 g. (0.00230 mole) of

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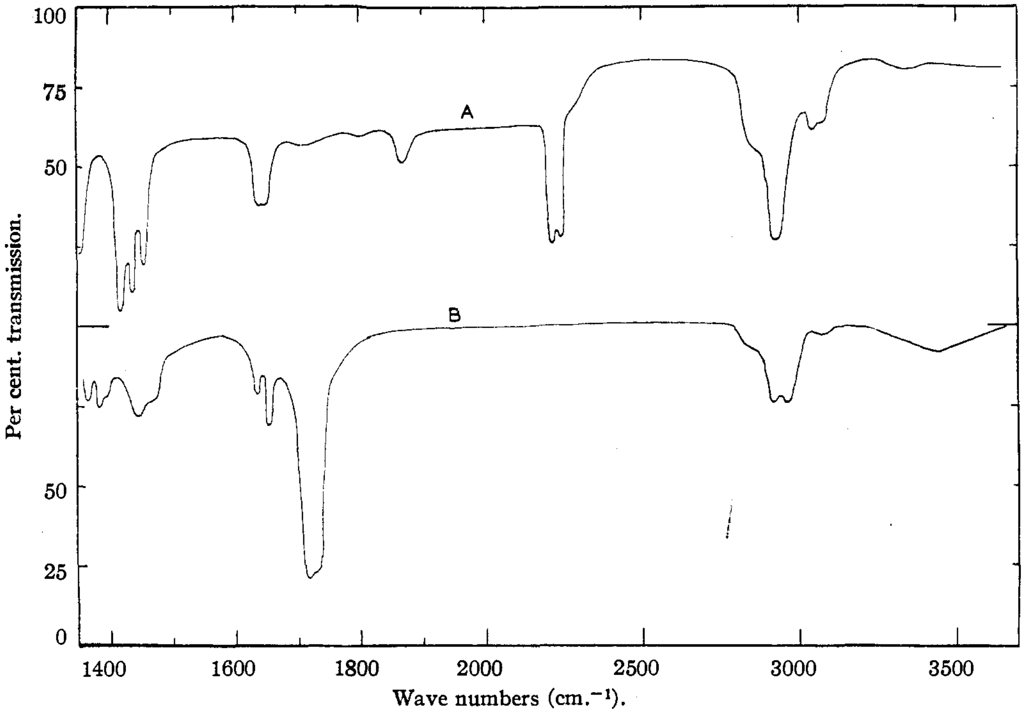
[7] Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 107.

[8] The microanalyses reported in this work were done by the Clark Microanalytical Laboratory, Urbana, Illinois.



recrystallized dimer (m. p. 53–55°) was added, and the solid washed down with 30 cc. of absolute methanol. The bottle was placed in the hydrogenation apparatus, evacuated and filled with hydrogen three times, and shaking was begun at 28° and 742 mm. In seven minutes the compound absorbed 58 cc. of hydrogen. This is the amount required by 0.00230 mole for one double bond. The hydrogenation rate then became slower, and a total of 116 cc. of hydrogen (30° and 742 mm.) was absorbed by the compound over a period of seven hours. The amount calculated for 0.00230 mole for two double bonds is 117.0 cc. at 29° and 742 mm.

The catalyst was filtered and the methanol evaporated. The residue was taken up with 95% ethanol and heated on the water-bath at 50° while water was added drop by drop until the solution began to get cloudy. The solution was placed in the ice-box. The reduced material separated as an oil. No crystalline isomer was separated from the mixture.

Saponification of the Dimer of 2-Cyano-1,3-butadiene.—Four and one-half grams (0.0286 mole) of the crude solid was heated under reflux with 6.7 g. (0.12 mole) potassium hydroxide in 30 cc. of water. During the heating ammonia was liberated. An additional 0.5 g. of potassium hydroxide was added and refluxing was continued for four hours. No more ammonia could be detected at the top of the reflux condenser. One gram of Darco was added to the resulting orange solution and the mixture was then filtered. The solution was cooled in ice and acidified with 50% sulfuric acid. The precipitated acid was collected on a Buchner funnel, redissolved in 95% ethanol, and concentrated some by evaporation. Then water was added and the solution was allowed to crystallize at room temperature. The first crop of crystals, silvery-white leaflets, amounted to 0.3 g.; m. p. 235–236° (sintered 230°). By further evaporation of the filtrate and crystallization from dilute alcohol solution a total of 2.6 g. of solid (*ca.* 50%), m. p. 235–236°, was collected. A portion of material was lost.

In a second experiment 3.6595 g. of the dimer was saponified by heating with 15 g. of sodium hydroxide in 50 cc. of water over a period of fourteen and one-half hours. The alkaline solution was added slowly with very rapid stirring to a solution of 41.5 cc. of 12 *N* hydrochloric acid and 50 cc. of water in a 250-cc. beaker. The precipitated acid was collected on a Buchner funnel, washed with distilled water and dried in an oven at 55° for two hours, m. p. 231–232° (sintered 229°). The yield was 3.0881 g. or 70.5%. The acid was recrystallized from alcohol–water solution, m. p. 235°.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17; neutral. equiv., 98.1. Found: C, 60.80, 60.73; H, 6.11, 6.34; neutral. equiv., 100.4.

This acid was soluble in alcohol and hot water, and sparingly soluble in ether, benzene and acetone. It decolorized dilute potassium permanganate solution when dissolved in 95% ethanol. It did not decolorize bromine in carbon tetrachloride solution.

Determination of the Number of Double Bonds in the Unsaturated Acid by Hydrogenation.—A hydrogenation apparatus designed to measure quantitatively the amount of hydrogen taken up by an unsaturated compound was used in this experiment. There were placed in the reduction bottle 50 cc. of absolute ethanol, 0.5 g. of 10% palladium-on-charcoal and 0.1962 g. (0.001 mole) of the unsaturated acid. The system was evacuated and filled with hydrogen twice, the volume of hydrogen at 737 mm. and 23.8° was noted and shaking begun. In one minute 53.5 cc. of hydrogen was absorbed before stopping the shaker. The gas buret was refilled and shaking was resumed. In the next hour and twenty minutes, 42.9 cc. of hydrogen at 23° and 742 mm. was absorbed, making a total of 96.4 cc. of hydrogen.

In a blank determination, 0.500 g. of 10% palladium-on-charcoal in 50 cc. of absolute alcohol took up 40 ± 2 cc. of hydrogen at 22° and 749 mm. pressure. This is equivalent to 42 cc. at 742 mm. and 23°. In other words, the unsaturated compound itself absorbed 54 ± 2 cc. of hydrogen. The amount calculated for two double bonds is 50.0 cc. at 23.8° and 742 mm.

Dehydrogenation of the Unsaturated Acid with Palladium-on-Charcoal.—In an 18 × 150 mm. Pyrex test-tube were placed 1.00 g. (0.00510 mole) of the unsaturated acid, 0.100 g. of 10% palladium-on-charcoal catalyst, and 0.01 g. of copper chromite catalyst. The materials were mixed and the test-tube closed with a one-hole rubber stopper fitted with a 6-in. length of glass tubing. The tube was connected by means of rubber tubing to a U-shaped capillary glass tubing immersed in a pan of water and extending part way up into a 50-cc. buret filled with water and standing in the water.

The evolved gas was collected in the buret and the volume, temperature, and pressure of the gas noted as the dehydrogenation was carried out. As one buret became filled with gas another was put in its place.

The test tube was placed in a Wood's metal-bath heated with a Bunsen burner to an initial temperature of 220°. Gas bubbles began to appear after a few minutes of heating and, as they began to slacken, the temperature of the bath was raised over a period of four hours. The final temperature was 320°. A total volume of 163.5 cc. of gas at standard temperature and pressure (corrected for water vapor pressure) was collected. The theoretical amount of hydrogen at standard temperature and pressure is 114 cc. for 0.00510 mole. An equal amount of carbon dioxide should be evolved, and this explains the excess over the theory for hydrogen. Most of the carbon dioxide was lost by solution in the water over which the gas was collected.

The residue in the test-tube was extracted with ether. The ether solution was filtered and evaporated. The oily residue solidified on cooling. It was dissolved in alcohol, treated with Darco, and filtered. Two successive attempts at crystallization by adding water to the hot solution and cooling yielded only gummy precipitates. The alcohol solution was transferred to a 10-cc. distilling flask, the alcohol removed, and the residue subjected to distillation at reduced pressure. Only a drop or two collected in the side-arm (b. p. 145–150° (19 mm.)), but when the distilling flask cooled, solid crystals appeared on the sides. The crystals, which were removed, amounted to 0.053 g., m. p. 98–105°. After recrystallization from alcohol-water solution, the melting point was 112°. The literature gives 110–111°[9] and 112–113°[10] for the melting point of *p*-ethylbenzoic acid. *m*-Ethylbenzoic acid is reported to melt at 47°.[11]

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.50; H, 6.99.

Esterification of the Unsaturated Dibasic Acid.—In a 50-cc., ground-glass, round-bottom flask attached to a 2-ft., water-cooled condenser were placed 0.98 g. (0.005 mole) of the unsaturated acid (m. p. 235°), 5 cc. of absolute alcohol (0.085 mole) and 2 drops of concentrated sulfuric acid. The reactants were refluxed on the steam-bath for four hours. Then 10 cc. of benzene was added, the water-cooled condenser replaced by a 10-in. Vigreux column and a total reflux-partial take-off head and the solution heated under practically total reflux as the azeotropic mixture of alcohol, benzene, and water was taken off at 65–72° over a period of four and one-half hours. The remaining traces of benzene and alcohol were removed by distillation under water pump pressure.

The residue was dissolved in 50 cc. of distilled ether and washed three times with 15-cc. portions of 5% aqueous potassium hydroxide solution, dried over anhydrous sodium sulfate, filtered, and distilled under reduced pressure in a 10-cc. distilling flask. The ester boiled at 131–133° (3 mm.) and amounted to 15–20 drops; n^{20}_{D} 1.4801[12]; d^{20}_{4} 1.0639[12]; M_D calcd. 67.04; M_D found 67.38 (exaltation of 0.34).

The ester was soluble in alcohol, ether and chloroform. It was insoluble in dilute potassium hydroxide and 10% sodium bicarbonate solution. The ester decolorized dilute aqueous potassium permanganate solution but did not decolorize bromine in chloroform solution.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.54; H, 7.95.

Acidification of the potassium hydroxide wash solution with concentrated hydrochloric acid gave 0.128 g. of recovered acid, m. p. 233–234°.

Summary

2-Cyano-1,3-butadiene dimerizes on standing at 5° in the presence of a trace of picric acid to yield a solid whose structure is that of the Diels–Alder condensation product, 1-vinyl-1,4-dicyano-Δ^4-cyclohexene. Proof of the six-membered ring structure was obtained by converting the dimer to an unsaturated dibasic acid which was dehydrogenated and decarboxylated to *p*-ethylbenzoic acid.

The infrared absorption spectra of the dimer and of the diester prepared from it indicate the presence of a conjugated and an unconjugated nitrile group and ester group, respectively, thus confirming the structure assigned on the basis of degradation. No evidence for an eight-membered dimer was noted. Smaller amounts of other dimers may have been lost in working up the mixture.

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(9) Fittig and König, *Ann.*, **144**, 290 (1867).

(10) Aschenbrandt, *ibid.*, **216**, 218 (1882).

(11) "Handbook of Chemistry and Physics," 29th ed., Chemical Rubber Publishing Company, Cleveland, Ohio, 1945, p. 640.

(12) These data determined by Clark Microanalytical Laboratory, Urbana, Illinois.

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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Orthoesters and Related Compounds from Malono- and Succinonitriles

BY S. M. McELVAIN AND JUEL P. SCHROEDER[1]

The study of the preparation of orthoesters from nitriles, which has been in progress for some time in this Laboratory[2] in connection with work on the ketene acetals, has been extended to malono- and succinonitriles. The present paper reports the preparation and alcoholysis of the various iminoester hydrochlorides that may be obtained from these dinitriles and describes certain related products resulting from these reactions.

Treatment of each of these dinitriles with equivalent amounts of methanol and hydrogen chloride gave the monoimino salts (I and III) readily and methanolysis of these salts gave good yields of the corresponding cyanoörthoesters (II and IV). In the case of II it was necessary to remove all traces of acid from the reaction product with aqueous sodium carbonate solution before distillation to prevent the pyrolysis of the orthoester to cyanoketene dimethylacetal.

Attempts to convert II to the corresponding iminoester with equivalent amounts of methanol

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[1] Wisconsin Alumni Research Foundation Research Assistant, 1946–47; University Fellow, 1947–48.

[2] McElvain and (a) Nelson, THIS JOURNAL, **64**, 1825 (1942); (b) Clarke, *ibid.*, **69**, 2661 (1947); (c) Stevens, *ibid.*, **69**, 2663 (1947).