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, $\lambda_{max}^{CHCl_3}$ 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, $\lambda_{max}^{CHCl_3}$ 5.91; and n.m.r. ($CDCl_3$), 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-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°, $\lambda_{max}^{CHCl_3}$ 5.90 μ.

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

(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-Pentadienoate[1]

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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 8a-pyrrolidino-1,4,4a,5,6,7,8,8a-octahydro-1-naphthoate (**13**) and methyl 8a-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 8a-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-hexahydronaphthalenes.

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 acid[7] 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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(3) National Institutes of Health Predoctoral Fellow (Fellowship No. 5-F1-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. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 1 (1963).

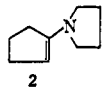
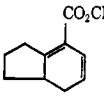
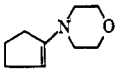
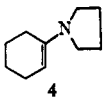
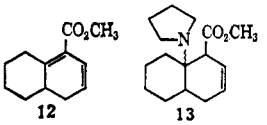
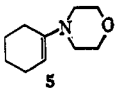
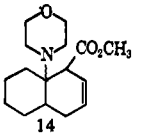
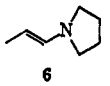
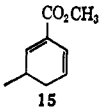
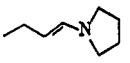
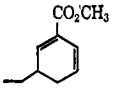
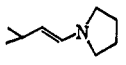
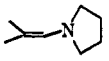
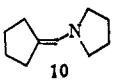
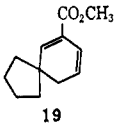
(6) S. Hunig and H. Kahanek, *Chem. Ber.*, **90**, 238 (1957).

(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.

TABLE I

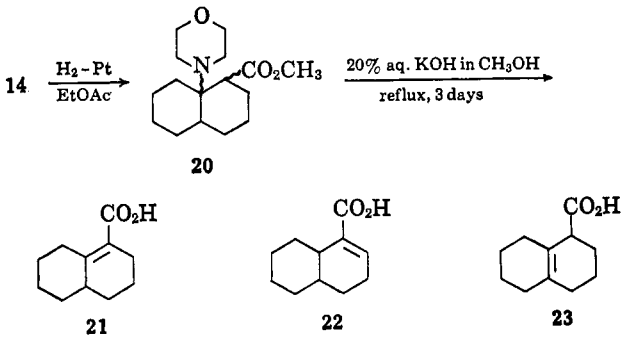
PRODUCTS FROM THE REACTION OF ENAMINES WITH METHYL *trans*-2,4-PENTADIENOATE

Enamine	Products	Yield, %
 2	 11	91
 3	11	18
 4	 12 13	10, 60
 5	 14	35
 6	 15	30
 7	 16	29
 8	 17	23
 9	 18	26
 10	 19	53

fication of **20** with 20% aqueous methanolic potassium hydroxide resulted in the elimination of the elements of morpholine and gave 2,3,4,4a,5,6,7,8-octahydro-1-naphthoic acid (**21**) in 70% yield. The properties of **21**, however, are different from those reported for the compound obtained by a bromination–dehydrobromination sequence on *cis,cis*-decahydro-1-naphthoic acid.[9,10] The compound reported by Ungnade and Ortega was readily obtained by their reported procedure.[10] The n.m.r. spectrum of this product in chloroform-*d* showed absorption for one vinyl proton as a complex multiplet centered at 7.12 p.p.m. On the basis of this absorption the compound reported by these workers must be assigned the isomeric structure **22**. The spectral data of **21** and its methyl ester, prepared by reaction of **21** with ethereal diazomethane, clearly eliminates the alternative structure **23** for the product obtained by refluxing **20** with aqueous potas-

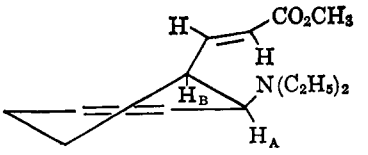
(9) H. E. Ungnade and F. V. Morriss, *J. Am. Chem. Soc.*, **72**, 2112 (1950).

(10) H. E. Ungnade and I. Ortega, *ibid.*, **73**, 1564 (1951).



sium hydroxide in methanol. The n.m.r. spectrum of **21** shows a broad doublet (J = 11 c.p.s.) for one hydrogen atom at 3.53 p.p.m. This low-field absorption is that expected of the quasi-equatorial hydrogen atom at C-8 due to deshielding by the carboxyl carbonyl group. The carbonyl stretching vibration of **21** occurs at 1675 cm.$^{-1}$ and the ultraviolet spectrum of the compound shows an absorption maximum at 224 mμ (ϵ 7140) in ethanol. Similarly, the n.m.r. spectrum of the methyl ester of **21** shows a broad doublet (J = 11 c.p.s.) for one hydrogen at 3.29 p.p.m., the carbonyl stretching vibration occurs at 1705 cm.$^{-1}$ and the ultraviolet spectrum in ethanol shows an absorption maximum at 228 mμ (ϵ 8330).

It was of interest to determine the structure of the condensation product from reaction of the electron-poor diene **1** with the electron-rich 1-diethylamino-1,3-butadiene (**24**). Reaction occurred readily yielding a 1:1 adduct. This product showed a carbonyl stretching vibration at 1715 and an olefinic stretching vibration at 1652 cm.$^{-1}$ (shoulder at 1640 cm.$^{-1}$) in addition to a maximum at 205 mμ (ϵ 16,200) in the ultraviolet spectrum in *n*-heptane. These data indicate that the dienamine condensed at the γ,δ positions of **1**.[11] The n.m.r. spectrum of the adduct is in agreement with this conclusion. The absorption for the β hydrogen atom of the α,β-unsaturated ester moiety appears as a quartet (J = 16 and 9 c.p.s.) centered at 7.3 p.p.m. The absorption for the α hydrogen atom appears as a quartet (J = 16 and 1.5 c.p.s.) centered at 5.94 p.p.m. The complex absorption of two other olefinic hydrogen atoms is observed at 5.6–6.0 p.p.m. Complex absorption for one hydrogen atom is also observed at 3.3–3.7 p.p.m. with no adjacent line separations greater than 3 c.p.s. The line width at half-height is approximately 10 c.p.s. This absorption may be assigned to H_A in **25**. Since this proton



25

appears not to be coupled to H_B by more than 3 c.p.s., **25** represents the most probable stereochemical assignment. The assignment of *cis* stereochemistry to the substituents on the cyclohexene ring of **25** is in agreement with the stereochemistry of the adducts reported

(11) The dimerization of methyl *trans*-2,4-pentadienoate and 2,4-pentadienoic acid proceeds in a similar manner: see H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **28**, 27 (1963), and K. Alder and W. Vogt, *Ann.*, **570**, 190 (1950), respectively.

by Hunig and Kahanek from the reaction of 1-diethylamino-1,3-butadiene with electrophilic olefins.[6]

Treatment of **25** with concentrated hydrochloric acid under reflux for 15 hr. resulted in the elimination of diethylamine and isomerization to hydrocinnamic acid.

Experimental Section[12]

N-Pyrrolidinomethylenecyclopentane (10).—Into a 500-ml. round-bottom flask equipped with a magnetic stirrer, water separator, reflux condenser, and gas inlet tube were placed cyclopentanecarboxaldehyde (56.9 g., 0.580 mole), redistilled pyrrolidine (159 g., 2.23 moles), 125 ml. of reagent grade benzene, and a trace of *p*-toluenesulfonic acid. The mixture was refluxed under nitrogen for 13 hr. after which time 5 ml. of water was collected in the water separator. The benzene was removed and the residual oil was distilled under reduced pressure to give 76 g. (86%) of **10** as a colorless liquid: b.p. 49–51° (0.02–0.03 mm.), $\nu_{max}^{CHCl_3}$ 1665 cm.$^{-1}$. $\lambda_{max}^{cyclohexane}$ 254 mμ (ε 4500). The n.m.r. spectrum of the pure liquid showed absorption at δ 1.3–1.85 (8H, aliphatic CH_2), 2.0–2.5 (4H, $-CH_2-C=$), 2.8–3.2 (4H, $-CH_2-N$), and 5.83 (1H, quintet, J = 2 c.p.s., C–H).

Anal. Calcd. for $C_{10}H_{17}N$: C, 79.40; H, 11.34; N, 9.26. Found: C, 79.63; H, 11.37; N, 9.41.

Methyl 8a-Pyrrolidino-1,4,4a,5,6,7,8,8a-octahydro-1-naphthoate (13) and Methyl 4,4a,5,6,7,8-Hexahydro-1-naphthoate (12).—Into a 50-ml. three-neck flask equipped with a magnetic stirrer, thermometer, reflux condenser, and gas inlet tube were placed 25 ml. of anhydrous benzene, 5.00 g. (0.0446 mole) of methyl *trans*-2,4-pentadienoate,[13] and 6.74 g. (0.0446 mole) of 1-(N-pyrrolidino)cyclohexene.[5] An immediate deep yellow coloration was observed upon addition of the reagents. The mixture was refluxed 4.5 hr. under nitrogen and kept at room temperature overnight. The benzene was removed and the residue was acidified with cold 5% hydrochloric acid. The aqueous mixture was extracted with two 50-ml. portions of ether and the combined etheral extract was washed with 10 ml. of water and dried over anhydrous magnesium sulfate. Concentration followed by distillation of the neutral residue afforded 0.85 g. (10%) of methyl 4,4a,5,6,7,8-hexahydro-1-naphthoate (**12**): b.p. 77–79° (0.17 mm.); $\nu_{max}^{CCl_4}$ 1713 (s), 1638 (w), and 1595 (w) cm.$^{-1}$; $\lambda_{max}^{C_2H_5OH}$ 286 mμ (ε 2790), inflection at 232 mμ (ε 3040). The n.m.r. spectrum in carbon tetrachloride showed absorption at δ 0.9–2.5 (11H, complex multiplets, aliphatic H), 3.71 (3H, singlet, $-OCH_3$), 5.3–5.8 (1H, complex multiplet, vinyl H), and 6.0–6.3 (1H, broad doublet, J = 10 c.p.s., vinyl H).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.79; H, 8.39.

The aqueous solution was made basic with 5% potassium carbonate solution and extracted with one 100-ml. portion and two 50-ml. portions of ether. The combined extract was dried over anhydrous magnesium sulfate and concentrated to give 10.0 g. of a crude, partially crystallized oil. Methanol was then added and, after further crystallization, the product was filtered and washed with cold methanol and dried to give 4.6 g. (39%) of methyl 8a-pyrrolidino-1,4,4a,5,6,7,8,8a-octahydro-1-naphthoate (**13**) as white crystals. Further crystallization from the mother liquor afforded an additional 2.4 g., over-all yield 7.0 g. (60%): m.p. 65–66°; $\nu_{max}^{CHCl_3}$ 2930 (s), 1727 (s), 1665 (w), 1472 (m), 1437 (s), 1330 (s), 1150 (s), and 1015 (s) cm.$^{-1}$. The n.m.r. spectrum in chloroform-*d* had absorption at δ 1.0–2.0 (19H, aliphatic H), 3.1–3.35 (1H, $-CH-C=O$), 3.62 (3H, singlet, $-OCH_3$), and 5.4–5.9 (2H, multiplet, olefinic H).

Methyl 8a-Morpholino-1,4,4a-5,6,7,8,8a-octahydro-1-naphthoate (14).—Into a 100-ml. three-neck flask equipped with heating mantle, magnetic stirrer, reflux condenser, and gas inlet tube were placed 6.66 g. (0.0594 mole) of methyl *trans*-2,4-pentadienoate, 40 ml. of anhydrous benzene, and 9.92 g. (0.0593 mole) of 1-(N-morpholino)cyclohexene.[5] The mixture was refluxed under nitrogen for 5 days. The benzene solution was washed with four 10-ml. portions of 5% hydrochloric acid, two 20-ml. portions of saturated sodium chloride solution, and one 10-ml. portion of saturated sodium chloride solution. The combined aqueous solution (including the sodium chloride washings) was extracted with 10 ml. of ether. The aqueous solution was made basic with 5% potassium carbonate solution and extracted with three 25-ml. portions of ether. The combined ether extract was washed with 10 ml. of saturated sodium chloride solution and dried over magnesium sulfate. Removal of the ether from the basic extraction afforded 5.8 g. (35%) of methyl 8a-morpholino-1,4,4a,5,6,7,8,8a-octahydro-1-naphthoate (**14**) as a white crystalline solid. The compound was twice recrystallized from ether to give white needles: m.p. 96.5–97.5° (a third recrystallization raised the melting point to 97.5–98.5°); $\nu_{max}^{CHCl_3}$ 1730 (s), 1660 (w), and 1115 (s) cm.$^{-1}$. The n.m.r. spectrum in chloroform-*d* had absorption at δ 1.51 (8H, complex multiplet, aliphatic H), 2.26 (2H, multiplet, allylic H), 2.68 (5H, quintet, $-CH_2-N$ and tertiary H), 3.03 (1H, multiplet, $-CH-CO_2-CH_3$), 3.62 (7H, multiplet, $O-CH_2$ and $-O-CH_3$), and 5.71 (2H, multiplet, olefinic H).

Anal. Calcd. for $C_{16}H_{25}NO_3$: C, 68.78; H, 9.02; N, 5.01. Found: C, 68.51; H, 9.02; N, 4.82.

Preparation of 11, 15, 16, 17, 18 and 19.—These compounds were prepared by refluxing the enamine and **1** in benzene. The quantities used and the period of reflux are indicated in Table II. The product was obtained by one of the following procedures as indicated in Table II.

TABLE II

Product	Enamine[a] (g., mole)	1, g. (mole)	Benzene, ml.	Reflux period, hr.	Work-up procedure
11	2 (6.45, 0.0470)	5.00 (0.0446)	25	6.5	A[b]
11	3 (7.70, 0.0502)	5.56 (0.0496)	40	96	B
15	6 (3.27, 0.0294)	3.39 (0.0302)	30	12	B
16	7 (3.92, 0.0313)	3.51 (0.0313)	30	23	B
17	8 (4.16, 0.030)	3.36 (0.030)	30	17	B
18	9 (11.2, 0.089)	10.0 (0.089)	0	36 (90°)	
19	10 (1.06, 0.0070)	0.731 (0.0065)	5	20	A

[a] See ref. 5. [b] The combined aqueous extracts were basified with 5% sodium carbonate and extracted with ether to obtain an additional amount of **11** after this ether extract was washed with saturated sodium chloride solution, dried over magnesium sulfate, concentrated, and distilled.

Procedure A.—The benzene was removed and the residue was acidified with 5% hydrochloric acid. The mixture was extracted with ether, and the combined ether extracts were dried over anhydrous magnesium sulfate. The product was obtained by concentration of the ether and distillation of the residue.

Procedure B.—The benzene solution was washed with 5% hydrochloric acid and saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The product was obtained by concentration of the benzene and distillation of the residue.

4-Carbomethoxy-7,7a-dihydroindan (11).—The yield was 7.23 g. (91%): b.p. 63–64° (0.12 mm.); $\nu_{max}^{CCl_4}$ 2920 (s), 2845 (m), 2800 (m), 1708 (s), 1638 (w), 1590 (w), 1435 (m), 1262 (s), 1199 (m), and 1088 (m) cm.$^{-1}$; $\lambda_{max}^{C_2H_5OH}$ 292 mμ (ε 2620) and 235 mμ (ε 13,300). The n.m.r. spectrum in carbon tetrachloride showed absorption at δ 0.8–3.4 (9H, multiplet, aliphatic H), 3.82 (3H, singlet, $-OCH_3$), 5.6–6.2 (1H, multiplet, olefinic H), and 6.59 (1H, quartet, J = 3 and 10 c.p.s., olefinic H).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.08; H, 7.91. Found: C, 73.98; H, 7.87.

2-Carbomethoxy-6-methyl-1,3-cyclohexadiene (15).—The yield was 1.34 g. (30%): b.p. 36–37° (0.12 mm.); $\nu_{max}^{CHCl_3}$ 3000 (m), 2948 (m), 2920 (m), 2855 (m), 2810 (m), 1705 (s), 1635 (m), 1598 (m), 1578 (w), 1450 (m), 1435 (s), 1375 (m), 1298 (s), 1267 (s), 1100 (s), and 1000 (s) cm.$^{-1}$; $\lambda_{max}^{C_2H_5OH}$ 282 mμ (ε 2649). The n.m.r. spectrum in carbon tetrachloride showed absorption at δ 1.08 (3H, doublet, J = 7 c.p.s., $-CH_3$), 1.7–2.9 (3H, complex multiplet, allylic H), 3.67 (3H, singlet, $-OCH_3$), 5.55–6.45 (2H, complex multiplet, olefinic H), and 6.5–6.75 (1H, broad singlet, olefinic H).

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.79; H, 7.82.

(12) All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Perkin-Elmer, Model 21, 237, or 337. The ultraviolet spectra were determined with a Cary recording spectrophotometer, Model 14. The microanalyses were performed by Dr. S. M. Nagy and his associates, by the Scandinavian Microanalytical Laboratory, and by Midwest Microlab. The n.m.r. spectra were determined with a Varian A-60 spectrometer. The values are reported in parts per million downfield from tetramethylsilane. The mass spectra were obtained with a CEC, Model 21-130, mass spectrometer.

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

2-Carbomethoxy-6-ethyl-1,3-cyclohexadiene (16).—The yield was 1.49 g. (29%): b.p. 47–47.5° (0.05 mm.); $\nu_{max}^{CHCl_3}$ 2975 (m), 2950 (s), 2915 (s), 2855 (m), 2805 (m), 1703 (s), 1635 (w), 1599 (m), 1450 (m), 1435 (s), 1365 (m), 1265 (s), 1100 (s), and 1035 (m) cm.$^{-1}$; $\lambda_{max}^{C_2H_5OH}$ 284 mμ (ε 2455). The n.m.r. spectrum in carbon tetrachloride showed absorption at δ 1.06 (3H, triplet, J = 7 c.p.s., $-CH_3$), 1.2–2.7 (5H, complex multiplet, aliphatic H), 3.67 (3H, singlet, $-OCH_3$), and 5.5–6.8 (3H, complex multiplet, olefinic H).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.11; H, 8.17.

2-Carbomethoxy-6-isopropyl-1,3-cyclohexadiene (17).—The yield was 1.26 g. (23%): b.p. 56–57° (0.12 mm.); $\nu_{max}^{CHCl_3}$ 2950 (s), 2860 (s), 2810 (m), 1703 (s), 1635 (m), 1578 (m), 1460 (m), 1435 (s), 1395 (w), 1380 (m), 1367 (m), 1260 (s), and 1087 (s) cm.$^{-1}$; $\lambda_{max}^{C_2H_5OH}$ 283 mμ (ε 2687). The n.m.r. spectrum in carbon tetrachloride showed absorption at δ 0.95 (6H, doublet, J = 7 c.p.s., $-CH_3$), 1.2–2.0 (1H, multiplet, aliphatic H), 2.05–2.25 (3H, multiplet, allylic H), 3.67 (3H, singlet, $-OCH_3$), 5.6–5.9 (1H, doublet of triplets centered at 5.75, J = 10 and 4 c.p.s., olefinic H), 6.1–6.4 (1H, doublet of quartets centered at 6.23, J = 10 and 1.5 c.p.s., olefinic H), and 6.68 (1H, finely split multiplet, olefinic H).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.29; H, 8.95. Found: C, 73.33; H, 8.88.

2-Carbomethoxy-6,6-dimethyl-1,3-cyclohexadiene (18).—The yield was 3.90 g. (29%): b.p. 45–46° (0.25 mm.); $\nu_{max}^{CHCl_3}$ 2950 (s), 2910 (m), 2855 (m), 2810 (m), 1710 (s), 1640 (m), 1587 (m), 1465 (m), 1437 (s), 1398 (w), 1360 (m), 1338 (m), 1310 (s), 1265 (s), 1175 (m), 1080 (s), and 1000 (s) cm.$^{-1}$; $\lambda_{max}^{heptane}$ 278 mμ (ε 2390). The n.m.r. spectrum in chloroform-*d* showed absorption at δ 1.08 (6H, singlet $>C<^{CH_3}_{CH_3}$), 2.13 (2H, quartet, J = 2 and 5 c.p.s., allylic CH_2), 3.81 (3H, singlet, $-OCH_3$), 5.7–6.1 (1H, doublet of triplets, J = 5 and 10 c.p.s., vinyl H), 6.3–6.6 (1H, doublet of multiplets, J = 10 c.p.s., vinyl H), and 6.73 (1H, finely split multiplet, vinyl H).

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.06; H, 8.49. Found: C, 72.46; H, 8.50.

Methyl Spiro[4.5]-1,3-decadiene-2-carboxylate (19).—The yield was 0.668 g. (53%): b.p. 88–88.5° (0.18 mm.); $\nu_{max}^{CCl_4}$ 2940 (s), 2860 (m), 1735 (s), 1641 (w), 1590 (w), 1440 (m), 1265 (s), 1115 (m), and 1087 (m) cm.$^{-1}$; $\lambda_{max}^{C_2H_5OH}$ 284 mμ (ε 3270). The n.m.r. spectrum in carbon tetrachloride showed absorption at δ 1.64 (8H, broad singlet, aliphatic H), 2.15 (2H, quartet, J = 4.5 and 2 c.p.s., allylic H), 3.70 (3H, singlet, $-OCH_3$), 5.45–6.0 (1H, multiplet, olefinic H), 6.38 (1H, broad doublet, J = 9 c.p.s., olefinic H), and 6.7 (1H, broad singlet, olefinic H).

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.66; H, 8.57.

Spiro[4.5]-1,3-decadiene-2-carboxylic Acid.—Into a 25-ml. flask equipped with magnetic stirrer, reflux condenser, and oil bath were placed 4.89 g. (0.0254 mole) of 2-carbomethoxyspiro-[4.5]-1,3-decadiene (19) and 9 ml. of 4 *N* aqueous sodium hydroxide solution.The mixture was heated for 5.5 hr. at 100°, cooled, and extracted with three 25-ml. portions of ether. The aqueous solution was acidified with 5% hydrochloric acid and extracted with three 25-ml. portions of ether. The ethereal extracts from the acidic solution were combined and dried over anhydrous magnesium sulfate. The ether was removed and the residue was subjected to molecular distillation at 80–100° (0.12 mm.) to yield the acid as a white solid: 3.29 g. (73%); m.p. 73.0–74.5°; $\nu_{max}^{CCl_4}$ 3400–2400 (broad), 1690 (s), 1640 (m), and 1585 (m) cm.$^{-1}$; $\lambda_{max}^{C_2H_5OH}$ 283 mμ (ε 3110); the molecular ion peak in the mass spectrum appeared at *m/e* 178. The n.m.r. spectrum in chloroform-*d* showed absorption at δ 1.66 (1H, singlet, aliphatic $-CH_2-$), 2.18 (2H, quartet, J = 4.5 and 2 c.p.s., $=C-CH_2-$), 5.78 (1H, doublet of triplets, J = 10 and 4.5 c.p.s., $-\overset{H}{\underset{|}{C}}-\overset{}{C}=$), 6.31 (1H, complex doublet, J = 10 c.p.s., $=\overset{O=C\ H}{\underset{|\quad|}{C}}-\overset{}{\underset{|}{C}}=$), 6.85 (1H, finely split multiplet, $\overset{H\ CO}{\underset{|\quad|}{C}}=C$), and 12.33 (1H, singlet, $-COOH$).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.99; H, 7.88.

Methyl 4,4a,5,6,7,8-Hexahydro-1-naphthoate (12) from 13.—Methyl 8a-pyrrolidino-1,4,4a,5,6,7,8,8a-octahydro-1-naphthoate (3.09 g., 0.0117 mole) was refluxed in a mixture of 20 ml. of methanol and 15 ml. of aqueous 5% hydrochloric acid under a nitrogen atmosphere for 3 days. A second liquid phase settled to the bottom of the flask. Saturated sodium chloride solution (30 ml.) was added to the mixture which then was extracted with three 10-ml. portions of ether. The combined extract was dried over anhydrous magnesium sulfate. Concentration of the ethereal extract yielded 2.12 g. of a slightly yellow oil. Short-path distillation under reduced pressure afforded 1.64 g. (73%) of methyl 4,4a,5,6,7,8-hexahydro-1-naphthoate (12) as a colorless liquid, b.p. 77–79° (0.17 mm.). The infrared, ultraviolet, and n.m.r. spectra were identical with those of 12 prepared as described earlier.

Methyl 8a-Morpholinodecahydro-1-naphthoate (20).—Adams catalyst (platinum oxide, 0.454 g.) in 10 ml. of ethyl acetate was prereduced under hydrogen over a 30-min. period at atmospheric pressure and room temperature. A solution of 2.05 g. (7.35 mmoles) of methyl 8a-morpholino-1,4,4a,5,6,7,8,8a-octahydro-1-naphthoate (13) in 25 ml. of ethyl acetate was injected into the flask by means of a syringe. The theoretical amount of hydrogen was absorbed over a 2-hr. period. Removal of the ethyl acetate after filtration afforded 2.02 g. (98%) of methyl 8a-morpholinodecahydro-1-naphthoate as a white crystalline solid: m.p. 112.5–114.0° (two recrystallizations from ether raised the melting point to 117.0–117.5°); $\nu_{max}^{CHCl_3}$ 1720 (s) and 1114 (s) cm.$^{-1}$. The n.m.r. spectrum in chloroform-*d* showed broad absorption at δ 0.8–2.1 (14H), 2.1–2.8 (6H), and 3.4–3.8 (7H).

Anal. Calcd. for $C_{16}H_{27}NO_3$: C, 68.29; H, 9.67; N, 4.98. Found: C, 68.09; H, 9.80; N, 5.09.

2,3,4,4a,5,6,7,8-Octahydro-1-naphthoic Acid (21).—Methyl 8a-morpholinodecahydro-1-naphthoate (20) (0.559 g., 1.98 mmoles) in 15 ml. of 20% potassium hydroxide solution prepared from 1:1 water–methanol was refluxed 3 days. To the clear solution was added 20 ml. of saturated sodium chloride solution. The mixture was extracted with three 10-ml. portions of ether, acidified with concentrated hydrochloric acid, and extracted with three 10-ml. portions of ether. The ether extracts after acidification were combined, washed with 5 ml. of saturated sodium chloride solution, and dried, and the ether was removed to yield 0.250 g. (70%) of 21 as a white solid. The acid was sublimed twice at 68° (0.02 mm.) to give 0.177 g. (49%), m.p. 106.5–107.5°. The resublimed acid was recrystallized from aqueous ethanol: m.p. 107.5–108.0°; $\nu_{max}^{CHCl_3}$ 3400–2400 (broad), 1675 (s), and 1620 (m) cm.$^{-1}$; $\lambda_{max}^{C_2H_5OH}$ 224 mμ (ε 7140). The n.m.r. spectrum in chloroform-*d* showed absorption at δ 1.0–3.5 (14H, aliphatic H), 3.53 (1H, broad doublet, J = 11 c.p.s.), and 11.4 (1H, singlet, $-COOH$).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.33; H, 9.10.

***cis,cis*-Decahydro-1-naphthoic Acid.**—This compound was prepared in 85% yield by the platinum-catalyzed reduction of 1,2,3,4-tetrahydro-1-naphthoic acid in glacial acetic acid according to the procedure of Ungnade and Morriss,[9] m.p. 123.0–123.5° (lit. m.p. 124–125°,[9] 123.5–124°[14]).

***cis*-3,4,4a,5,6,7,8,8a-Octahydro-1-naphthoic Acid (22).**—This compound was prepared according to the procedure of Ungnade and Morriss[8] to which structure 21 had been assigned.[9] The product was recrystallized twice from aqueous ethanol after sublimation: m.p. 162–163° (lit. m.p. 158.5–160°,[8] 158–159°[9]); $\nu_{max}^{CHCl_3}$ 3400–2400 (broad), 1680 (s), and 1635 (m) cm.$^{-1}$; $\lambda_{max}^{C_2H_5OH}$ 218.5 mμ (ε 7820). The n.m.r. spectrum in chloroform-*d* showed absorption at δ 0.9–2.1 (11H, multiplet, aliphatic H), 2.1–2.8 (3H, multiplet, allylic H), 7.12 (1H, complex multiplet, vinyl H), and 10.88 (1H, broad singlet, $-CO_2H$).

Methyl 2-Diethylamino-1,2,5,6-tetrahydro-*trans*-cinnamate (25).—Freshly distilled 1-diethylamino-1,3-butadiene (10.40 g., 0.0830 mole), methyl *trans*-2,4-pentadienoate (9.312 g., 0.0830 mole), and 20 ml. of anhydrous benzene were added to a 100-ml. pear-shaped flask equipped with a magnetic stirrer, reflux condenser, and gas inlet tube. The red-brown mixture was stirred in the dark under nitrogen for 3 days at room temperature. After the addition of 25 ml. of ether, the mixture was extracted three times with 50 ml. of 5% hydrochloric acid solution. The combined acid extract was made basic with a saturated solution of sodium bicarbonate and extracted four times with 50 ml. of

(14) W. G. Dauben, R. C. Tweit, and C. Mannerskantz, *J. Am. Chem. Soc.*, **76**, 4420 (1954).

ether. The combined ethereal extract was washed twice with 25 ml. of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the ether followed by short-path distillation under reduced pressure gave 13.663 g. (69%) of **25** as a light yellow liquid: b.p. 90–92° (0.04–0.05 mm.); $\nu_{max}^{CHCl_3}$ 1710 (s), 1650 (m), and 1640 cm.$^{-1}$ (sh); $\lambda_{max}^{heptane}$ 205 mμ (ε 16,200). The n.m.r. spectrum of **25** in chloroform-*d* showed absorption at δ 0.98 (6H, triplet, J = 7 c.p.s.), 1.5–2.3 (4H, broad multiplet), 2.4–2.8 (5H, quartet, J = 7 c.p.s.), 3.4–3.7 (1H, broad multiplet), 3.75 (3H, singlet), 5.6–6.0 (2H, multiplet), 5.93 (1H, quartet, J = 16 and 1.5 c.p.s.), and 7.32 (1H, quartet, J = 16 and 9 c.p.s.).

Anal. Calcd. for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 71.04; H, 9.95; N, 6.19.

The picrate had m.p. 163.0–163.5°; recrystallization from methanol gave m.p. 163.5–164.0°.

Anal. Calcd. for $C_{20}H_{26}N_4O_9$: C, 51.50; H, 5.62; N, 12.01. Found: C, 51.51, 51.69; H, 5.61, 5.79; N, 11.83, 11.83.

Hydrocinnamic Acid from 25.—Adduct **25** (1.450 g., 0.00611 mole) and 15 ml. of concentrated hydrochloric acid (37%) were refluxed for 15 hr. in a 50-ml. round-bottomed flask equipped with heating mantle, magnetic stirrer, and reflux condenser. The mixture was extracted three times with 10 ml. of ether and the combined ether solution was extracted three times with 10 ml. of aqueous 5% sodium bicarbonate. After acidification with concentrated hydrochloric acid, the mixture was extracted twice with 10 ml. of ether and the combined extract was washed with 5 ml. of saturated sodium chloride solution and finally dried over anhydrous magnesium sulfate. Removal of the ether afforded 0.470 g. (51%) of hydrocinnamic acid as a light brown oil which crystallized upon addition of a seed crystal. Molecular distillation under reduced pressure (60–80° at 0.04 mm.) afforded 0.334 g. (36%) of the acid as a white solid, m.p. 46.5–48.0; a mixture melting point showed no depression and the infrared spectrum was identical with that of authentic hydrocinnamic acid (m.p. 49.0–49.5°).

The Influence of Solvent and Chloramine Structure on the Free-Radical Rearrangement Products of N-Chlorodialkylamines

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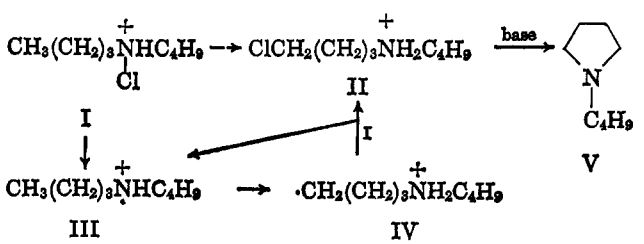
The influence of certain acidic solvents and chloramine structure on the photolytic Hofmann–Loeffler reaction has been studied. The δ-chloramine from N-chlorodi-*n*-butylamine was formed in 71% or better yield in the solvents 3.9 *M* sulfuric acid in acetic acid, nitromethane, or acetonitrile and in trifluoroacetic acid. The conversion of some δ-chloramines to the corresponding δ-hydroxyamines was demonstrated. In the aminium radical derived from N-chloro-N-methyl-5-phenylbutylamine only 62% of intramolecular hydrogen abstraction occurred at C-4 of the 5-phenylbutyl chain; 38% occurred at C-5 in the largest deviation from the usually high selectivity towards the C-4 position yet observed for an aminium radical. N-*t*-Butylchloramines were photolytically rearranged in acetic acid in order to observe any effect on the reaction efficiency and the selectivity due to the bulky N-alkyl group; the expected pyrrolidines were obtained in acceptable yields, and attack of the aminium radical occurred almost exclusively at C-4.

We wish to report some illustrations of the influence of solvent and of chloramine structure on the products obtained from photolytic rearrangements of N-chloramines (the Hofmann–Loeffler reaction[1]); the data should be useful in the further application of this reaction to organic synthesis.

Dependence on Solvent.—The literature does not reveal which of a variety of potential acidic solvents (Table I) are useful for effecting the desired rearrangement I → II or, perhaps, related reactions involving intermediate aminium radicals $R_2\overset{+}{N}H$, such as the addition of chloramines to unsaturated hydrocarbons.[2,3] We have studied mainly the rearrangement of N-chlorodi-*n*-butylamine, since we have already described in detail its reactions under varying conditions in sulfuric acid–acetic acid media.[4]



Our observations are summarized in Table II; entries 2–4 recall certain of our earlier results in sulfuric acid–acetic acid[4] for comparison with the new results, which follow. Thus, 83–88% yields of the pyrrolidine V are realized under several conditions of the photolytic reaction in acetic acid; in this solvent, the photolysis must be followed by basification to convert the primary product II to the isolable base V.

One useful alternative to sulfuric acid in acetic acid is trifluoroacetic acid (TFA, entries 7 and 8), claimed to be generally the solvent of choice for the chloramine rearrangement.[1] However, neither Wawzonek[5] nor we have found TFA to be superior, in terms of product yield, to sulfuric acid systems; for example, compare entries 2 and 7 in Table II and 1–3 in Table III. TFA may excell for steroidal chloramines[6] because it increases substrate solubility or decreases ionic side reactions involving other functional groups present in the steroid, such as C=C and C=O.

However, TFA does offer distinct advantages, as pointed out earlier[1,6]; principally, it allows simple isolation of the salt II. When II is isolated, derivatives other than V may then be obtained, such as the corresponding alcohol. Example 8 of Table II illustrates such a process; a primary chlorine atom was

(1) Reviewed by M. E. Wolff, *Chem. Rev.* **63**, 55 (1963).
(2) R. S. Neale, *J. Am. Chem. Soc.*, **86**, 5340 (1964).
(3) R. S. Neale and R. L. Hinman, *ibid.*, **85**, 2666 (1963).
(4) R. S. Neale and M. R. Walsh, *ibid.*, **87**, 1255 (1965).
(5) S. Wawzonek and T. P. Culbertson, *ibid.*, **81**, 3367 (1959).
(6) J. F. Kerwin, M. E. Wolff, F. F. Owings, B. B. Lewis, B. Blank, A. Magnani, C. Karash, and V. Georgian, *J. Org. Chem.*, **27**, 3628 (1962).