

observed in the n.m.r. spectrum of 20 (τ 4.20, 1H) as was a quaternary N-methyl peak (τ 6.73).

Methylation of the Enamines from "1-Methyl- $\Delta^{4(9)}$ -dehydroquinolizidinium Perchlorate" (21 and 26).—A sample of the iminium salt 21 prepared¹⁵ by the mercuric acetate oxidation of 1-methylquinolizidine (23) was recrystallized to a constant melting point of 253–255° which agreed well with that reported in the literature¹⁷ (252–253°). After the methylation experiment described below had been carried out, this salt was shown¹⁴ to consist of a 2:1 mixture of the iminium perchlorates 21 and 26.

The basic fraction obtained by methylation of the above mixed salt according to the usual procedure was, according to its vapor phase chromatogram, a mixture of at least six components which were not readily separable. An n.m.r. spectrum (D_2O) of the noncrystalline quaternary fraction (28) (ca. 70% yield based on the amount of 21 actually present in the starting mixed salt) displayed sharp peaks at τ 6.7 and 8.4. After several recrystallizations from methanol-ether with the aid of some Norit, the white TNBS derivative of 28 melted at 185–187°.

Anal. Calcd. for $C_{17}H_{22}N_4O_6S$: C, 44.53; H, 4.83. Found: C, 44.75; H, 4.73.

Reaction of Quaternary Salt 11 with Base.—A mixture of 0.6 g. of the crude salt 11, 2 ml. of water, and 10 ml. of a saturated solution of sodium hydroxide was directly steam distilled until the distillate was no longer basic. Approximately 0.15 g. of 11 was recovered from the distillate by extraction with chloroform. The distillate was worked up in the same way as the methylation reactions to give 0.4 g. of a crude perchlorate salt which was catalytically hydrogenated to give a basic substance whose v.p.c. indicated the presence of three compounds. The compound formed in highest yield had a v.p.c. retention time similar to 8-methylindolizidine (16), but its picrate melted at 105–107° as compared to 203–204° for that of 16.¹⁵ Furthermore, the infrared spectrum of this material was similar to that of N-methylpiperidine and not 16.

The product of highest retention time had an infrared spectrum similar to that of N-methylpyrrolidine, while that of lowest retention time was not present in sufficient quantity for isolation.

Acknowledgment.—This research was supported in part by funds from the Research Committee of the University of California.

The Reaction of Enamines with Activated Butadienes. A One-Step Synthesis of Benzenes¹

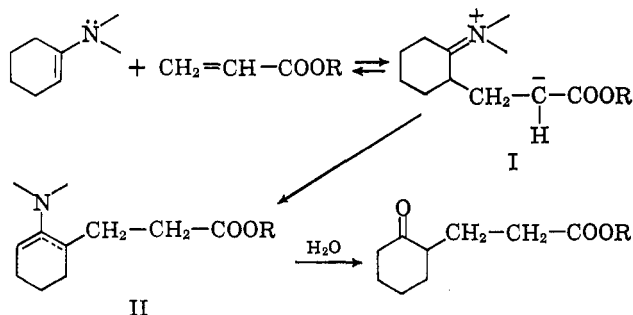
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The reaction of enamines with ethyl sorbate and ethyl 2,4-pentadienoate was studied. Under appropriate conditions, cycloaddition, retro-Michael elimination, and aromatization were realized, thus affording a one-step synthesis of benzenes.

Stork and co-workers² demonstrated the ability of electrophilic olefins to undergo nucleophilic attack with enamines. A typical over-all process is shown below.



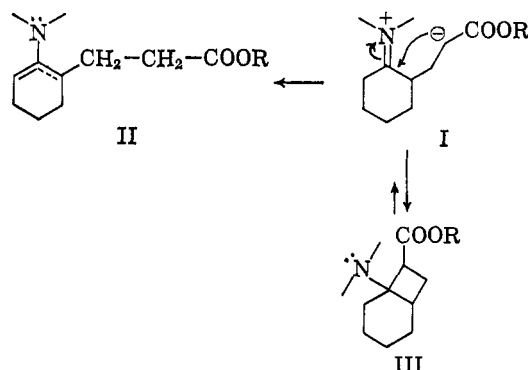
Brannock and co-workers³ found that, under appropriate conditions, cyclobutane derivatives of the type III may be observed. It is not certain whether they arise from direct cycloaddition or *via* a two-step (Michael–Mannich) sequence. From the results of the Columbia workers,¹ it would appear that III could well be in equilibrium with I (Mannich–retro-Mannich), an equilibrium which is presumably irreversibly displaced toward II by proton transfer.

The purpose of this communication is to disclose preliminary results of a study of this type of reaction

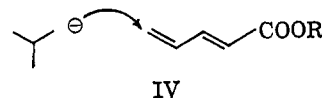
(1) This work was supported by a Grant from the National Institutes of Health, No. AM-08695-0. The efforts of Mrs. Celia B. Lerman are gratefully acknowledged.

(2) G. Stork, A. Brizzolara, H. Landesman, J. Smuszkoicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

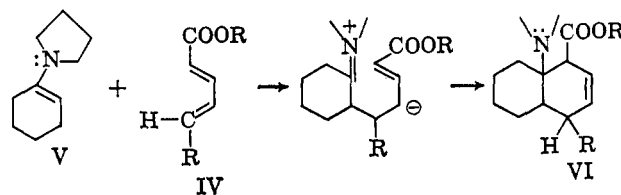
(3) K. C. Brannock, R. D. Burpitt, V. M. Goodlett, and J. G. Thweatt, *J. Org. Chem.*, **29**, 813 (1964).



on a system vinylogously related to the one considered above. Derivatives of β -vinylacrylates are well known⁴ to undergo 1,6 addition preferentially. We therefore



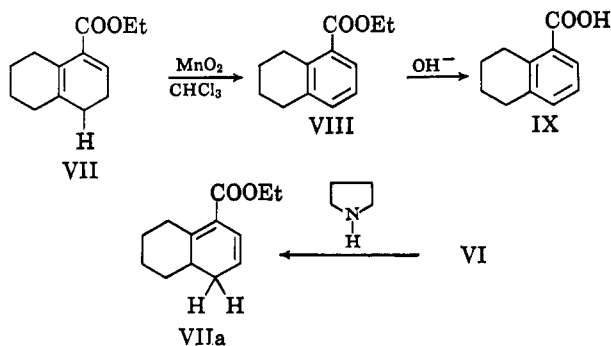
felt it of interest to examine the enamine reaction on derivatives of IV with the hope of realizing terminal addition and attendant (or concurrent by a cycloaddition process) six-membered ring formation.



(4) E. P. Kohler and F. R. Butler, *J. Am. Chem. Soc.*, **48**, 1041 (1926).

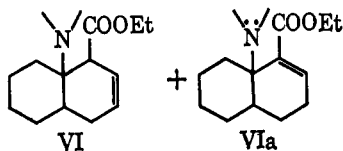
In the event, when freshly distilled, colorless samples of V and IV ($R = H$, $R' = Et$) were mixed in a nitrogenous environment, a bright yellow color developed. Distillation of this solution at 10^{-3} mm. resulted in a fractionation into starting components.

Of more interest is the fact that in refluxing, dry tetrahydrofuran a 1:1 molar ratio of IV and V after 17 hr. gave, upon removal of the solvent at reduced pressures, a residue whose ultraviolet spectrum indicated a virtual absence (*ca.* 3%) of the butadiene IV. The neutral portion of this material is assigned the structure VII on the basis of the fact that upon oxidation with "active" $MnO_2^{5,6}$ followed by aqueous hydrolysis it afforded the known⁷ 5,6,7,8-tetrahydro-1-naphthoic acid IX in 72% yield starting from the oily neutral fraction.

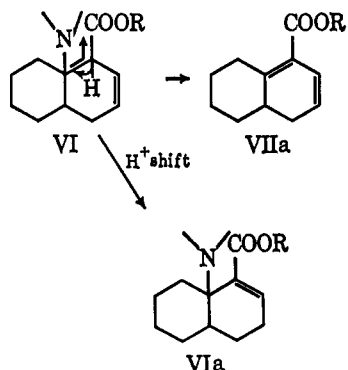


That this material is not pure VIIa is vouchsafed by the fact that its n.m.r. spectrum exhibits at least four different kinds of vinylic hydrogens. Its vapor phase chromatogram exhibits two peaks.

Upon basification, the acid-soluble fraction gave rise to material whose spectral and chromatographic properties are consistent with its being a mixture of VI + VIa.



These results, while of little synthetic utility owing to partitioning, are suggestive of the intermediacy of the hoped for product VI which, during the course of the reaction and subsequent treatment, underwent reverse Michael addition and tautomerization.

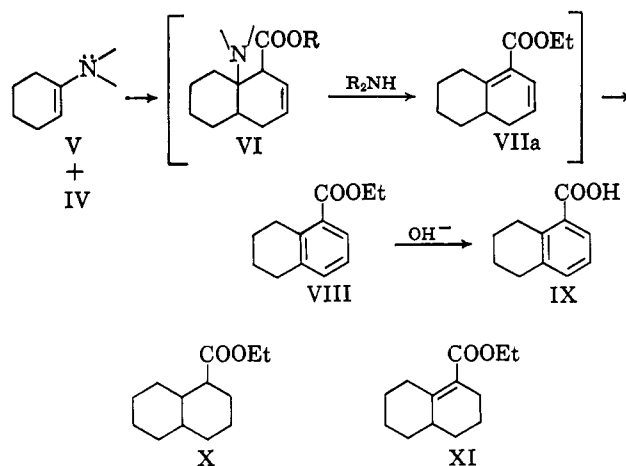


(5) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(6) We have found this reagent very convenient for oxidizing certain dihydroquinolines and dihydrobenzenes to the corresponding aromatic systems.

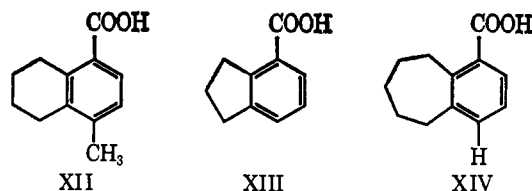
(7) J. J. Cason and D. D. Phillips, *J. Org. Chem.*, 17, 298 (1952).

It thus seemed plausible that more vigorous treatment would rectify part of this problem and lead to a more nearly homogeneous mixture. These expectations were realized. Heating the β -vinylacrylate IV and the enamine in dry diglyme under pressure at 200° followed by fractional distillation afforded, as the major product, the already encountered VIII. Saponification gave the crystalline IX in 43% over-all yield. The presumed sequence is shown below.



In three runs, the ester VIII was obtained in 58% average yield, contaminated with nonaromatic material, which tentatively could well be a mixture of X and XI. However, the sum of these did not exceed (v.p.c.) 7% of the ester fraction. Hence, either they are resinified in the course of the reaction or, more likely, the aromatization also occurs by a process other than disproportionation.

The over-all reaction has been extended, with minor modification, to the commercially available ethyl sorbate (IV, $R = CH_3$) and the morpholine enamine of cycloheptanone² as well as to the pyrrolidine enamine of cyclopentanone. The sorbate was recovered virtually unreacted from the refluxing tetrahydrofuran reaction conditions, whereas IV ($R = H$) is virtually all reacted under these conditions. The morpholinocycloheptene does not afford the yellow color upon admixture with IV ($R = H$) at room temperature. However, at elevated temperatures both these systems (sorbate and the morpholinocycloheptene) react in a qualitatively similar manner to the ethyl 2,4-pentadienoate and the pyrrolidine enamines. Thus, we prepared in two steps the following crystalline acids in 40–50% yield.



In summary, we are dealing with a process which permits the elaboration of a benzo derivative of a cycloalkane starting with an enamine of the corresponding cycloalkanone in one step. This raises mechanistic questions particularly as to the nature of the cycloaddition step. The yellow color observed on admixture of the components is reminiscent of many types of

Diels-Alder reactions. The Diels-Alder process itself is not without certain mechanistic ambiguities. It does, however, suggest a *cis* addition. Whether our reaction is a Diels-Alder in that sense, or a Michael followed by a Mannich-type closure capable, in principle, of cyclizing in a *trans* sense kinetically, is a question we cannot answer now. Our inability, thus far, to isolate the key adduct VI in pure form deprives us of the required stereochemical facts necessary for interpretation. Current studies are being conducted to correct this situation as well as to determine the feasibility of more challenging applications of this reaction.^{8,9}

Experimental Section¹⁰

Materials.—Tetrahydrofuran was distilled from lithium aluminum hydride. Dioxane was purified according to Fieser,¹¹ flushed with a stream of nitrogen, and stored. Diglyme (Eastman) was refluxed over calcium hydride and distilled from it at atmospheric pressure. Ethyl sorbate (IV, R = CH₃) was distilled from hydroquinone at 61–64° (16–18 mm.) prior to use. The ethyl 2,4-pentadienoate was prepared so that a direct comparison with commercially available ethyl sorbate could be made. In our hands, an exact adaptation of the method used for the methyl ester¹² afforded IV (R = H) in only 16–20% yield (in six runs) as a free-flowing liquid, b.p. 53–55° (19 mm.), $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.90 μ , $\lambda_{\text{max}}^{\text{EtOH (95\%)}}$ 247 $m\mu$ (ϵ 27,600). All the enamines were prepared according to Stork and co-workers.² Efforts were made to rigorously exclude air from all the enamine reactions.

The Reaction of Ethyl 2,4-Pentadienoate (IV, R = H) with Δ^1 -Pyrrolidino-cyclohexene (V). A. In Tetrahydrofuran.—A solution of the ester IV (R = H) (12.8 g., 0.10 mole) and the enamine V (15.6 g., 0.11 mole) in 150 ml. of tetrahydrofuran was heated under reflux. Aliquots were removed. After 17 hr. the absorption at 247 $m\mu$ had dropped to ca. 3% of its original intensity. Upon removal of most of the solvent at atmospheric pressure, the residue was dissolved in ca. 200 ml. of ether and this solution treated with 200 ml. of 10% hydrochloric acid containing several chips of ice to keep the mixture cold. The acid layer was quickly neutralized with ice-cold caustic alkali to pH 9. Extraction with ether, drying the ether extract over sodium sulfate, followed by removal of the solvent under vacuum afforded 13.7 g. of a residue. All efforts to crystallize this material or its derivatives (saponified or hydrogenated) were abortive. The n.m.r. spectrum of this material exhibited two different, overlapping types of O-CH₂ quartets in the region $\tau = 5.5$ –6.2 p.p.m. A thin layer chromatogram on silica gel eluted with 5% triethylamine in ethyl acetate exhibited two distinct major spots (sulfuric acid). Its infrared spectrum exhibited bands at 5.75 and 5.83 μ . This material is tentatively assigned as a mixture of tautomers VI + VIa. The neutral extract afforded a residue of 3.6 g. whose n.m.r. spectrum, $\tau = 3.9$ –5.1 p.p.m., exhibited a minimum of four different vinylic hydrogens, a minimum of two ethyl groups was clearly discernible. Treatment of 1.7 g. of this material with 3 g. of "active" manganese dioxide⁶ in 40 ml.

(8) During the preparation of this manuscript, it was brought to our attention that this work intersects at certain points with that done by G. A. Berchtold, J. Ciabattomi, and A. A. Tunick: see Abstracts of the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p. 35; *J. Org. Chem.*, **29**, 3679 (1965). We gratefully acknowledge an enlightening conversation with Professor G. Berchtold of the Massachusetts Institute of Technology.

(9) It will be noted that the underlying assumptions of this work were not unlike those which prompted us to examine the reaction of appropriate vinyl pyridines with enamines. That cycloaddition products were not realized in that case [cf. G. Singerman and S. Danishefsky, *Tetrahedron Letters*, **33**, 2249 (1964)] is presumably related to a disruption of aromaticity, which would be inherent in that case. Another decisive difference could well be the presence of a basic nitrogen to facilitate proton transfer.

(10) All boiling points are uncorrected. The infrared spectra were determined on a Beckman IR-8 spectrophotometer. Ultraviolet measurements were made on a Cary 14. The n.m.r. spectra were measured at 60 Mc. with a Varian Model A-60 instrument. The values are quoted on the τ scale in parts per million relative to tetramethylsilane ($\tau = 10$ p.p.m.).

(11) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath and Co., Boston, Mass., 1957, p. 85, method a.

(12) E. Adlerova, et al, *Collection Czech. Chem. Commun.*, **25**, 226 (1960).

of chloroform under reflux, followed by filtration afforded, upon removal of the solvent, a residue which was distilled at 0.10 mm., affording a major cut of 1.2 g. at 86–89°. This material exhibited four peaks upon vapor phase chromatography. The major peak, ca. 90%, had a retention time identical with authentic VIII obtained from esterification of the authentic, crystalline IX.

B. In Diglyme.—A solution of IV (6.2 g., 0.05 mole) and the enamine V (7.7 g., 0.05 mole) in 30 ml. of diglyme was heated in a stainless steel bomb at 135° for 8 hr. In a typical experiment ca. 25 min. was necessary to reach this point from room temperature. The temperature was raised to 200° and heated for an additional 12 hr. After cooling and rapid distillation of the volatiles from 0 to 40° at 0.01 mm., the residue was distilled through a 2-ft. Vigreux column, affording a major cut from 86–94° (0.10 mm.) of 7.7 g. Of this material, 4.7 g. was saponified in 100 ml. of 10% ethanolic potassium hydroxide containing 3 ml. of water. The solvent was concentrated under vacuum and the residue was taken up in ca. 100 ml. of water. The water layer was extracted several times with ether and acidified to pH \approx 3. Extraction with ether afforded an orange solution which was nearly decolorized with charcoal, and the ether was removed, leaving a residue of 3.7 g., m.p. 144–148° (crude yield 43%). Recrystallization from ether-hexane afforded 3.1 g. of needles: m.p. 148–149, lit.⁷ 147–149.5°; n.m.r. (CDCl₃), τ 1.9 (1), 2.2 (1) doublet ($J = 6$ c.p.s.), 2.6–3.1 (2) multiplet, 6.8 (2) poorly resolved triplet, 7.5 (2) poorly resolved triplet, and 8.1–8.4 (4) multiplet.

The Reaction of Ethyl Sorbate (IV, R = CH₃) with the Enamine V. A. In Dioxane, a Two-Step Synthesis of XII.—A solution of IV (7.02 g., 0.05 mole) and V (7.39 g., 0.05 mole) in 75 ml. of dioxane was heated under reflux for 16 hr. Volatiles were removed at water pump pressure. The residue was dissolved in ether, extracted with 10% hydrochloric acid, and dried over sodium sulfate. The solution was filtered; the solvent was removed at the water pump. The residue was distilled at 0.04 mm. affording a major cut from 90 to 105° of 6.8 g., which was added to 10 g. of manganese dioxide in 40 ml. of chloroform. Immediate evolution of heat was noted. The mixture was stirred and heated under reflux for 2 days. After filtration through sintered glass, the solvent was removed at the water pump and the residue was taken up in a solution of ethanol (100 ml.), water (3 ml.), and potassium hydroxide (10 g.). This solution was heated at reflux temperature under a blanket of nitrogen for ca. 12 hr. It was then concentrated at the water pump and added to 100 ml. of water. The aqueous layer was extracted with ether until it was clear orange, acidified to pH \approx 2, and extracted again with three 100-ml. portions of ether. The combined ether extract was dried over sodium sulfate and boiled with charcoal. Filtration and removal of the solvent under vacuum afforded 4.5 g. of a glassy residue. Trituration with ether-hexane afforded 3.7 g. (31% crude) of a yellow crystalline solid, m.p. 171–183°. Recrystallization of 2.0 g. of this material from ether afforded 1.3 g. of white plates, m.p. 184–186°, unequivocally¹³ assigned the structure XII on the basis of its n.m.r. spectrum (CDCl₃): τ 1.8 (1), 2.3 (1) doublet ($J = 7$ c.p.s.), 2.9 (1) doublet ($J = 7$ c.p.s.), 6.9 (2) triplet, 7.4 (2) triplet, 7.8 (3) singlet, and 8.2 (4) multiplet.

Anal. Found: C, 74.00; H, 8.12.

B. In Diglyme.—A solution of IV (7.12 g., 0.5 mole) and V (7.47 g., 0.05 mole) in 30 ml. of diglyme was flushed with nitrogen and heated to 200° in a stainless steel bomb. Heating was continued for an additional 20 hr. The contents were transferred to a flask fitted with a 1-ft. Vigreux column. Upon exposure of this system to a vacuum of ca. 0.01 mm. copious evolution of gas was observed. In a Dry Ice cooled trap 2.1 g. of material was obtained, identified as pyrrolidine¹⁴ (contaminated with traces of diglyme) by its n.m.r. spectrum. The diglyme was removed from room temperature to -40° (0.10 mm.). The residue was fractionally distilled and a major cut of 8.9 g. was collected from 79–98°. This was saponified as in the previous experiment, whereupon 4.5 g. of XII (49%), m.p. 180–183°, was obtained.

(13) We have been unable to find a reference to this particular isomer of methyl tetrahydronaphthoic acid.

(14) A reasonably relevant analogy to a retro-Michael elimination of an angular pyrrolidino function is found in the work of Stork and co-workers⁵ in the reaction of the enamine of cyclohexanone with methyl vinyl ketone, affording the enamine of $\Delta^4,8$ -octalone.

The Pyrrolidine Enamine of Cyclopentanone with IV (R = H). A Two-Step Synthesis of XIII.—A solution of the enamine (6.7 g., 0.05 mole) and ethyl 2,4-pentadienoate in 35 ml. of diglyme was heated exactly as in the previous experiment. Fractional distillation afforded a major fraction from 86 to 93° (0.25 mm.) of 6.2 g. An infrared spectrum, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.80 μ , indicated it to be primarily ethyl indan-1-carboxylate. This material was saponified exactly as before, affording 3.9 g. (49%) of a crude acid, m.p. 140–147°. Recrystallization of this material from ether afforded 2.9 g., m.p. 147–149°. This was assigned the structure XIII because of its melting point (lit.¹⁵ 151.5–152.5); infrared, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.91; and n.m.r. (CDCl₃), τ 1.2 (1), 2.2 (1) doublet, 2.6–3.1 (2) multiplet, 6.7 (2) triplet ($J = 8$ c.p.s.), 7.1 (2) triplet ($J = 8$ c.p.s.), and 7.6–8.1 (2) multiplet.

The Reaction of the Morpholine Enamine of Cycloheptanone with IV (R = H). A Two-Step Synthesis of Benzosuberane-1-

(15) L. F. Fieser, and E. B. Hershberg, *J. Am. Chem. Soc.*, **59**, 396 (1937).

carboxylic Acid.—Slight modifications had to be introduced to bring the yield in this case up to the 40% level. Thus, a solution of the enamine (6.30 g., 0.034 mole) and IV (6.62 g., 0.05 mole) in 30 ml. of diglyme was heated to 120° for 14 hr. The temperature was then increased to 215°, and the solution was heated for an additional 13 hr. Distillation of the low-boiling material afforded ca. 12:1 mixture of diglyme–morpholine (v.p.c.) as a codistillate at 25–40° (0.01 mm.). The remainder was fractionated, affording a major cut from 89 to 103° (0.10 mm.). This material was saponified directly as in the previous experiments. Evaporation of the ether left an oily residue of 4.7 g. Trituration with ether–pentane afforded 3.5 g. of crystalline material, m.p. 93–101°, crude yield. Three recrystallizations from ether–hexane afforded 2.2 g., m.p. 109–110°, lit.¹⁶ 108°, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.90 μ .

(16) R. Granger, H. Orzalési, and A. Muratelle, *Compt. rend.*, **252**, 1478 (1961).

Synthesis of 1,3-Cyclohexadienes by the Reaction of Enamines with Methyl *trans*-2,4-Pentadienoate¹

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Enamines react with methyl *trans*-2,4-pentadienoate (1) to give intermediate 1:1 adducts arising from 1,4-cycloaddition. These intermediate amino esters readily lose the elements of pyrrolidine or morpholine under the reaction conditions affording methyl 3,4-dihydrobenzoate derivatives. The reaction has been shown to be general for pyrrolidine enamines of both cyclic ketones and simple aldehydes. In two cases the amino esters are obtained as the major product. The cycloaddition of 1-(*N*-pyrrolidino)cyclohexene and 1-(*N*-morpholino)cyclohexene with 1 gives methyl 8 α -pyrrolidino-1,4,4a,5,6,7,8,8a-octahydro-1-naphthoate (13) and methyl 8 α -morpholino-1,4,4a,5,6,7,8,8a-octahydro-1-naphthoate (14), respectively. Upon treatment with aqueous methanolic hydrochloric acid 13 gives methyl 4,4a,5,6,7,8-hexahydro-1-naphthoate. Catalytic hydrogenation of 14 affords methyl 8 α -morpholinodecahydro-1-naphthoate (20). Aqueous potassium hydroxide converts 20 to 2,3,4,4a,5,6,7,8-octahydro-1-naphthoic acid (21). Bromination and subsequent dehydrobromination of *cis,cis*-decahydro-1-naphthoic acid yields exclusively *cis*-3,4,4a,5,6,7,8,8a-octahydro-1-naphthoic acid and not the isomeric compound 21 reported earlier. 1-Diethylamino-1,3-butadiene reacts with 1 to produce methyl 2-diethylamino-1,2,5,6-tetrahydro-*trans*-cinnamate (25).

The use of enamines as intermediates in organic syntheses has been studied in considerable detail.⁵ Alkylations, acylations, and 1,2-cycloaddition reactions of enamines, in particular, have been thoroughly investigated. The 1,4-cycloaddition of 1-diethylamino-1,3-butadiene with electrophilic olefins to produce 4-substituted 3-diethylaminocyclohexenes is well documented,⁶ but no studies of the 1,4-cycloaddition of an electron-poor butadienyl system to the simple electron-rich enamine moiety have been reported. This manuscript is concerned with such a study in order to develop the reaction as a useful synthesis of substituted 1,3-cyclohexadienes and substituted 4,4a,5,6,7,8-hexahydro-naphthalenes.

The electron-poor diene chosen for study was methyl *trans*-2,4-pentadienoate (1). The enamines and 1 were refluxed in benzene under a nitrogen atmosphere for the period of time indicated in the Experimental Section. The enamines employed and the products obtained as well as per cent yields are listed in Table

I. Since the morpholine enamines 3 and 5 gave substantially poorer yields of cycloadducts than the corresponding pyrrolidine enamines 2 and 4, the pyrrolidine enamines were used in all subsequent reactions.

The work-up conditions ordinarily were such that the amino esters were not obtained but eliminated the elements of secondary amine to afford the substituted 1,3-cyclohexadiene derivative as the reaction product. In cases where the amino ester was obtained, it could be converted to the corresponding diene with refluxing aqueous methanolic hydrochloric acid. The stereochemistry of the amino esters was not determined.

The structure of the diene 11 has been established by House and Cronin who converted it to the known indan-4-carboxylic acid⁷ by aromatization with 2,3-dichloro-5,6-dicyanobenzoquinone and subsequent saponification with sodium hydroxide in aqueous methanol.⁸ The structures of the other products are assigned on the basis of the structure of 11, elemental analysis, and their spectral characteristics listed in the Experimental Section. The spirodiene ester 19 was converted to its corresponding acid by treatment with aqueous base at 100° and acidification.

Adduct 14 was readily reduced with hydrogen over platinum in ethyl acetate to 20 in 98% yield. Saponi-

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(2) Alfred P. Sloan Fellow, 1963–1965.

(3) National Institutes of Health Predoctoral Fellow (Fellowship No. 5-FI-GM-20,133 from the National Institute of General Medical Sciences).

(4) National Science Foundation Undergraduate Research Participant 1962–1963.

(5) (a) G. Stork, et al., *J. Am. Chem. Soc.*, **85**, 207 (1963); (b) J. Szmuszcz, *Advan. Org. Chem.*, **4**, 1 (1963).

(6) S. Hunig and H. Kahanek, *Chem. Ber.*, **90**, 238 (1957).

(7) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **59**, 396 (1937).

(8) H. O. House and T. H. Cronin, *J. Org. Chem.*, **30**, 1061 (1965). We wish to express our appreciation to these workers for carrying out this transformation.