than 1,2-hexadiene or a mixture of the two. The two allenes had identical retention times, but the nmr spectrum in the olefinic proton region clearly differentiated between the two allenes.

Efforts were made to agitate the reactions at a uniform rate and good and reproducible values were found. Some variations were noticed when different lots of sodium amide were used. This could have been caused by differences in the particle size of the sodium amide or by qualitative differences caused by deterioration during preparation and/or storage. Within a given lot the values were consistent and reproducible.

Reactions of Enamines. VIII. The Reaction of Eniminium Salts with Trichloroacetate[1]

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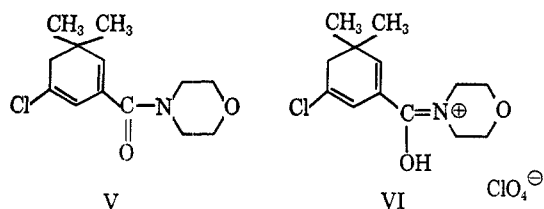
The relatively unstable compound isolated from the reaction of trichloroacetyl chloride with 5,5-dimethyl-3-N-morpholinylcyclohex-2-en-1-one has been shown to be N-1-(1-trichloromethyl-3-chloro-5,5-dimethylcyclohex-2-enyl)morpholine. The mechanism of formation of the latter from N-(3-chloro-5,5-dimethylcyclohex-2-en-1-ylidene)morpholinium trichloroacetate is discussed. The generality of this reaction of eniminium trichloroacetates is demonstrated.

In a previous paper in this series[2] it was shown that reaction of the enamino ketone I with trichloroacetyl chloride gave the chloroeniminium salt II (X = Cl). A second major product, a somewhat unstable oil, was induced to crystallize from aqueous acetone. Elemental analysis indicated the empirical formula $C_{13}H_{19}Cl_4NO$. Dimers were excluded by a molecular weight determination. In contrast to the starting material and II, the
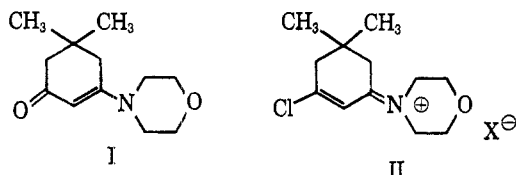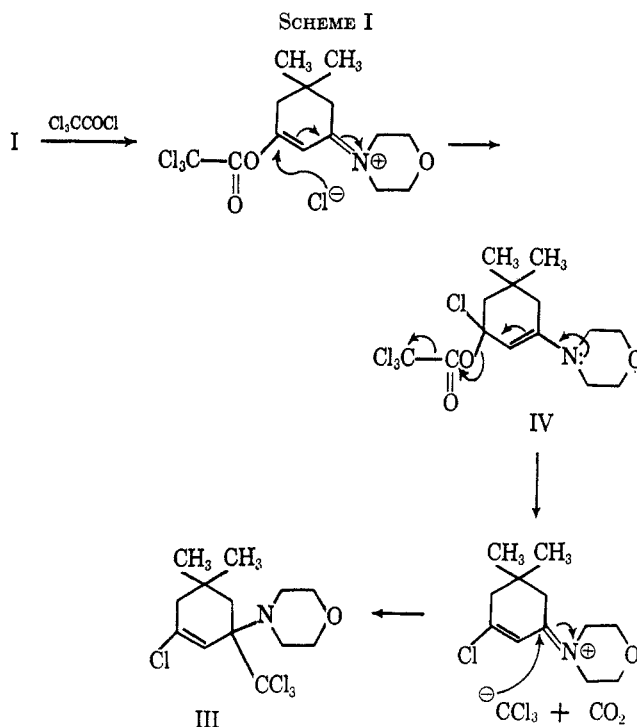

compound showed only end absorption in the ultraviolet so that the chromophores present cannot be in conjugation. The nuclear magnetic resonance (nmr) spectrum showed the presence of one vinyl hydrogen, and the presence of a carbon–carbon double bond was confirmed by a band at 6.10 μ in the infrared spectrum. On the basis of this evidence structure III may be assigned to the compound. The formation of III could proceed by the series of reactions I → IV → III (Scheme I). Initial O-acylation is followed by addition of chloride ion to give the intermediate IV which can collapse by loss of trichloroacetate ion to the chloroeniminium cation, which is precipitated in part as II (X = Cl). Under the reaction conditions, the trichloroacetate anion undergoes decarboxylation to the trichloromethyl anion, which adds[1] to the chloroeniminium cation to produce the observed product III. Further evidence for structure III was provided by degradation. Heating III with aqueous acetone or ethanol effected its conversion to an oil, the morpholide V. The nmr spectrum of
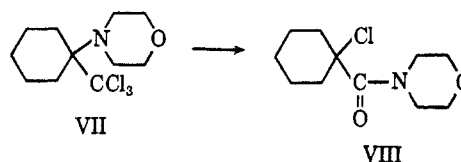

SCHEME I

V showed the presence of two vinyl protons at τ 4.10 and 4.30. Bands at 6.05 and 6.12 μ in the carbonyl region of the infrared spectrum may be assigned to amide carbonyl and carbon–carbon double bonds, respectively. The presence of a cross-conjugated diene acid chromophore was confirmed by the ultraviolet absorption at 279 mμ. The morpholide V formed a crystalline perchlorate, which had the correct elemental analysis and spectral data compatible with structure VI.[3]

The formation of V from III must have taken place by a mechanism similar to that involved in the rearrangement of the trichloromethyl derivative VII to

(1) Part VII: G. H. Alt and A. J. Speziale, *J. Org. Chem.*, **31**, 1340 (1966).

(2) G. H. Alt and A. J. Speziale, *ibid.*, **29**, 794 (1964).

(3) See G. H. Alt and A. J. Speziale, *ibid.*, **30**, 1407 (1965), and references there cited for the site of protonation of amides.

the α-chloroamide VIII.[1] In the case of III this must involve conversion to the aziridinium salt IX (X = Cl) (Scheme II) which can easily undergo ring opening to the intermediate X (X = Cl) in the manner demonstrated by Leonard and Jann.[4] Further hydrolysis to XI (X = Cl) followed by dehydrohalogenation over alumina would then give V. Although doubts have been expressed about the existance of aziridinium salts such as IX,[5] we were able to isolate IX (X = ClO₄) by treatment of III with an ethanolic solution of silver perchlorate.

SCHEME II
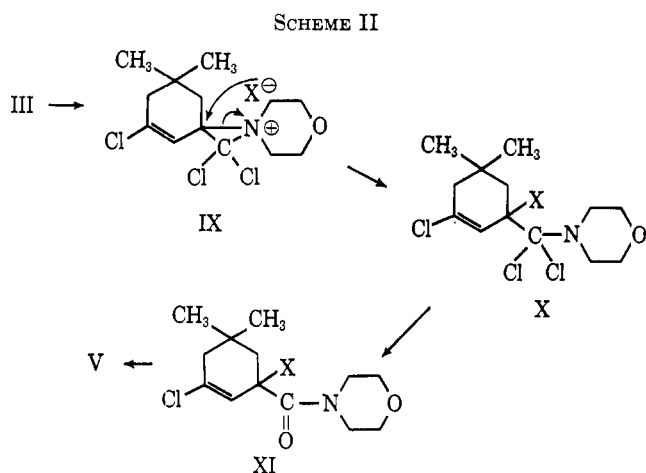
Vigorous basic hydrolysis of III led directly to the diene acid XII. The nmr spectrum of XII showed two vinyl protons at τ 3.0 and 4.12 as well as a broad multiplet centered at τ 1.92 due to the acidic proton. The infrared spectrum showed bands at 5.93 and 6.12 μ (C=O and C=C, respectively). Evidence for the linear conjugation of the chromophores in XII was provided by the ultraviolet absorption at 295 mμ. The known cross conjugated diene ester XIII (R = CH₃)[6] has ultraviolet absorption at 278 mμ.
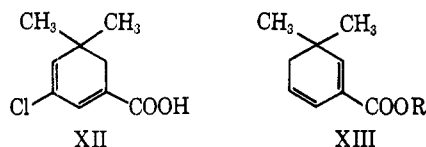
It was found that derivatives of XIII (R = CH₃ or H) could not be isomerized by treatment with strong base under conditions at least as vigorous as those used for the hydrolysis of III to XII. Hence it follows that V cannot be an intermediate in the basic hydrolysis of III, and that the basic and essentially neutral hydrolyses of III take place by different mechanisms.

It must be assumed that under basic conditions the trichloromethyl group of III is hydrolyzed to an intermediate XIV which suffers attack at one of the
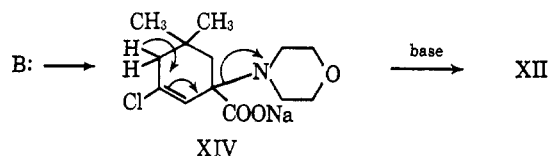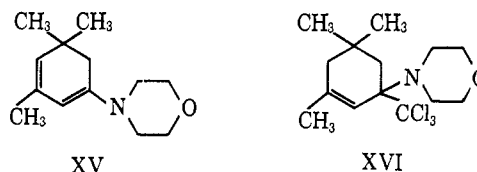
(4) N. J. Leonard and K. Jann, J. Am. Chem. Soc., 84, 4806 (1962).

(5) A. Lukasiewicz, Tetrahedron, 20, 1113 (1964); see, however, ref 4.

(6) G. A. Berchtold, J. Ciabattoni, and A. A. Tunick, J. Org. Chem., 30, 3679 (1965). Thanks are due to Professor G. A. Berchtold for making his manuscript available to us prior to publication.

protons at C-4 with subsequent loss of morpholine to give the linearly conjugated diene acid XII.

Preferential attack at C-4 could be due to a lesser degree of steric hindrance at this position, to the somewhat greater acidity of the allylic protons, or to a combination of both effects.

Attempts were made to prepare III by the reaction of II (X = ClO₄) with sodium trichloroacetate. Although the formation of II (X = Cl₃CCOO) must have taken place as evidenced by the isolation of sodium perchlorate, further reaction did not occur as carbon dioxide evolution was not observed and II (X = ClO₄) was recovered from the reaction mixture by the addition of perchloric acid. The only neutral product isolated was identified as 3-chloro-5,5-dimethylcyclohex-2-en-1-one the known hydrolysis product of II.[2]

To demonstrate the generality of the reaction of trichloroacetate with eniminium salts, the dienamine XV[7] was treated with 1 mole of trichloroacetic acid in refluxing benzene. A vigorous reaction with evolution of carbon dioxide took place. The product was an unstable benzene-soluble oil showing one vinyl hydrogen at τ 4.45 in the nmr spectrum. The presence of a carbon–carbon double bond was confirmed by a band at 6.05 μ in the infrared spectrum. The absence of con-

jugated chromophores was shown by only end absorption in the ultraviolet spectrum. This evidence and its properties, which were similar to those of III, led us to assign structure XVI to this compound. Vigorous basic hydrolysis of XVI afforded a diene acid XVII. The nmr spectrum showed two vinyl protons at τ 3.00 and 4.42 as well as a complex multiplet at τ −1.11 due to acidic proton. The infrared spectrum showed a carbonyl band at 5.98 μ as well as carbon–carbon double bond absorption at 6.10 μ. The ultraviolet absorption at 296 mμ confirmed the presence of a linearly conjugated chromophore.
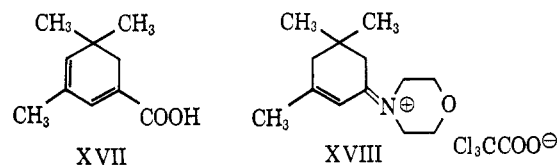
The formation of XVI must have taken place by protonation of XV at C-4 to give the eniminium salt XVIII[8] which can then react by decarboxylation and addition of trichloromethyl anion to give XVI by a scheme similar to that outlined for the conversion of II (X = Cl₃CCOO) to III.

An attempt was made to prepare a cross-conjugated acid derivative in this series (corresponding to V). Hydrolysis of XVI under mild conditions led to a mixture of acids with ultraviolet absorption at 265 and 296 mμ. The latter is probably due to XVII; however,

(7) G. Opitz and W. Merz, Ann., 652, 139 (1962).

(8) The site of protonation in dienamines such as XV is well established. See ref 7.

the absorption at 265 mμ is more likely to be due to the diene acid formed by abstraction of a proton from the methyl group at C-3 rather than to the cross-conjugated diene acid.

Experimental Section[9]

N-(3-Chloro-5,5-dimethylcyclohex-2-en-1-ylidene)morpholinium Chloride (II, X = Cl).—To a solution of the enamino ketone I[2] (5.23 g, 0.025 mole) in carbon tetrachloride (70 ml) was added trichloroacetyl chloride (4.7 g, 0.0255 mole) in carbon tetrachloride over a period of 0.5 hr. The reaction mixture was heated under reflux for 3 hr, during which time a solid was precipitated. The reaction mixture was cooled, and the solid (2.0 g, 30%) was filtered. The solid was washed with benzene, dried in a vacuum dessicator to give pure II (X = Cl): mp 200–205° dec.

Evaporation of the filtrate gave 7.5 g of a colorless oil. In a similar experiment the off gases were passed through barium hydroxide solution. Filtration gave 2.5 g (0.13 mole) of barium carbonate.

N-1-(1-Trichloromethyl-3-chloro-5,5-dimethylcyclohex-2-enyl)-morpholine.—Careful recrystallization of the colorless oil (above) from aqueous acetone gave III: mp 96–98° (3.5 g, 41%).

Anal. Calcd for $C_{13}H_{19}Cl_4NO$: C, 45.24; H, 5.55; Cl, 41.10; N, 4.06; mol wt, 345.12. Found: C, 45.20; H, 5.60; Cl, 41.33; N, 3.90; mol wt, 353.

Hydrolysis of III. A.—Compound III (3 g) in aqueous ethanol was boiled for several hours. The solvents were removed *in vacuo* and the residue taken up in benzene and chromatographed over neutral alumina. Elution with benzene and benzene ether mixtures gave approximately 1.5 g of colorless oil (V), λ_{max}^{EtOH} 279 mμ (ϵ 6000), showing two vinyl protons (τ 4.10 and 4.30) in the nmr and two bands in the carbonyl region of the infrared at at 6.05 and 6.12 μ.

The compound gave a crystalline perchlorate (VI) on treatment of its ethanol solution with 70% perchloric acid: mp 217–220°; λ_{max}^{EtOH} 280 mμ (ϵ 5800).

Anal. Calcd for $C_{13}H_{19}Cl_2NO_6$: C, 43.83; H, 5.38; Cl, 19.91; N, 3.93. Found: C, 43.76; H, 5.03; Cl, 20.11; N, 3.90.

B.—Compound III (3 g) in aqueous ethanol was treated with 20 ml of 10% NaOH and heated under reflux for 8 hr. The reaction mixture was cooled and extracted with chloroform to remove any basic and neutral materials. The aqueous layer was acidified and extracted with chloroform. The extracts were dried with magnesium sulphate and evaporated *in vacuo* to give approximately 1 g (XII): mp 130–132°; λ_{max}^{EtOH} 295 mμ (ϵ 5800). Infrared showed a carbonyl band at 5.93 μ and a carbon–carbon double bond at 6.12 μ. Nmr spectrum showed two vinyl protons at τ 3.00 and 4.12 as well as a broad multiplet at τ 1.92 due to the acidic proton.

Anal. Calcd for $C_9H_{11}ClO_2$: C, 57.91; H, 5.94; Cl, 19.00. Found: C, 58.10; H, 5.85; Cl, 19.17.

Aziridinium Salt IX (X = ClO₄).—Compound III (1.06 g, 0.031 mole) in acetone (20 ml) was treated with a solution of

silver perchlorate (0.635 g, 0.031 mole) in ethanol (10 ml) at room temperature for 30 min. The precipitated silver chloride (0.43 g, 97%) was filtered and the solvents were evaporated to give a crystalline hygroscopic salt. Recrystallization of the salt from ethanol gave material of mp 138–145°.

Anal. Calcd for $C_{13}H_{19}Cl_4NO_5$: C, 37.98; H, 4.66; N, 3.41; Cl, 34.50. Found: C, 37.91; H, 4.53; N, 3.65; Cl, 35.32.

1-Morpholino-3,5,5-trimethylcyclohexa-1,3-diene (XV). Prepared by the Method of Opitz and Merz.[7]—Isophoron (69.0 g, 0.5 mole), morpholine (50.0 g, 0.6 mole), and p-toluenesulphonic acid (0.1 g) in 200 ml of toluene were heated under a Dean-Stark trap until no more water separated. After removal of the toluene, the residue was fractionated *in vacuo*. The dienamine XV had bp 78.5° (0.3 mm), n^{23}D 1.5309, and λ_{max}^{hexane} 274 mμ (ϵ 12,000).

Anal. Calcd for $C_{13}H_{21}NO$. C, 75.31; H, 10.21; N, 6.76. Found: C, 75.48; H, 10.37; N, 6.77.

Opitz and Merz[7] reported bp 112–114° (0.1 mm), n^{21}D 1.5275, and λ_{max}^{hexane} 277 mμ (ϵ 12,800), but no elemental analysis.

The dienamine XV afforded a crystalline perchlorate XVIII (X = ClO₄) upon treatment of an ethanolic solution with 70% perchloric acid. Recrystallized from ethanol it had mp 215–217°, λ_{max}^{EtOH} 278 mμ (ϵ 19,700).

Anal. Calcd for $C_{13}H_{22}ClNO_5$: C, 50.73; H, 7.21; N, 4.55; Cl, 11.52. Found: C, 50.92; H, 7.25; N, 4.47; C., 11.75.

Reaction of Dienamine XV with Trichloroacetic Acid.—The dienamine XII (6.2 g, 0.03 mole) in benzene (70 ml) at 70° was treated with a solution of trichloroacetic acid (4.9 g, 0.03 mole) in benzene (30 ml) dropwise over 30 mins so as to maintain a temperature of 70°. Carbon dioxide was evolved during the addition and the reaction mixture was refluxed for a further hour when this was complete. The solvent was then removed *in vacuo* giving XVI, 9.5 g (100% wt yield), as an oil having no ultraviolet and showing a C=C bond at 6.05 μ in the infrared spectrum. The nmr showed one vinyl proton at τ 4.45.

Hydrolysis of XVI.—The above oil (1 g) in 30 ml of ethanol was treated with 10 ml of 10% sodium hydroxide solution and heated under reflux overnight. After evaporating the ethanol, the mixture was diluted with water and extracted with chloroform to remove any basic and neutral material. The aqueous layer was acidified with concentrated hydrochloric acid and the precipitated solid was extracted with chloroform. Evaporation of the chloroform extract afforded 350 mg of solid: mp 90–95°. Recrystallization from aqueous methanol afforded analytically pure XVII: mp 102–104°; λ_{max}^{EtOH} 296 mμ (ϵ 6700).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.08; H, 8.43.

The infrared showed a carbonyl band at 5.98 μ and a carbon–carbon double bond at 6.10 μ. The nmr spectrum showed two vinyl protons at τ 3.00 and 4.42, as well as a broad multiplet at τ −1.11 due to the acidic proton.

Reaction of Chloroeniminium Salt II (X = ClO₄) with Sodium Trichloroacetate.—The chloroeniminium salt II (X = ClO₄)[2] (3.3 g, 0.01 mole) and sodium trichloroacetate (1.9 g, 0.01 mole) in ethylene dichloride (50 ml) were heated under reflux for 18 hr. Some solid which came out was filtered and appeared to be sodium perchlorate. The filtrate was evaporated and the residue was triturated with benzene. There was some benzene insoluble-salt which on treatment with perchloric acid gave II (X = ClO₄) (1 g). Evaporation of the benzene filtrate gave a yellow oil. Infrared spectra showed that it was not compound III but probably impure (carbonyl band at 5.95 μ, double bond at 6.20 μ). 3-Chloro-5,5-dimethylcyclohex-2-en-1-one was formed by hydrolysis of II (see ref 2).

(9) Boiling points and melting points are uncorrected. Melting points were taken with a Mel-Temp capillary melting point apparatus. Ultraviolet spectra were taken with a Beckman DK2A spectrometer. Infrared spectra were taken with a Perkin-Elmer Infracord Model 137 in chloroform solution. Nuclear magnetic resonance spectra were taken with a Varian A-60 instrument in deuteriochloroform solution using tetramethylsilane as the internal standard.