The Reaction of Ethyl Azodicarboxylate with Conjugated Dienes[1]

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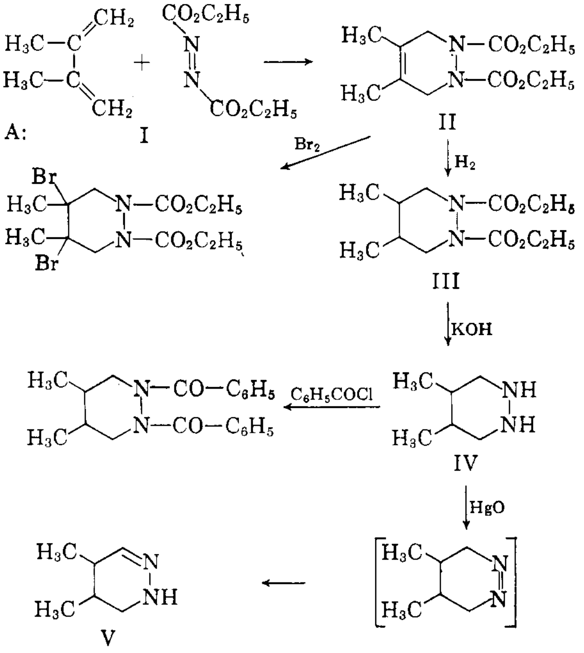
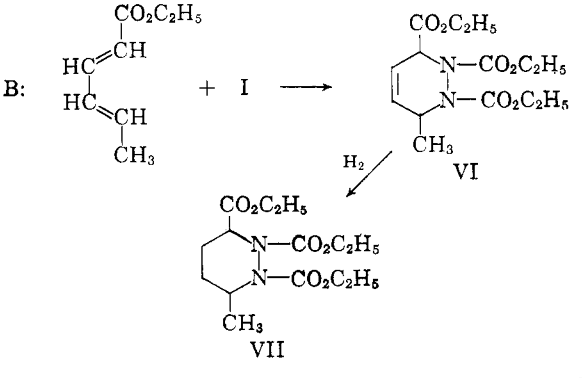
The reaction of ethyl azodicarboxylate (I) with simple conjugated dienes resulted in Diels-Alder 1,4- addition, whereas with more highly substituted conjugated dienes addition occurred by a cyclic mechanism. These results indicated that steric factors influence the course of reaction. The reaction of I with 2,3-dimethylbutadiene and ethyl sorbate gave 1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine (94%) and 6-methyl-1,2,3-tricarbethoxy-1,2,3,6-tetrahydropyridazine (80%), respectively. Treatment of 2,5-dimethyl-2,4-hexadiene with I gave VIII (65%) shown to be a mixture of 1,2-dicarbethoxy-1-[3-(2,5-dimethyl-2,4-hexadienyl)]hydrazine (83%) and 1,2-dicarbethoxy-1-[1-(2,5-dimethyl-2,4-hexadienyl)]hydrazine (15%). Reaction of I with 1,3-cyclohexadiene yielded 1,2-dicarbethoxy-1-(2,5-cyclohexadienyl)hydrazine (77%). The cyclic mechanism operative in the latter reactions proceeded with a shift of the double bond to destroy conjugation.

The addition of ethyl azodicarboxylate (I) to conjugated diene and triene systems is known to result in several types of reaction. One type is the familiar Diels-Alder or 1,4-addition[2–4] and the other, addition in the allyl position.[5,6] These reactions present a good synthetic route for the preparation of various pyridazines and other hydrazine derivatives. The present investigation was carried out in order to determine the factors which influence 1,4- addition *vs.* "allylic addition" and to clarify the position of attachment in the latter reaction.

The relatively simple dienes, 2,3-dimethylbutadiene and ethyl sorbate, reacted readily with I to give normal 1,4- addition. Thus, 1,2-dicarbethoxy-4,5-dimethyl-1,2,3,6-tetrahydropyridazine (II) was formed in 94% yield from 2,3-dimethylbutadiene and I. A solid dibromide derivative of II was prepared. Hydrogenation of II using 10% palladium-on-charcoal catalyst in ethanol on a Parr apparatus gave an 84% yield of 1,2-dicarbethoxy-4,5-dimethylhexahydropyridazine (III). Hydrolysis of III was affected by refluxing the compound in ethanolic potassium hydroxide for six hours under nitrogen. The product, 4,5-dimethylhexahydropyridazine (IV) was obtained in 84% yield. A dibenzoyl derivative of IV was prepared in 88% yield. Oxidation of IV was carried out under a nitrogen atmosphere using mercuric oxide in anhydrous ether. The only compound isolated corresponded to 4,5-dimethyl-1,4,5,6-tetrahydropyridazine (V), which was characterized by analyses, infrared, and ultraviolet spectra. The isolation of V indicated that an azo compound was formed, but an isomerization to the more stable structure V had taken place under the reaction conditions. These reactions are presented in scheme A.



Ethyl sorbate and I reacted at 80° to form the adduct 6-methyl-1,2,3-tricarbethoxy-1,2,3,6-tetrahydropyridazine (VI) in 80% yield. The adduct VI was hydrogenated to 6-methyl-1,2,3-tricarbethoxyhexahydropyridazine (VII) also 80% yield; see scheme B.



Recently the addition of I to two conjugated diene systems has been reported by Levina, and co-workers.[5] They claimed, *a priori*, that addi-

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[1] This research was carried out under grant #G7279 from the National Science Foundation, whose support is gratefully acknowledged.

[2] O. Diels, J. H. Blom, and W. Koll, *Ann.*, **443**, 242 (1925).

[3] K. Alder and K. Niklas, *Ann.*, **585**, 81 (1954).

[4] P. Baranger and J. Levisalles, *Bull. soc. chim. France*, 704 (1957).

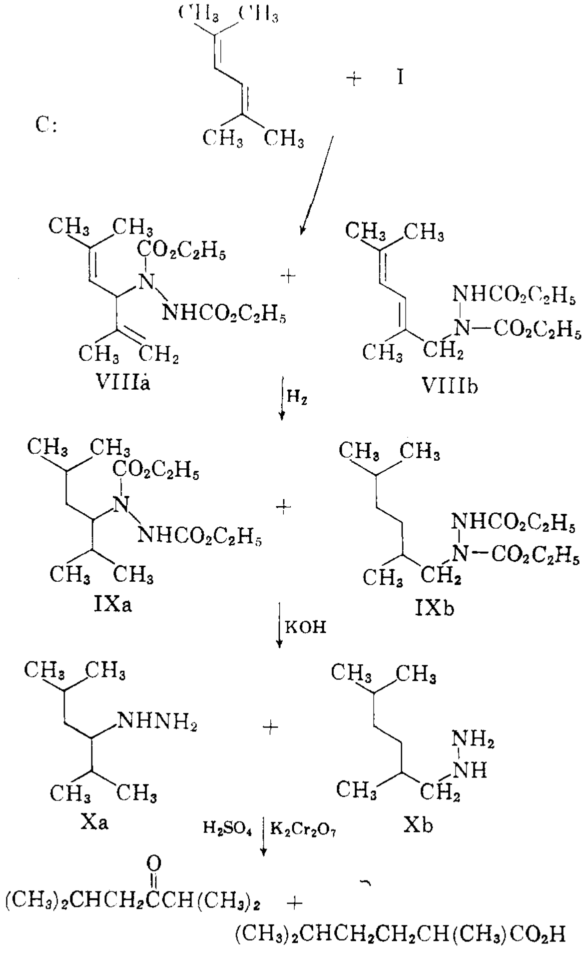
[5] R. Y. Levina, U. S. Skabarow, and M. H. Kuzmin, *Doklady Akad. Nauk., S.S.S.R.*, **131**, 1080 (1960).

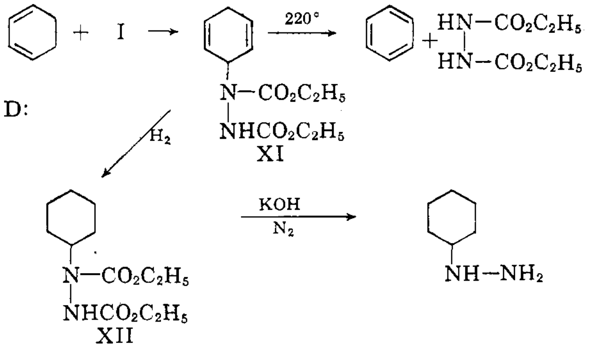
[6] J. M. Cinnamon and K. Weiss, *J. Org. Chem.*, **26**, 2644 (1961).

tion of I to the dienes took place in the allyl position, but presented no evidence to support their proposed structures. Since the mode of addition and the point of attachment were not established, it was necessary to investigate this type of addition in detail and to prove rigorously the structure of the product, or products.

To clarify whether this "allylic addition" occurred with a shift of the double bonds, 2,5-dimethyl-2,4-hexadiene was allowed to react with I in refluxing benzene. The adduct formed in 65% yield and showed infrared absorption at 2.93 μ (N—H) and a doublet in the carbonyl region at 5.72 and 5.89 μ. Ultraviolet spectra of this material exhibited a maximum at 242 $m\mu$ (ϵ 3100) and indicated that the product contained 15% of a highly substituted conjugated diene. Gas chromatography showed the adduct to consist of a mixture of three products with the composition 2%, 83%, and 15%, respectively. Assignment of the structures to the products as 1,2-dicarbethoxy-1-[3-(2,5-dimethyl-1,4-hexadienyl)]hydrazine (VIIIa) (the 83% component) and 1,2-dicarbethoxy-1-[2,5-dimethyl-2,4-hexadienyl)]hydrazine (VIIIb) (the 15% component) was made on the basis of the ultraviolet data and the evidence given below. Mixture VIII absorbed two molar equivalents of hydrogen in ethanol using palladium-on-charcoal catalyst to furnish a 71% yield of product. Gas chromatography of the latter material showed the composition was 84% 1,2-dicarbethoxy-1-[3-(2,5-dimethyl-*n*-hexyl)]hydrazine (IXa) and 15% 1,2-dicarbethoxy-1-(2,5-dimethyl-*n*-hexyl)]hydrazine (IXb). Both VIII and IX were thick viscous oils that were purified by evaporative distillation. Hydrolysis of IX with potassium hydroxide in refluxing ethylene glycol furnished an 82% yield of the alkylhydrazine mixture X. The mixture was oxidized with potassium dichromate in dilute sulfuric acid solution. The neutral extract of the reaction mixture gave a 45% yield of isopropyl isobutyl ketone. The physical constants of this product agreed well with those reported. The semicarbazone and oxime derivatives of this ketone were prepared. From the acidic fraction of the oxidation mixture, 2,5-dimethylhexanoic acid was isolated, characterized as the amide, m.p. 100°. These reactions are shown in scheme C.

The addition of I to 1,3-cyclohexadiene proceeded at room temperature to yield 77% of 1,2-dicarbethoxy-1-[1-(2,5-cyclohexadienyl)]hydrazine (XI). Compound XI, m.p. 53–54°, showed infrared absorption at 2.90 μ (N—H) and a doublet in the carbonyl region at 5.70 and 5.85 μ. The ultraviolet spectrum gave a maximum at 226 $m\mu$ (ϵ 15) characteristic of a 1,4-cyclohexadiene.[7] Compound XI was labile to heat. A thermal decomposition at 220° gave a 94% yield of benzene and a 97% yield of ethyl hydrazodicarboxylate. Two molar equivalents of hydrogen were absorbed by XI and gave 1,2-dicarbethoxy-1-cyclohexylhydrazine (XII) in 88% yield. Hydrolysis of XII in refluxing ethanolic potassium hydroxide under nitrogen produced the known cyclohexylhydrazine in 63% yield. The hydrochloride derivative was prepared and corresponded also with the known compound. These reactions are given in scheme D.





The results of our investigation with conjugated dienes and I have indicated that when the 1,4-position of the diene is highly substituted Diels-

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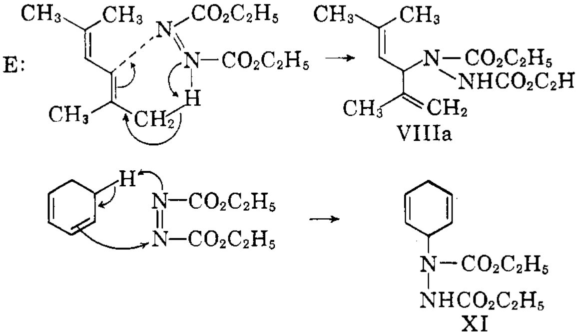
(7) L. W. Pickett and E. Sheffield, *J. Am. Chem. Soc.*, **68**, 216 (1946).

Alder addition is prevented and addition takes place by other pathways. This hindrance toward 1,4- addition is clearly steric in nature. In view of the *trans* configuration of the dienophile, even the presence of a dimethylene bridge was sufficient to change the course of the reaction.

The two pathways which the reaction followed using 2,5-dimethyl-2,4-hexadiene were addition in the allyl position which is similar to that reported for simple olefins[8] and a cyclic mechanism resulting in addition (reaction scheme E) similar to that reported for 1,3-diarylpropenes.[9] The cyclic mechanism proposed in the case of the 1,3-diarylpropenes and possibly for cycloheptatriene[10] proceeded with a shift of the double bond and the retention of conjugation in the product presumably provided the driving force of the reaction.

The results of the present investigation have shown however, that retention of conjugation is not a requisite of adduct formation. The cyclic mechanism was the *major* mode of addition in the reaction of I with sterically hindered conjugated dienes and resulted in a shift of the double bond out of conjugation. The *minor* mode of addition was that of free radical allylic addition.

E:



VIIIa

XI

Experimental[11]

1,2-Dicarbethoxy-4,5-dimethyl-1,2,3,6-tetrahydropyridazine (II).—Treatment of 9.45 g. (0.115 mole) of 2,3-dimethylbutadiene[12] with 20.0 g. (0.115 mole) of ethyl azodicarboxylate[13] (I) produced a colorless liquid. Distillation of this liquid gave 27.37 g. (94%) of II, b.p. 103–106° (0.5 mm.),[14] n^{25}_D 1.4640, d^{25} 1.0820.

Anal. Calcd. for $C_{12}H_{20}N_2O_4$: C, 56.23; H, 7.87. Found: C, 56.33; H, 7.82.

1,2-Dicarbethoxy-4,5-dimethyl-4,5-dibromohexahydropyridazine.—To a solution of 2.3 g. (0.013 mole) of II in 10 ml. of carbon tetrachloride, 2.6 g. of bromine in 10 ml. of the same solvent was added slowly. Evolution of heat occurred and the bromine was discolored. The solvent was evaporated to a small volume on a hot plate and the remaining solvent evaporated on standing to yield a light brown solid. Recrystallization from ether-petroleum ether gave 3.86 g. (72%) of the dibromide, m.p. 90–92°.

Anal. Calcd. for $C_{12}H_{20}N_2O_4Br_2$: C, 34.63; H, 4.84. Found: C, 34.79; H, 4.69.

1,2-Dicarbethoxy-4,5-dimethylhexahydropyridazine (III).—The adduct II (31.58 g., 0.122 mole) was hydrogenated in 185 ml. of 95% ethanol over 1.5 g. of 10% palladium-on-charcoal catalyst at 56 p.s.i. at room temperature on a Parr apparatus. The solution was filtered and the ethanol removed under vacuum. The residual liquid was distilled to give 26.43 g. (84%) of III, b.p. 103–105° (0.43 mm.), n^{25}_D 1.4564, d^{25} 1.0668.

Anal. Calcd. for $C_{12}H_{22}N_2O_4$: C, 55.79; H, 8.58. Found: C, 55.83; H, 8.56.

4,5-Dimethylhexahydropyridazine (IV).—A solution of 20 g. of potassium hydroxide in 150 ml. of 95% ethanol containing 21.40 g. (0.083 mole) of III was refluxed for 6.5 hr. under nitrogen. The solution was cooled, precipitated potassium salts were removed by filtration, and the ethanol removed under reduced pressure. The residual liquid was distilled and furnished 7.97 g. (84%) of IV, b.p. 90° (30 mm.), n^{25}_D 1.4712, d^{25} 0.9319.

Anal. Calcd. for $C_6H_{14}N_2$: C, 63.11; H, 12.37. Found: C, 63.40; H, 12.64.

1,2-Dibenzoyl-4,5-dimethylhexahydropyridazine.—Five milliliters of benzoyl chloride was added slowly to 1.0 g. (0.088 mole) of IV in 20 ml. of 10% sodium hydroxide solution with cooling. After extraction with chloroform, the product was crystallized by the addition of hexane. Recrystallization of the resulting solid, m.p. 181–185° from ethanol-water gave 2.48 g. (88%) of the product, m.p. 190°.

Anal. Calcd. for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88. Found: C, 74.46; H, 6.92.

4,5-Dimethyl-1,4,5,6-tetrahydropyridazine (V).—A solution of 4.42 g. (0.039 mole) of IV in 40 ml. of anhydrous ether was stirred with a magnetic stirrer under nitrogen and cooled with an ice bath. Twenty grams of mercuric oxide (yellow powder) was added slowly to this mixture. The mercuric oxide slowly darkened. Stirring was continued for 12 hr. The grey solid was filtered and the ether removed from the filtrate under vacuum. The residual pale yellow liquid was distilled and yielded 1.93 g. (45%) of V, b.p. 87° (19 mm.), n^{26}_D, 1.4839, d^{23} 0.9670, $\lambda^{C_2H_5OH}_{max}$ 234 mμ (ϵ 4290). Infrared spectrum ($CHCl_3$): bands at 2.92 μ (N—H) and 6.16 μ (C=N).

Anal. Calcd. for $C_6H_{12}N_2$: C, 64.24; H, 10.78; N, 24.98. Found: C, 64.16; H, 10.98; N, 24.60.

6-Methyl-1,2,3-tricarbethoxy-1,2,3,6-tetrahydropyridazine (VI).—A mixture of 17.4 g. (0.1 mole) of I and 14.1 g. (0.1 mole) of ethyl sorbate[15] was heated at 80° for 1.5 hr. After this time the mixture had turned to a yellow, thick viscous liquid. Distillation of this liquid gave 26.03 g. (80%) of the colorless product VI, b.p. 125–127° (0.23 mm.), n^{25}_D 1.4647, d^{23} 1.1420.

Anal. Calcd. for $C_{14}H_{22}N_2O_6$: C, 53.49; H, 7.05. Found: C, 53.65; H, 7.21.

6-Methyl-1,2,3-tricarbethoxyhexahydropyridazine (VII).—The adduct VI (22.73 g., 0.073 mole) was hydrogenated

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[8] N. Rabjohn, *J. Am. Chem. Soc.*, **70**, 1181 (1948). While acetaldehyde was isolated from the ozonolysis of the product from I and 2-methyl-2-butene, no yield was reported. The high carbon analysis of the other product of ozonolysis does not preclude the possibility of a mixture containing an additional carbon.

[9] R. Huisgen and H. Pohl, *Ber.*, **93**, 527 (1960).

[10] *Cf.* ref. 6. The retention of conjugation in the adduct obtained from I and cycloheptatriene renders it impossible to state which mechanism is operative.

[11] Boiling points and melting points are uncorrected. Microanalyses were performed by Drs. Weiler and Strauss, Oxford, England, and A. Bernhardt, Mülheim, Germany. Spectra of the compounds were measured with a Beckman Model DU ultraviolet spectrophotometer and a Perkin-Elmer Model 137 double beam infrared spectrophotometer. Gas chromatographic analyses were performed on an F & M Scientific Corp. Model 21B dual heater gas chromatography apparatus using one-fourth inch diameter Celite-Silicone grease columns.

[12] The authors wish to acknowledge the gift of a generous quantity of 2,3-dimethylbutadiene from the Houdry Process Corp., Philadelphia, Pa.

[13] Prepared by the method of N. Rabjohn, *Org. Syntheses*, **Coll. Vol. III**, 375 (1955).

[14] Baranger and Levisalles (ref. 4) report b.p. 145° (1 mm.), n^{14}_D 1.4795, d^{18}_4 1.1132.

[15] Prepared from sorbic acid, obtained from Union Carbide Co.

in 160 ml. of 95% ethanol over 1.5 g. of palladium-on-charcoal catalyst at 62 p.s.i. on a Parr apparatus. The solution was filtered and the ethanol removed under vacuum. The residual liquid was distilled and yielded 18.4 g. (80%) of VII, b.p. 127–130° (0.02 mm.), n^{25}_{D} 1.4568, d^{25} 1.1322.

Anal. Calcd. for $C_{14}H_{24}N_2O_6$: C, 53.15; H, 7.65. Found: C, 53.11; H 7.42.

2,5-Dimethyl-2,4-hexadiene.—The compound was purchased from Matheson, Coleman and Bell Co., and showed $\lambda_{\max}^{C_2H_5OH}$ 242 mμ (ϵ 20,900) (reported,[16] $\lambda_{\max}^{C_2H_5OH}$ 242 mμ (ϵ 21,500)) and was found to be 98% pure by both ultraviolet and gas chromatographic analysis.

Reaction of 2,5-Dimethyl-2,4-hexadiene with I.—One-tenth mole (17.4 g.) of I and 15.0 g. (0.136 mole) of 2,5-dimethyl-2,4-hexadiene in 30 ml. of benzene were refluxed for six hr. The colorless solution was vacuum concentrated to a thick viscous liquid. Purification by evaporative distillation yielded 18.34 g. (65%) of VIII, b.p. 195° (1.3 mm.),[17] by column, b.p. 122–125° (0.4 mm.), n^{26}_{D} 1.4712, d^{28} 1.0441. Infrared spectrum ($CHCl_3$): bands at 2.93 μ (N—H), 5.72 μ and 5.89 μ (C=O).

Anal. Calcd. for $C_{14}H_{24}N_2O_4$: C, 59.13; H, 8.51. Found: C, 59.24; H, 8.41.

Ultraviolet analysis of the product exhibited $\lambda_{\max}^{C_2H_5OH}$ 242 mμ (ϵ 3100) and indicated that 15% of a conjugated diene was present. Gas chromatography of the product in a chloroform solvent on a 2-ft. column gave the composition as 2%, 83%, and 15%, respectively, as determined by the peak area method.[18]

Hydrogenation of VIII.—The addition product VIII, (26.74 g., 0.094 mole) was hydrogenated over 1.0 g. of 10% palladium-on-charcoal catalyst in 150 ml. 95% ethanol on a Parr apparatus and absorbed 1.87 equivalents of hydrogen. The catalyst was removed by filtration and the ethanol removed under vacuum. Purification of the clear, thick, viscous liquid by evaporative distillation yielded 21.67 g. (71%) of IX, b.p. 160° (0.12 mm.),[17] by column, b.p. 102–104° (0.18 mm.), n^{26}_{D} 1.4485, d^{28} 1.0108.

Anal. Calcd. for $C_{14}H_{28}N_2O_4$: C, 58.10; H, 10.10. Found: C, 57.90; H, 9.75.

Gas chromatography of the product in a chloroform solvent on a 2-ft. column gave the composition as 1.2%, 84.2%, and 14.6%, respectively, as determined by the peak area method.[19]

Hydrolysis of IX.—A solution of 26.0 g. (0.0874 mole) of IX in 200 ml. of ethylene glycol containing 50 g. of potassium hydroxide was refluxed for 36 hr. The mixture was cooled and 300 ml. of water added; the resulting solution was extracted three times with 200-ml. portions of ether. The ether extracts were combined, dried over calcium sulfate, and the ether removed. The residual liquid was distilled and 9.83 g. (82%) of the alkylhydrazine mixture X, b.p. 92–97° (20 mm.), n^{26}_{D} 1.4415, obtained.

Oxidation of X.—To 40 g. (0.136 mole) of potassium dichromate in 250 ml. of 10% sulfuric acid solution which was stirred with a magnetic stirrer, 12.0 g. (0.0835 mole) of X was added dropwise. After the addition was completed, the reaction was stirred for 1 hr. and allowed to come to room temperature. The mixture was extracted twice with 200-ml. portions of ether. The combined ether extracts were washed twice with 100-ml. portions of 5% sodium hydroxide solution and once with water. The ether phase was dried over calcium sulfate and removed, whereupon distillation of the residual liquid gave 4.8 g. (45%) of isopropyl isobutyl ketone, b.p. 142–146°, n^{25}_{D} 1.4018, d^{25} 0.7942.[20] A semicarbazone derivative melted at 141°.[20] The oxime derivative was prepared, b.p. 190°,[21] n^{25}_{D} 1.4377, d^{25} 0.8668.

The basic extract was acidified and extracted with two 200-ml. portions of ether. The ether was dried over calcium sulfate and then removed. The infrared spectrum of the crude residual liquid indicated that a carboxylic acid was present. The amide was prepared from the crude liquid and gave 0.11 g. of 2,5-dimethylhexanoic acid amide, m.p. 86–88°. Recrystallization from petroleum ether gave amide, m.p. 100°.[22]

1,2-Dicarbethoxy-1-[1-(2,5-cyclohexadienyl)]hydrazine (XI).—One-tenth mole (17.4 g.) of I was added slowly with swirling to 10.0 g. (0.125 mole) of 1,3-cyclohexadiene.[23] The resulting colorless liquid was concentrated under vacuum to a thick viscous oil. Ether–petroleum ether was added and 19.76 g. (77%) of the white solid XI crystallized, m.p. 48–50°. Recrystallization of the solid from ether–petroleum ether gave material m.p. 53–54°; $\lambda_{\max}^{\text{hexane}}$ 226 mμ (ϵ 15). Infrared spectrum ($CHCl_3$): bands at 2.90 μ (N—H), 5.70 μ and 5.85 μ (C=O).

Anal. Calcd. for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.14; Found: C, 56.51; H, 6.88.

Thermal Decomposition of XI.—When 7.62 g. (0.03 mole) of XI was heated in a small distillation apparatus for 3 hr. at 220°, a colorless liquid distilled. On cooling, a white solid crystallized in the distillation flask.

Two cuts of the liquid distillate were taken, 1.45 g. n^{26}_{D} 1.4860 and 0.74 g., n^{26}_{D} 1.4785. Total yield was 2.19 g. (94%), b.p. 78° (micro method). Comparison of the infrared spectrum of this liquid with the spectrum of benzene showed them to be identical.

The white solid, 5.1 g. (97%), had a melting point 128–129°. A mixed melting point with an authentic sample of ethyl hydrazodicarboxylate was undepressed, and infrared spectra of the two samples were identical.

1,2-Dicarbethoxy-1-cyclohexylhydrazine (XII).—The addition product XI (32.0 g., 0.126 mole) was hydrogenated over 1.5 g. of 10% palladium-on-charcoal catalyst in 160 ml. of 95% ethanol at 59 p.s.i. in a Parr apparatus. Two equivalents of hydrogen were absorbed. The catalyst was removed by filtration and the ethanol removed under vacuum to leave a thick oil. A white solid, m.p. 64–65°, was crystallized in three crops on the addition of ether–petroleum ether. The yield of XII was 28.07 g. (88%).

Anal. Calcd. for $C_{12}H_{22}N_2O_4$: C, 55.79; H, 8.58. Found: C, 55.83; H, 8.50.

Cyclohexylhydrazine.—A solution of 24.5 g. (0.097 mole) of XII in 300 ml. of 95% ethanol containing 30 g. of potassium hydroxide was refluxed for 7.5 hr. under nitrogen. The precipitated potassium carbonate was filtered and the ethanol removed under vacuum. The residual liquid was dissolved in water and extracted with ether. The ether was dried and removed. The yield was 6.74 g. (62%) of cyclohexylhydrazine, m.p. 45–48°.[24] The hydrochloride was prepared in 85% yield. Upon recrystallization from ethanol–ether, the cyclohexylhydrazine hydrochloride melted 109–110°.[24]

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(16) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1425 (1952).

(17) Levina, *et al* (ref. 5) reported for VIII, b.p. 185–187° (15 mm.), n^{20}_{D} 1.4738, d^{20}_{4} 1.0390; for IX, b.p. 175–176° (8 mm.), n^{20}_{D} 1.4570, d^{20}_{4} 1.0120.

(18) Retention times of the peaks were 0.25 min., 0.97 min., and 1.75 min., respectively. Flow rate of helium was 68 ml. per min. with column temperature 198° and the detector temperature 272°.

(19) Retention times of the peaks were 0.31 min., 1.19 min., and 2.09 min., respectively. Flow rate of helium was 58 ml. per min. with the column temperature 165° and the detector temperature 205°.

(20) E. B. Sokolova, *Zhur. Obshchei. Khim.*, **23**, 2002 (1953) reported b.p. 144–146°, n^{20}_{D} 1.4083, d^{20}_{20} 0.8303; semicarbazone m.p. 142°.

(21) G. Ponzio, *Gazz. chim. ital.*, **30**, 25 (1900) reported b.p. 201–203°.

(22) P. Barbier and R. Locquin, *Compt. rend.*, **156**, 1443 (1913) reported m.p. 99–100°.

(23) Prepared by the method of K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann.*, **551**, 109 (1942).

(24) M. Busch and K. Linsenmeier, *J. pract. Chem.*, **115**, 216 (1927), reported m.p. 46–50°. Hydrochloride, m.p. 110–111°.

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The Reaction of Ethyl Azodicarboxylate with 1,3- and 1,4-Cyclohexadienes

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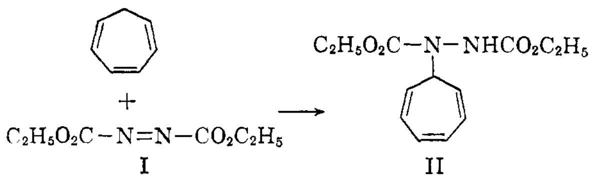
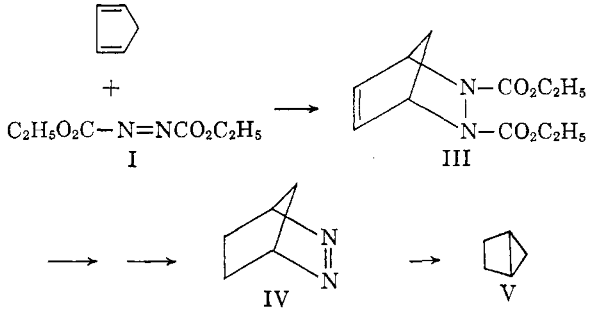
The reaction of 1,3-cyclohexadiene with ethyl azodicarboxylate does not proceed *via* a Diels-Alder adduction, but presumably by an addition-abstraction mechanism to form diethyl 2,5-cyclohexadien-1-yl bicarbamate. The product from the reaction of 1,4-cyclohexadiene with the azo ester is diethyl 2,4-cyclohexadien-1-yl bicarbamate. The structure proof for these compounds resided in infrared and ultraviolet spectral data and was confirmed by NMR analysis along with hydrogenation of each of these products to diethyl cyclohexylbicarbamate.

The reaction of ethyl azodicarboxylate (I) with conjugated dienes can proceed *via* additive substitution with carbons bearing allylic hydrogens, as shown by the reaction of ethyl azodicarboxylate with cycloheptatriene to form diethyl cycloheptatrienylbicarbamate (II).[1] On the other hand, ethyl azodicarboxylate (I) can behave as a dienophile with dienes such as cyclopentadiene to form *N*,*N*′-dicarboxyethyl-1,3-*endo*-hydrazocyclopentene (III).[2] This work has been repeated by Criegee and Rimmelin[3] as a preliminary step in the formation of 1,3-*endo*-azocyclopentane (IV) and thence to formation of bicyclo[2.1.0]pentane (V).



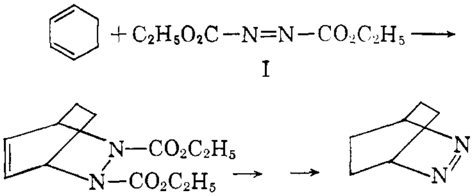
I II



I III IV V

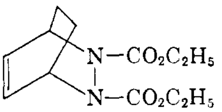
The reaction of 1,3-cyclohexadiene with ethyl azodicarboxylate has been studied in these laboratories to determine whether additive substitution or a Diels-Alder adduction has occurred.

The "synthesis" of 1,4-*endo*-azocyclohexane (VI) has been described by Pirsch and Jorgl[4]; this synthetic method follows a procedure originally developed by O. Diels[2] for the preparation of III. The first step of the synthesis, as described by Pirsch and Jorgl is supposedly a Diels-Alder adduction of 1,3-cyclohexadiene with ethyl azodicarboxylate (I) to form *N*,*N*′-dicarboxyethyl-1,4-*endo*-hydrazocyclohexene (VII).

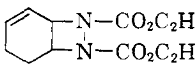


I VII VI

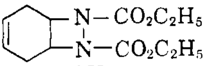
Although, *a priori*, it is convenient to assume formation of VII, the "normal" Diels-Alder adduct, there can be no reason to exclude structures such as the 1,2-adducts,[5] VIII and IX, or products such as X or XI.



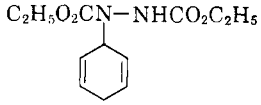
VII



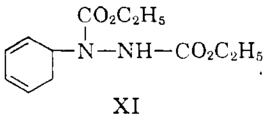
VIII



IX



X



XI

Indeed, the investigations from this laboratory show that *N*,*N*′-dicarboxyethyl-1,4-*endo*-hydrazo-

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(1) J. M. Cinnamon and K. Weiss, *J. Org. Chem.*, **26**, 2644 (1961).

(2) O. Diels, J. H. Blom, and W. Koll, *Ann.*, **443**, 242 (1925).

(3) R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957).

(4) J. Pirsch and J. Jorgl, *ibid.*, **68**, 1324 (1935).

(5) Private communication from Prof. S. J. Cristol.