Acknowledgment.—The authors wish to acknowledge funds toward the purchase of the F&M Scientific Corp. gas chromatography apparatus used in this work from the National Institutes of Health and a grant-in-aid from the Society of the Sigma Xi. Funds toward the purchase of the Perkin-Elmer Infrared were obtained from the National Science Foundation.

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

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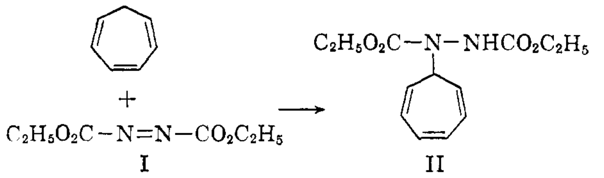
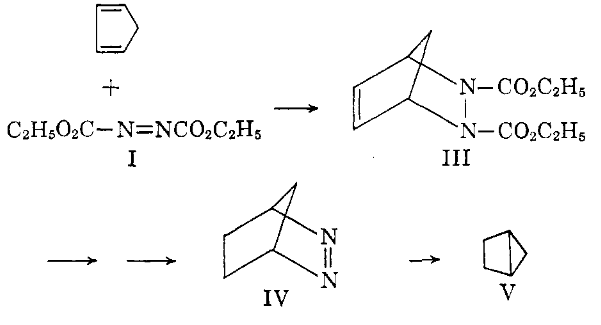
The reaction of 1,3-cyclohexadiene with ethyl azodicarboxylate does not proceed *via* a Diels-Alder adduction, but presumably by an addition-abstraction mechanism to form diethyl 2,5-cyclohexadien-1-yl bicarbamate. The product from the reaction of 1,4-cyclohexadiene with the azo ester is diethyl 2,4-cyclohexadien-1-yl 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.

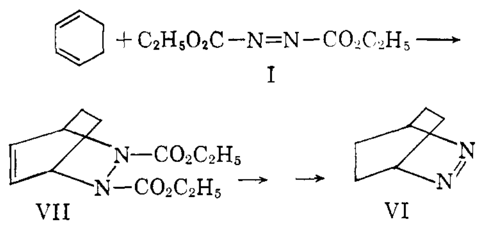
The reaction of ethyl azodicarboxylate (I) with conjugated dienes can proceed *via* additive substitution with carbons bearing allylic hydrogens, as shown by the reaction of ethyl azodicarboxylate with cycloheptatriene to form diethyl cycloheptatrienylbicarbamate (II).[1] On the other hand, ethyl azodicarboxylate (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).



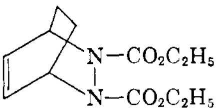


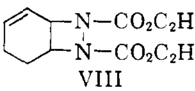
The reaction of 1,3-cyclohexadiene with ethyl azodicarboxylate has been studied in these laboratories to determine whether additive substitution or a Diels-Alder adduction has occurred.

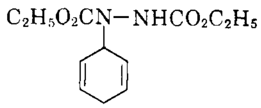
The "synthesis" of 1,4-*endo*-azocyclohexane (VI) has been described by Pirsch and Jorgl[4]; this synthetic method follows a procedure originally developed by O. Diels[2] for the preparation of III. The first step of the synthesis, as described by Pirsch and Jorgl is supposedly a Diels-Alder adduction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

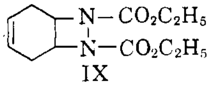


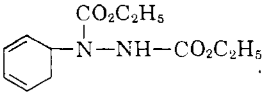
Although, *a priori*, it is convenient to assume formation of VII, the "normal" Diels-Alder adduct, there can be no reason to exclude structures such as the 1,2-adducts,[5] VIII and IX, or products such as X or XI.


VII


VIII


X


IX


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.

cyclohexene (VII) was *not* the product of the reaction.[6]

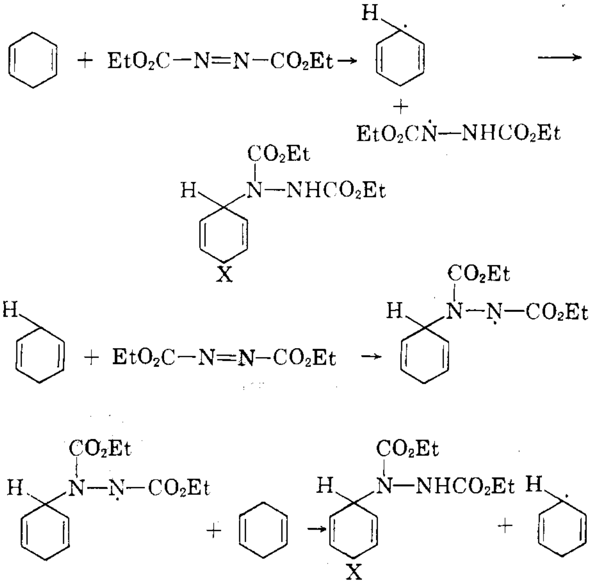
The adduction of 1,3-cyclohexadiene with ethyl azodicarboxylate proceeds smoothly with the formation of three products (as shown by vapor phase chromatography); the main product, after distillation, definitely indicates the one-to-one adduct. Compounds X and XI can be distinguished as a class from compounds VII, VIII, and IX by such gross differences as active hydrogen, N—H bond in the infrared, and different hydrogen areas as shown by NMR. Thus, neither VII, VIII, nor IX can be the adduct resulting from the reaction of 1,3-cyclohexadiene with ethyl azodicarboxylate for the following reasons: (a) the adduct contains a N—H bond ruling out structures VII, VIII, and IX but not structures X and XI, and (b) the NMR correlates perfectly with X and XI but not with VII, VIII, or IX as shown in Table I. Part of the evidence for the N—H bond resides in the 3300 cm.$^{-1}$ band in the infrared. This band shifts to 2450 cm.$^{-1}$ on substitution of deuterium for hydrogen as anticipated by theory.[7] The N—H bond is further confirmed by NMR and by its disappearance after substitution of deuterium for hydrogen. Final confirmation of the N—H bond resides in the determination of active hydrogen by treatment of the adduct with lithium aluminum hydride; this analysis gave 1.1 moles of hydrogen per mole of compound, thereby supporting only structures X and XI.

TABLE I

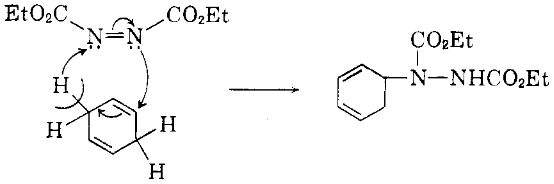
COMPARISON OF NMR HYDROGEN AREAS

NMR Relative area of hydrogens	Calculated for VII, VIII, and IX	Calculated for X and XI	Found
OCH_2	4	4	4.16
CH_3	6	6	6.60
Ring CH_2	4	2	1.88
Tertiary-H	2	1	0.94
Vinyl-H	2	4	3.51
N—H	0	1	0.94

Since C, H, N analysis and molecular weight clearly indicated the one-to-one adduct, and all other evidence pointed to either X or XI, there remained only the question of differentiating between X and XI. Indeed one would initially anticipate that XI would have an ultraviolet spectrum similar to that of 1,3-cyclohexadiene whereas X should have no significant ultraviolet spectrum. Since the adduct does not significantly absorb in the ultraviolet, one would anticipate that the adduct is compound X. It will also be noted that spin-spin splitting in the NMR should easily differentiate between X and XI, and indeed the NMR spectrum coincides with the predicted spectrum of compound X. If it is assumed that the reaction of 1,3-cyclohexadiene with ethyl azodicarboxylate results in formation of compound X, then the reaction of 1,4-cyclohexadiene with ethyl azodicarboxylate proceeding *via* hydrogen abstraction at the allyl position in a chain process would also result in formation of X.[8]



On the other hand a concerted addition-abstraction mechanism[9] would result in the formation of compound XI.



Under both radical and radical-inhibition conditions, ethyl azodicarboxylate reacted with 1,4-cyclohexadiene. Vapor phase chromatography indicated three compounds; a viscous oil, the major component, had the same vapor phase chromatographic retention time as the adduct of ethyl azodicarboxylate with 1,3-cyclohexadiene. This adduct, however, had a slightly different infrared spectrum even though the N—H stretching frequency was still quited istinct. The ultraviolet spectrum of this compound, however, was characteristic of a conjugated diene with λ_{max} 258 mμ and ϵ_{max} 3570; this compares quite closely to 1,3-cyclohexadiene, λ_{max} 258 mμ and ϵ_{max} 4580. The NMR

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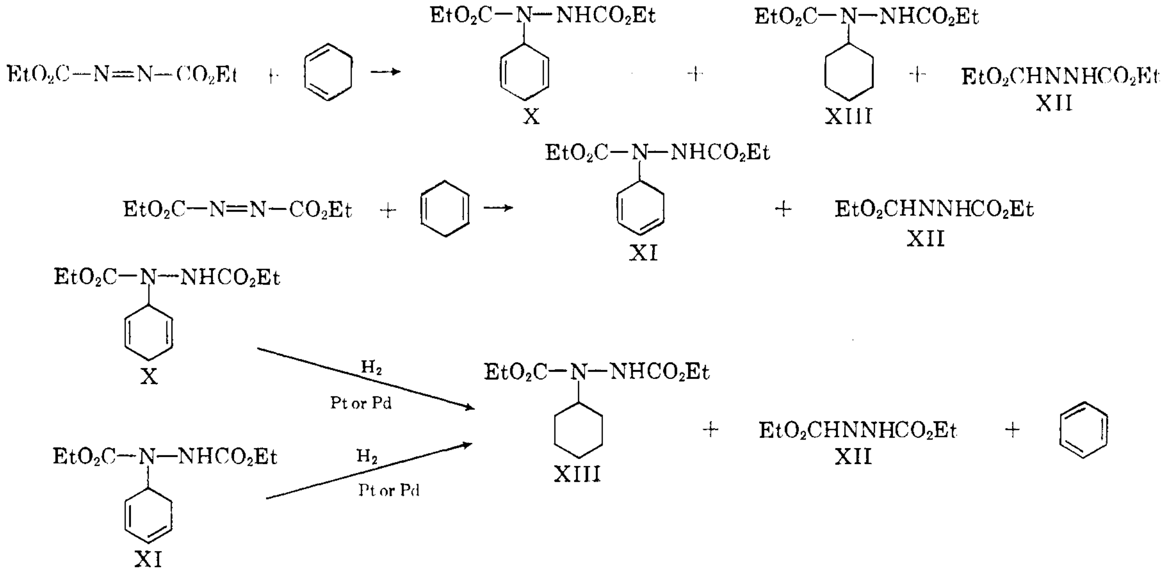
(6) While this manuscript was being reviewed, a paper by Cohen and Zand [S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962)] appeared, reporting the formation of VII and XI from 1,3-cyclohexadiene and ethylazodicarboxylate. The referee has kindly suggested that the difference between our work, in which compound X was formed, and that of Cohen and Zand is due to a minor difference in experimental procedure. Thus we added the azo compound to the diene whereas Cohen and Zand used the inverse addition.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1957, p. 207.

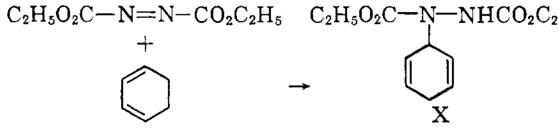
(8) R. Huisgen and F. Jakob, *Ann.*, **590**, 37 (1954).

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

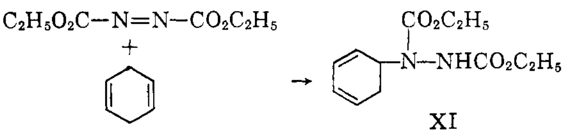
Scheme I



spectrum of this compound coincides with the spectrum predicted for XI. The fact that both compounds X and XI were available and could be compared side by side by ultraviolet and NMR made the assignments of X and XI quite clear. The reactions 1,3 and 1,4-cyclohexadiene with ethyl azodicarboxylate are shown in equations 1 and 2.



(1)



(2)

Because of the fact that 1,3-cyclohexadiene and ethyl azodicarboxylate might react under radical conditions to produce X but under nonradical conditions to form VII,[10] a sample of very carefully distilled 1,3-cyclohexadiene (see Experimental) was reacted under a nitrogen atmosphere with ethyl azodicarboxylate and with 1% hydroquinone as inhibitor. Hydroquinone was still present at the end of the reaction, but the course of reaction remained unchanged. Under all of our experimental conditions, at −25, −14, room temperature, 38, and at about 90°, with and without solvent, the formation of compound X was invariant, and at no time were compounds VII, VIII, or IX ever in evidence. In summary the evidence for structure X is (1) correct C, H, N analysis, (2) correct molecular weight, (3) correct molar refraction, (4) one active hydrogen per mole of compound, (5) the active hydrogen attached to a nitrogen atom as shown in the infrared spectra for N—H stretching at 3300 cm.$^{-1}$ and the further proof of the N—H bond by substitution of D for H by deuterium exchange and observing the expected shift of about 830 cm.$^{-1}$ due to the isotope effect.[7] Finally, structure proof is fully confirmed by NMR analysis giving the anticipated spectrum for X. The N—H bond assignment was fully confirmed by NMR on spectra of X before and after deuterium exchange.

For structure XI, resulting from the adduction of 1,4-cyclohexadiene with ethyl azodicarboxylate, the proof of structure is identical to that of X; the only additional difference is the expected spin-spin splitting in the NMR and the anticipated ultraviolet spectra of the conjugated diene.

In the adduction of ethyl azodicarboxylate with both 1,3-cyclohexadiene and 1,4-cyclohexadiene there were three products formed in each of the reactions. In the case of the 1,4-cyclohexadiene adduction two of the products formed are XI and ethyl hydrazodicarboxylate (XII); the structure of the latter compound was confirmed by isolation of XII and by its melting point, mixed melting point with an authentic sample, analysis, molecular weight, infrared comparison with an authentic sample, and comparison of vapor phase chromatographic retention times with an authentic sample. The third product having a very long vapor phase chromatographic retention time and representing about 3 to 4% of the total reaction has not been identified. The three compounds resulting from adduction of 1,3-cyclohexadiene with ethyl azodicarboxylate are X (isolated), ethyl hydrazodicarboxylate (isolated), and the product from hydrogenation of X, compound XIII (not isolated). The identity of compound XIII resides only in the fact that vapor phase chromatographic analysis on the hydrogenation of the above three component mixture results only in formation of peaks cor-

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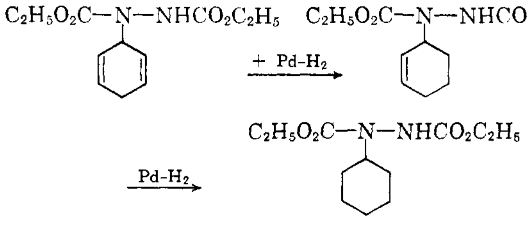
(10) Suggestion from Prof. W. E. von Doering.

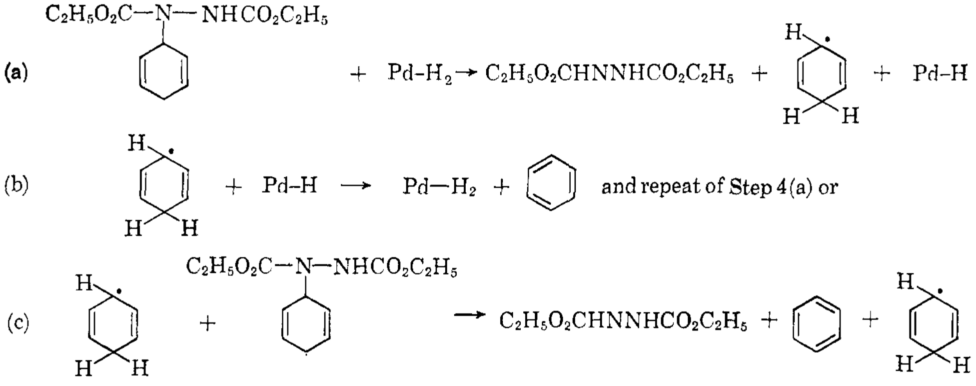
responding to XII and XIII. Thus, after hydrogenation of X, compound XIII was indeed isolated. Elemental analysis, molecular weight, molar refraction, active hydrogen, infrared analysis (N—H stretching) on XIII before and after deuterium exchange, and NMR analysis on XIII before and after deuterium exchange all confirm XIII as the correct structure for the hydrogenation of X. This, of course, further substantiates structure X and indeed hydrogenation of XI to form XIII completes the structure proof. The results are summarized in Scheme I.

It will be noted that hydrogenation of X (or XI) results not only in the anticipated hydrogenation product (XIII) but also in ethyl hydrazodicarboxylate and benzene. This is in variance with Pirsch and Jorgl[4] who postulated that hydrogenation of their adduct gave *N,N'*-dicarboxyethyl-1,4-*endo*-hydrazocyclohexane, ethyl hydrazodicarboxylate, and cyclohexane. The formation of benzene was quite clear both by ultraviolet analysis and by vapor phase chromatography and, of course, structure XIII which has been proven must of necessity rule out *N,N'*-dicarboxyethyl-1,4-*endo*-hydrazocyclohexane.

It had been noted that merely stirring compound X in palladium–charcoal and ethanol for twenty-four hours led to complete formation of benzene and ethyl hydrazodicarboxylate; however, when the same adduct X was stirred with palladium–charcoal in dioxane for forty-eight hours no reaction occurred. If, however, the palladium–charcoal is first saturated with hydrogen (but not enough to hydrogenate to form XIII in extensive amounts) then even in dioxane, the formation of benzene and ethyl hydrazodicarboxylate is complete. Since hydrogen must be present to effect the decomposition of X and it is known that in ethanol the reaction Pd + $CH_3CH_2OH \rightarrow CH_3CHO$ + Pd—H_2 occurs to some extent,[11] then there seems to be no doubt that hydrogenation of X proceeds by two concurrent mechanisms: (1) the normal hydrogenation of olefinic bonds and (2) a chain reaction involving C—N scission in which the rate-determining step is hydrogenolysis of a carbon-nitrogen bond. This is shown in equations 3 and 4.



(3)

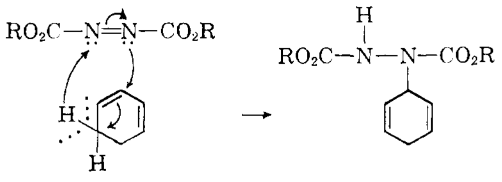


(4)

and Step 4(c) can be repeated.

There is no doubt that once hydrogenation of one of the double bonds is complete no C—N scission occurs since vapor phase chromatography shows no cyclohexene or cyclohexane. The only products observed (beside XIII) are benzene and ethyl hydrazodicarboxylate in equimolar quantities.

Although cyclopentadiene with a resonance stabilization of 2.9 kcal.[12] undergoes the Diels-Alder adduction with the azo ester,[2,3] 1,3-cyclohexadiene with a resonance energy of 1.9 kcal.[12] "apparently" undergoes an addition-abstraction mechanism to form a 1,4 diene with a loss of about 1.9 kcal. in resonance energy. At present we can conclude that only a slight structural difference can alter the course of a Diels-Alder reaction to that of an addition-abstraction reaction.



Experimental

All melting points are corrected and were taken on a Fisher-Johns melting point apparatus. Boiling points are uncorrected.

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(11) H. Wieland, *Ber.*, **45**, 484 (1912).

(12) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, 1955, p. 80.

Infrared spectra of ethyl hydrazodicarboxylate and ethyl azodicarboxylate were determined on a Baird Model 4-55 recording spectrophotometer. All other infrared spectra were determined using a Beckman IR-5 spectrophotometer. Ultraviolet spectra were obtained using a Cary Model 14-M recording spectrophotometer. NMR spectra were determined with Varian Associates A-60 and HR-60 spectrometers.

Vapor phase chromatographic analysis was carried out on a Perkin-Elmer Model 154-D Vapor Fractometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. Molecular weight analyses were determined by the Analytical Research Division of Esso Research and Engineering Co.

Ethyl Hydrazodicarboxylate.—This compound was prepared according to the method of N. Rabjohn.[13] After recrystallization from water with a little ethanol, the white crystals had a m.p. 133.5–134°.

Ethyl Azodicarboxylate.—This compound was purchased from Aldrich Chemical Co., Milwaukee, Wis., and had an infrared spectrum identical with a product prepared by the method of N. Rabjohn.[13] Purchased material was used in all reactions.

1,3-Cyclohexadiene.—The hydrocarbon was purchased from Farchan Research Laboratories, Wickliffe, Ohio; 1,4-cyclohexadiene was purchased from Columbia Organic Chemical Co., Columbia, S. C.

Diethyl 2,5-Cyclohexadien-1-yl Bicarbamate (X).—In a typical experiment 10.0 ml. (0.0996 mole) of 1,3-cyclohexadiene, 95% pure by vapor phase chromatographic[14] analysis, was heated to reflux (80°) in a 25-ml. three-necked flask equipped with magnetic stirrer, dropping funnel, thermometer, and condenser. Ethyl azodicarboxylate, 5.2 g. (0.0299 mole), was added dropwise over a 20-min. period. The temperature of the reaction mixture remained between 84–87° during addition of the azo compound. The reaction mixture was deep yellow during the addition but became almost colorless 5 min. after the addition was completed. The heat was removed 20 min. after the addition was completed, and the flask was allowed to cool. The reaction mixture was stripped of excess 1,3-cyclohexadiene by subjecting the reaction mixture to reduced pressure and heating at 50°; a very viscous, cloudy liquid, 7.2 g., resulted. Vapor phase chromatographic[15] analysis of the liquid showed three peaks. The major peak (67%) had a retention time of 9.3 min. The other two peaks, not completely resolved, had retention times of 5.4 min. and approximately 6.3 min. The 5.4 min. peak (18%) corresponded to an authentic sample of ethyl hydrazodicarboxylate. The product from an experiment larger in quantity but in every other respect identical to the above was distilled. Four fractions were taken; the last fraction, b.p. 120–125° (0.007 mm.), a clear, colorless, viscous liquid, corresponding in vapor phase chromatographic[15] retention time to the 9.3 min. peak had $n^{24}\text{D}$ 1.4909, d^{25} 1.1395. The infrared spectrum of this liquid showed the N—H stretching of secondary amides of 3300 cm.$^{-1}$ and a carbonyl absorption in the 1700–1750-cm.$^{-1}$ region. The remainder of the spectrum was characteristic but undefinitive. The ultraviolet spectrum of 0.11 g. of the liquid diluted up to 1000 ml. with ethanol gave no significant absorption. The NMR[16] spectrum showed a peak at 6.00 p.p.m. attributed to the methyl groups and appearing as a characteristic triplet. The ester methylenes appeared at 3.10 p.p.m. as two interlaced four-peak patterns, indicating that the two methylenes are shielded differently by the nitrogens and the ring. The ring methylene hydrogens at 4.60 p.p.m. would be expected to give a symmetrical A_2X_2 pattern, and two major peaks with shoulders were observed. The peaks at 2.00 p.p.m. for tertiary hydrogen and at 1.42 p.p.m. for vinyl hydrogen showed no clearly defined splitting pattern. The N—H peak appeared at −0.06 p.p.m.

Anal. Calcd. for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.02; mol. wt., 254 MRD, 64.54. Found: C, 56.48 H, 7.38; N, 10.81; mol. wt., 259, 257; MRD 64.55.

1,3-Cyclohexadiene and ethyl azodicarboxylate were also reacted at −25, −14, 25, and 38°, using the same molar ratios as in the experiment detailed above. At the lower temperatures the reactions proceeded more slowly. Judging completion by the disappearance of yellow color in the reaction mixture, it took 100 hr. for complete reaction at −25°; 22 hr., at −14°; 2 hr., at 38°. In all cases, the yields indicated a one-to-one adduction of diene to azo compound, and the major products had identical vapor phase chromatographic retention times and identical infrared spectra.

Nonradical conditions for the adduction were obtained by: (1) distilling 1,3-cyclohexadiene over hydroquinone and under a nitrogen atmosphere on a Todd distillation assembly using a Monel spiral column at a reflux ratio of 50:1 until a fraction was achieved, b.p. 80.5°, that was 96.7% 1,3-cyclohexadiene, 2.8% cyclohexene, 0.4% benzene, and 0.1% 1,4-cyclohexadiene by vapor phase chromatographic analysis[14]; (2) adding 12.4 g. (0.0713 mole) of ethyl azodicarboxylate dropwise to 15.0 ml. (0.15 mole) of the freshly distilled 1,3-cyclohexadiene refluxing with 1% hydroquinone in an apparatus similar to the one described in the experiment run at 84–87°. The entire apparatus had been thoroughly dried and purged with dry nitrogen before the reaction and was kept under dry nitrogen during addition of the ethyl azodicarboxylate. The reaction proceeded normally. The reaction mixture was extracted twice with 25 ml. of a 5% aqueous sodium hydroxide solution, the aqueous layer turning a brownish purple. This same color is observed on treatment of hydroquinone with base. The aqueous layers were combined and extracted with 25 ml. of dichloromethane. The organic layers were combined, dried over magnesium sulfate, and stripped of solvent under reduced pressure at room temperature, resulting in 17.3 g. of a cloudy, viscous residue. Vapor phase chromatographic[15] analysis showed this liquid to have the following composition: 2% of a peak corresponding in retention time to ethyl hydrazodicarboxylate; 15% of a peak with retention time of 6.3 min.; 83% of a peak with retention time of 9.3 min. The infrared spectrum and NMR spectrum of the peak occurring at 6.3 min. (isolated by liquid-liquid chromatography on acid-washed alumina) were identical to those of X.

Deuterium Exchange on X.—Compound X, 160 mg. (0.63 mmole), was dissolved in 0.5 ml. (85 mmoles) of deuterated ethanol (C_2H_5OD 99.5 atom %, purchased from Volk Radio-Chemical Co., Chicago, Ill.) under nitrogen drybox conditions. This solution was stirred for 185 hr. at room temperature, then was entirely stripped of solvent at 0.001 mm. pressure. Infrared spectrum of the residue was identical to compound X except for a shift of the N—H stretching at 3300 cm.$^{-1}$ to 2450 cm.$^{-1}$ for N—D stretching. Infrared clearly shows deuterium exchange from N—H to N—D. NMR[16] spectrum showed 40% disappearance of the peak at −0.06 p.p.m. for N—H, confirming the infrared evidence for deuterium change.

Reaction of Lithium Aluminum Hydride with X.—In a two-necked flask equipped with a magnetic stirrer and a rubber septum in one neck of the flask was dissolved 204.7 mg. (0.766 mmole) of X in 3.0 ml. of tetrahydrofuran. Compound X contained about 5% ethyl hydrazodicarboxylate as shown by vapor phase chromatographic[15] analysis. The above flask was connected to a gas analysis apparatus consisting of a gas buret and a mercury manometer.

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(13) N. Rabjohn, *Org. Syntheses*, Coll. Vol. III, 375 (1955).

(14) Determined with a 2 m. × 1/4 in. Perkin-Elmer Vapor Fractometer Column R at 55°.

(15) Obtained with a 1 m. × 1/4 in. 304 SS column packed with 20% ethylene glycol succinate on acid-washed Chromosorb W at 170° with 210 cc./min. of helium as carrier gas. This column packing was purchased from Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

(16) Carbon tetrachloride solution. Benzene = 0 as external reference.

Through the rubber septum of this flask was added 1.0 ml. of a 1.5 *M* lithium aluminum hydride solution in tetrahydrofuran. Evolution of hydrogen was immediate and was complete within 5 min. The amount of hydrogen evolved was 23.0 ml. corrected for volume of solution injected, a blank for the tetrahydrofuran and STP. Assuming X to have one active hydrogen and ethyl hydrazodicarboxylate to have two active hydrogens, the amount of hydrogen evolved should have been 19.7 ml.

Diethyl 2,4-Cyclohexadien-1-yl Bicarbamate (XI).—In an apparatus identical to the one described above in the preparation of X, 10.0 ml. (0.10 mole) of 1,4-cyclohexadiene (97% pure by vapor phase chromatographic analysis[14]) was heated to 60°. Ethyl azodicarboxylate 8.8 g. (0.0506 mole), was added dropwise over a 10-min. period, the temperature of the reaction mixture rising to 95° during the addition. Within 10 min. after the addition was completed the reaction mixture was only faintly yellow. The mixture was stripped of excess 1,4-cyclohexadiene under water aspirator vacuum at 50°. A white solid (2.5 g.) was precipitated from the residue by mixing with carbon tetrachloride. The remaining 8.6 g. of pale yellow, viscous liquid showed three peaks on vapor phase chromatographic[15] analysis; the first (21%) corresponding in retention time to ethyl hydrazodicarboxylate, the second, XI (76%), having a retention time of 9.3 min., and the third (3%) having a retention time of 26.0 min. This liquid was mixed with a small amount of dichloromethane, enough to make it sufficiently fluid, and place on a 25 in. × 1 in. chromatographic column containing 225 g. of aluminum oxide (Merck, acid-washed). Using dichloromethane as eluent 50-ml. fractions were taken. Fractions 13–25 contained a viscous liquid, corresponding to the peak with 9.3-min. retention time. This liquid was 98% pure.

Infrared spectrum of this liquid again showed the N—H stretching at 3300 cm.$^{-1}$ and a carbonyl absorption at 1670–1755 cm.$^{-1}$. Indeed this spectrum was *almost* identical to that of X. There was enough of a difference, however, to look at the ultraviolet spectra. The ultraviolet spectrum of 0.938 mmole of the liquid diluted up to 2500 ml. with absolute ethanol gave $\lambda_{\max}^{C_2H_5OH}$ 258 mμ, log ε 3.55. This compares to $\lambda_{\max}^{C_2H_5OH}$ 258 mμ, log ε 3.66 for 1,3-cyclohexadiene. NMR spectrum for this liquid was very similar to that of X. The differences are as follows: the peak at 2.00 p.p.m. for tertiary hydrogen in X shifted upfield to 2.29 p.p.m. Also a peak at 4.76 p.p.m. for ring methylenes showed more splitting than the corresponding peak at 4.60 p.p.m. in X. Presumably this is due to its becoming an A_2XY system instead of the simpler A_2X_2 system found in X. The hydrogen distribution by NMR is as follows:

	Theory	Found
CH_3	6	6.3
OCH_2	4	4.4
Ring CH_2	2	1.8
Tertiary H	1	0.9
Vinyl-H	4	3.4
N—H	1	1.2

Anal. Calcd. for $C_{12}H_{18}N_2O_4$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.70; H, 7.47; N, 11.20.

An attempted vacuum distillation at 130° of the crude product from a reaction similar to the above resulted in the formation of a dark, crystalline mass in the distillation flask and virtually no volatilized material.

Ethyl azodicarboxylate and 1,4-cyclohexadiene were reacted under nonradical conditions exactly as in the nonradical adduction of the 1,3 diene with the azo compound. Freshly distilled 1,4-cyclohexadiene (10 ml., 0.10 mole) and 8.8 g. (0.0506 mole) of ethyl azodicarboxylate yielded 3.3 g. of a white solid and 7.8 g. of a yellowish, viscous liquid whose vapor phase chromatographic[15] analysis gave three peaks; the first, corresponding in retention time, 5.4 min., to ethyl hydrazodicarboxylate, was 19% of the total area; the second, retention time 9.3 min., 76%; the third, retention time 26.0 min., 5%. Isolation of the second peak by chromatographing on an alumina column resulted in a viscous liquid whose infrared and NMR spectra were identical to XI.

Deuterium Exchange with XI.—Compound XI, 110 mg. (0.43 mmole), was stirred under nitrogen at room temperature for 41 hr. with 1.0 ml. (170 mmole) of deuterated ethanol (C_2H_5OD). Infrared spectrum of the residue remaining after stripping the solvent was identical to compound XI except for a shift of the band at 3300 cm.$^{-1}$ for N—H stretching to 2450 cm.$^{-1}$ for N—D stretching. This shift clearly demonstrates deuterium exchange. In the NMR spectrum the peak for N—H at −0.06 p.p.m. for XI showed a 90% disappearance, confirming the infrared evidence for deuterium exchange.

It was found that mixing the undistilled products from the preparations of X and XI with an equal volume of carbon tetrachloride precipitated a white solid (XII), m.p. 132–133°, after washing with carbon tetrachloride and drying. Intimate mixing with an authentic sample of ethyl hydrazodicarboxylate did not depress its melting point. As this solid was removed from the crude products the vapor phase chromatographic[15] peaks identical to ethyl hydrazodicarboxylate in retention time correspondingly disappeared. Infrared spectrum of the solid taken in a 0.2% KBr pellet was superimposable on that of an authentic sample of ethyl hydrazodicarboxylate.

Anal. Calcd. for $C_6H_{12}N_2O_4$: C, 40.90; H, 6.87; N, 15.90. Found: C, 41.01; H, 6.33; N, 15.86.

Diethyl Cyclohexylbicarbamate (XIII).—In a typical experiment, 1860 mg. of the crude product from the 1,3-cyclohexadiene and ethyl azodicarboxylate containing 67% (4.9 mmoles) of X, 15% of a component with 6.3 min. vapor phase chromatographic[15] retention time and 18% of ethyl hydrazodicarboxylate was diluted up to 10.0 ml. with ethanol. Mixed with 5.0 ml. of ethanol, 239 mg. of 10% palladium-on-charcoal were placed together with a magnetic stirrer in a two-necked flask equipped with a rubber septum, the flask being part of a gas buret type hydrogenation apparatus complete with leveling bulb and manometer. With the catalyst in the flask the entire apparatus was alternately evacuated and filled with hydrogen several times. Hydrogen uptake of the catalyst once stirring was started was 3.0 ml. within 3.0 min. Through the septum was injected 5.0 ml. of the ethanolic solution containing 2.5 mmoles of X. Hydrogen uptake occurred at once and continued for 2 hr. at an almost constant rate under an average overpressure of 5 mm. at 25°. The total hydrogen uptake was 105.7 ml. corrected for STP, or 1.9 mmole H_2/mmole X. The hydrogenated mixture was filtered and 1.0 ml. of the filtrate was diluted up to 10.0 ml. with absolute ethanol. The ultraviolet spectrum of this dilution showed the characteristic maxima for benzene at 261 mμ, 254 mμ, and 248 mμ. Based on A_{261} = 1.03, 0.772 mmole of benzene was found in the hydrogenated solution. The filtrate was stripped of solvent and any other volatile material by subjecting it to reduced pressure (200 mm.) and heat up to 110°. A white solid was precipitated from the viscous residue by mixing with carbon tetrachloride. Infrared spectrum of the solid in a 0.2% KBr pellet was identical with ethyl hydrazodicarboxylate. Vapor phase chromatographic[15] analysis of the residue gave three peaks: one had a retention time identical to ethyl hydrazodicarboxylate; the major one, a retention time of 6.3 min.; one, a retention time of 26.0 min. In a similar hydrogenation, run on a larger scale, the residue from the filtrate was distilled giving a colorless, viscous liquid, b.p. 125–128° (0.007 mm.), $n^{23}D$ 1.4797, d^{25} 1.1182. The NMR[16] spectrum showed peaks at −0.45 to −0.10 p.p.m., 3.10 p.p.m., 5.50 p.p.m., and 6.00 p.p.m. The peak at 3.10 p.p.m. was attributed to the four ester methylene hydrogens and the tertiary hydrogen. The latter had shifted upfield from 2.0–2.3 p.p.m. in X and XI due to the loss of the deshielding effect of the double bonds. The peak at 6.00 p.p.m. was partly attributed to the axial ring hydrogens. These would be expected to appear about 0.4 p.p.m. upfield from the equatorial hydrogens. The ring was assumed to have either slow inversion or no inversion at all due to the mass and steric effects of the hydrazine substituent. Dissection of this peak into an upper triplet having the correct 1:2:1 ratio and a lower segment, indicates that a peak equivalent to four hydrogens is buried beneath the methyl peak. The hydrogen distribution by NMR is as follows:

	Theory	Found
OCH_2 and *t*-H	5	5.5
CH_3 and ring CH_2	16	15.3
N—H	1	1.2

Anal. Calcd. for $C_{12}H_{22}N_2O_4$: C, 55.79; H, 8.59; N, 10.85; mol. wt., 258; MR_D, 65.48. Found: C, 55.67; H, 8.22; N, 10.95 mol. wt., 251, 246; MR_D, 65.51.

Reaction of Lithium Aluminum Hydride with XIII.—The method and apparatus used was the same as in the reaction of lithium aluminum hydride with X. To a tetrahydrofuran solution of 401.4 mg. (1.40 mmoles) of XIII containing 10% impurity by vapor phase chromatographic[15] analysis was added 1.0 ml. of a 1.5 *M* lithium aluminum hydride solution in tetrahydrofuran. The hydrogen evolved equaled 36.4 ml., corrected for the volume of solution injected, a blank for the tetrahydrofuran and STP. Assuming XIII to have one active hydrogen and the 10% impurity to be the dimer of XIII and therefore two active hydrogens the amount of hydrogen evolution should have been 35.1 ml.

Hydrogenation of XI.—Using an apparatus and method identical to that used in the hydrogenation of X, 580 mg. (2.16 mmoles) of XI, 95% pure by vapor phase chromatographic analysis,[15] took up 54.8 ml. of hydrogen or 1.13 mmoles H_2/mmole XI. The ultraviolet spectrum of the filtered hydrogenated solution showed 0.189 mmole of benzene to have been formed during the hydrogenation. Vapor phase chromatographic analysis[15] of the solution stripped of solvent showed it to contain 12% ethyl hydrazodicarboxylate, 73% of a compound corresponding in retention time (6.3 min.) to XIII and 15% of a compound with 26.0-min. retention time. The peak corresponding to XIII was isolated on an alumina chromatographic column and had infrared and NMR spectra identical to XIII.

Anal. Calcd. for $C_{12}H_{22}N_2O_4$: C, 55.79; H, 8.59. Found: C, 55.94; H, 8.53.

A hydrogenation of X was carried out in an identical manner to the hydrogenations of X and XI described above with the exception that 2.0 mmoles of X dissolved in 4.0 ml. of ethanol was placed in the flask with the catalyst before saturating the latter with hydrogen. The hydrogen uptake was 61.0 ml. or 1.4 mmoles H_2/mmole X. Benzene was found by ultraviolet analysis to the extent of 1.24 mmoles, and again ethyl hydrazodicarboxylate was formed, although the major product was still XIII.

In order to determine the reason for the formation of benzene and ethyl hydrazodicarboxylate, 1.22 mmoles of X was dissolved in 5.0 ml. of ethanol and stirred under nitrogen with 0.14 g. of 10% palladium-on-charcoal for 23 hr. The work-up of the solution was the same as for the hydrogenations. Ultraviolet analysis showed that 1.00 mmoles of benzene was formed; 83% of the possible amount. Vapor phase chromatographic[15] analysis showed that 91% of the original amount of X had disappeared, and that the amount of ethyl hydrazodicarboxylate had increased. The same experiment was repeated using *p*-dioxane as the solvent. Stirring under nitrogen was continued for 48 hr.; but ultraviolet spectrum showed no formation of benzene, and vapor phase chromatographic analysis[15] showed no change in amount of ethyl hydrazodicarboxylate present. Again using *p*-dioxane as solvent, 0.55 g. of 10% palladium on charcoal was placed in 4.0 ml. of the *p*-dioxane, the mixture then being saturated with 15.1 ml. of hydrogen. Compound X, 5.83 mmoles, was diluted up to 5.0 ml. with *p*-dioxane and was added to the saturated catalyst. The mixture was stirred for 49 hr. at room temperature under nitrogen. The mixture was filtered, and the filtrate was stripped of volatile material, which contained 4.59 mmoles of benzene. Ethyl hydrazodicarboxylate, 4.25 mmoles, was precipitated from the residue by mixing with carbon tetrachloride.

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Double Bond Migration in 1,2-Diaroyl-1-cycloalkenes[1]

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A number of 1,2-diaroyl-1-cycloalkenes have been found to undergo isomerization to the corresponding 1,6-diaroyl-1-cycloalkenes. The rearrangement is catalyzed by hydrochloric acid and by sodium hydroxide.

An attempt to prepare 1,2-dimesitoyl-1-cyclohexene (II) by the action of iodine on the enol salt of *trans*-1,2-dimesitoylcyclohexane (I) produced instead the unsymmetrical olefin, 1,6-dimesitoyl-1-cyclohexene (III).[2] It has now been found that a shorter reaction time gives the symmetrical olefin in 74% yield.

It seemed likely that the symmetrical olefin had rearranged to the unsymmetrical isomer when the reaction time was prolonged. Confirmation of this speculation was obtained by treating the symmetrical olefin with sodium hydroxide; when the solution was allowed to stand for seventy two hours, the unsymmetrical olefin was obtained in 93% yield.

It is possible that the rearrangement is due to purely steric factors. To explore this idea, the corresponding diduroyl compound, containing larger groups, was studied. Under the same conditions

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[2] R. C. Fuson, W. R. Hatchard, R. H. Kottke, and J. L. Fedrick, *J. Am. Chem. Soc.*, **82**, 4330 (1960).