This investigation has brought out the relative simplicity of the oxidation of cyclohexane to cyclohexanone at 100°, and the variety of the subsequent reactions of cyclohexanone at 80°. It has also indicated what reactions should become important in the presence of metals and at higher temperatures. Therefore, it should provide an improved point of departure for study of oxidations of cyclohexane at higher temperatures and for other aliphatic hydrocarbons at all temperatures.

Registry No.—Cyclohexane, 110-82-7; cyclohexanol, 108-93-0; cyclohexanone, 108-94-1; cyclohexyl hydroperoxide, 766-07-4; cyclohexyl acetate, 622-45-7; tricyclohexyl borate, 2467-16-5; cyclohexyl-*tert*-butyl peroxide, 15619-54-2; *tert*-butylperoxy isopropyl carbonate, 2372-21-6.

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Cycloaddition of an Enamine to an Activated Cyclopropane

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The cycloaddition of *N*-pyrrolidinylcyclohexene (**5**) to 1,1-dicyano-2,2-dimethylcyclopropane (**9**) proceeded by an SN2 route (across the 1–3 bond) rather than by way of a zwitterionic intermediate (across the 1–2 bond). The adduct (**12**) rearranged upon partial hydrolysis to a spiro structure (**13**) which was further hydrolyzed to 2-oxo-4,4-dimethylcyclopentanepentanoic acid (**14**). This keto acid was synthesized.

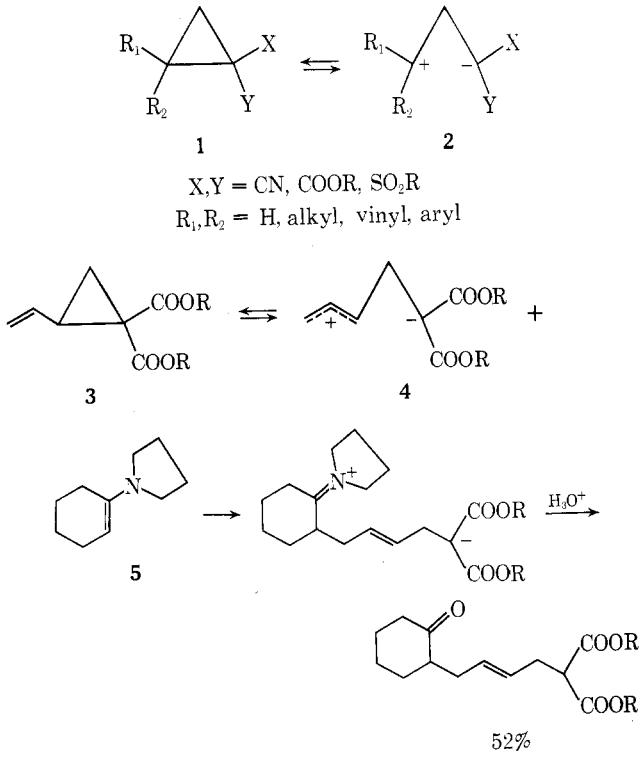
Considerable data now support the existence of zwitterionic intermediates (**2**) in the ring opening of suitably activated cyclopropanes (**1**). For instance, Cram[1] has demonstrated that nucleophiles, electrophiles, and polar solvents strongly increase the rate of racemization of such systems. In addition, both Cram[1] and Danishefsky[2] have shown that such systems suffer nucleophilic ring opening almost exclusively at the more highly substituted carbon (presumably by way of the more stable carbonium ion).

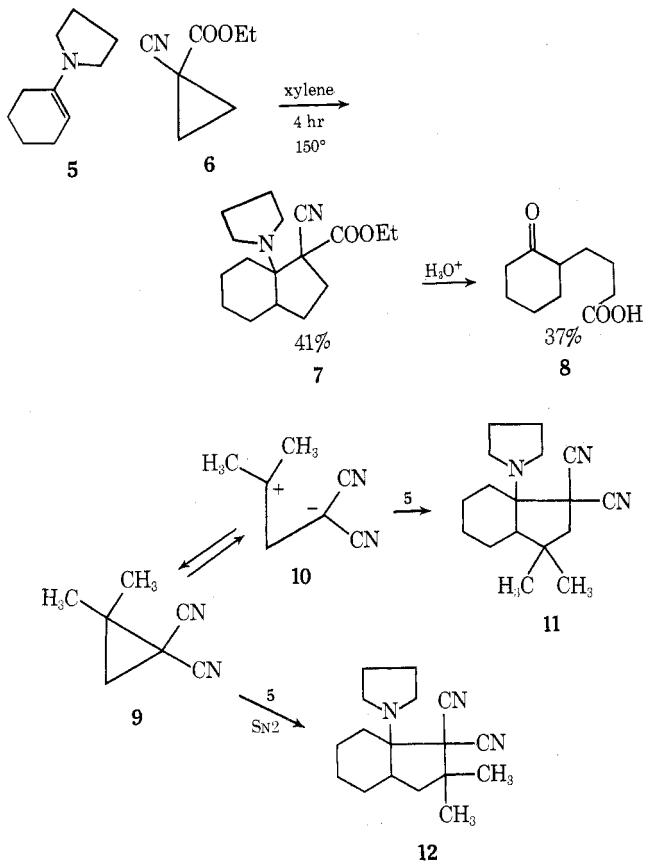
On the other hand, both authors have proven that nucleophilic attack occurs with *complete inversion*,[1,2a,b] leading to the conclusions that nucleophilic attack must be considerably faster than bond rotation and that racemization, at least in the presence of nucleophiles or polar solvents, probably involves a measure of nucleophilic participation as well (and also, perhaps, electrophilic aid).

Conversely, enamines attack **3** exclusively at the terminal carbon.[3] Danishefsky has suggested that the reaction involves zwitterionic intermediate **4**.

Where would an enamine attack cyclopropane **1**? Cycloaddition of enamine **5** to unalkylated cyclopropane **6** gave adduct **7** as shown by hydrolysis to keto acid **8**.[4]

We have examined the reaction of enamine **5** with 1,1-dicyano-2,2-dimethylcyclopropane (**9**).[5] A zwitterionic intermediate (**10**) would give **11**; SN2 attack would give **12**. In the event, **12** was produced in 47% yield. The results are summarized in Chart I.





Discussion

Adduct **12** showed a nitrile band at 2232 cm^{-1} in the ir; the NMR spectrum was characterized by two singlets at δ 1.38 and 1.45, attributable to the two methyl groups; the pyrrolidine group appeared in its characteristic form of an unresolved A_2B_2 multiplet. These data, and the lack of any ultraviolet absorption above 210 nm,[6] led us to formulate the cycloadduct as either **11** or **12**.

Recrystallization of **12** from hot 95% ethanol gave a crystalline product the formula of which denotes replacement of the pyrrolidinyl group by hydroxyl. Comparison of spectral bands with those of enaminonitrile **18**,[7] the presence of an additional ir band at 1701 cm^{-1}, two exchangeable protons (NMR), and the lack of a methine carbon (^{13}C NMR) convinced us that this hydrolysis product was **13** (position of the methyls still ambiguous). The hydrolysis and rearrangement of **12** to **13** is rationalized in Chart II.

Apparently the increased solvent polarity due to the presence of 5% water (**12** may be recrystallized without rearrangement from absolute alcohol) is sufficient to cause reopening of **12** to **19**.

Acid hydrolysis of both **12** and **13** gave keto acid **14** (which was synthesized as shown in Chart I), thereby fixing the position of the methyls as in **12** and not **11** (assuming that the structure shown for keto ester **16** is correct).

These results lead us to believe that terminal attack of enamine **5** on vinylcyclopropane **3** occurs by an S_N2' mechanism (in xylene). On the other hand, ring attack by pyrrolidine and other nucleophiles in *protic* solvents can be rationalized more readily in terms of solvent-, nucleophile-,

Chart I

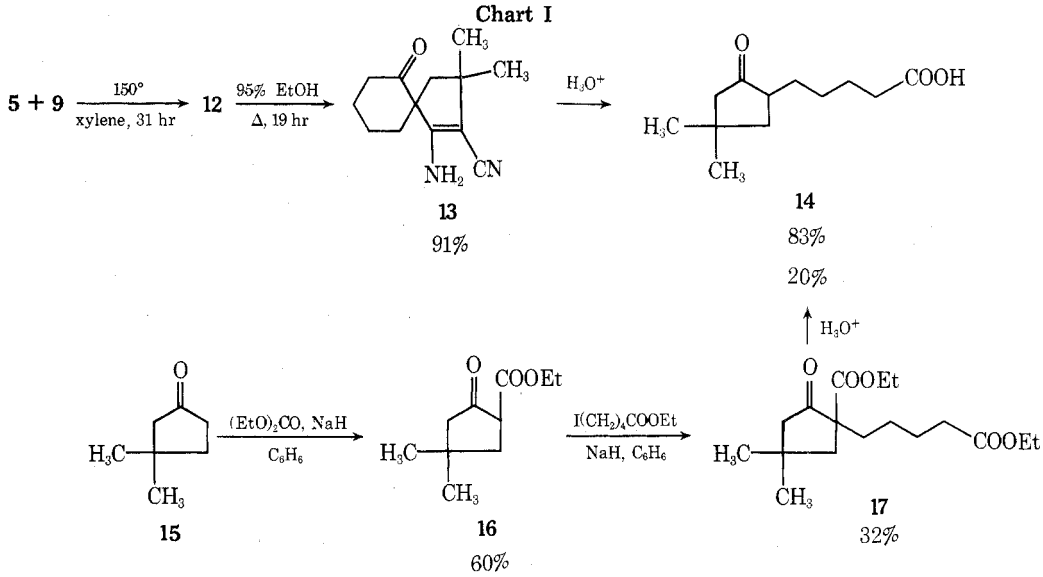
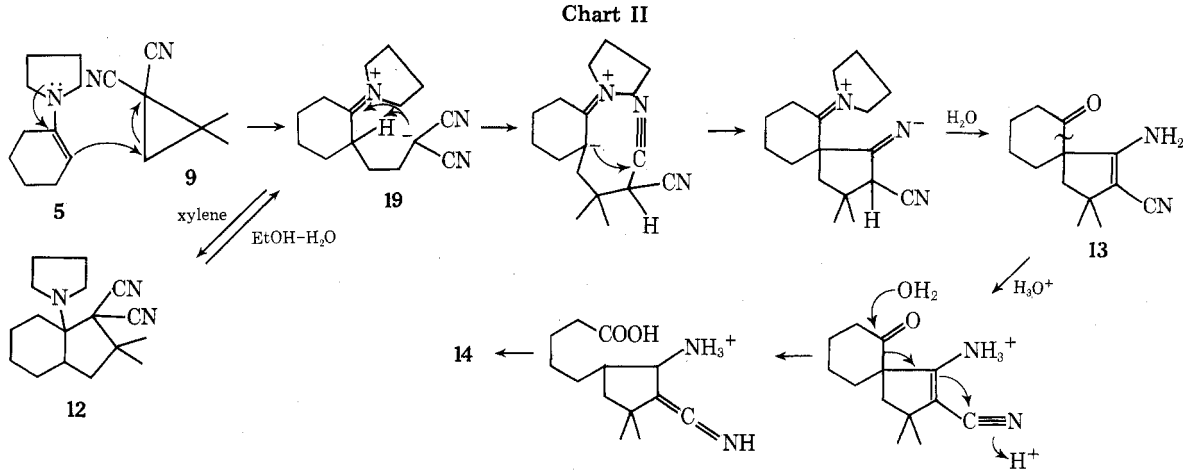


Chart II



or electrophile- (proton) assisted formation of a zwitterionic intermediate.

Experimental Section

Melting points (uncorrected) were determined on a Mel-Temp apparatus. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. GLC results were obtained on a Varian Aerograph A90-P3 thermal conductivity instrument. Infrared spectra were taken on a Perkin-Elmer 237-B or Beckman IR-20 grating spectrophotometer; ultraviolet spectra on a Cary 14; ^1H NMR spectra with a Varian A-60A or EM-360; ^{13}C NMR spectra with a Varian CFT-20 (Fourier transform); and mass spectra with a Varian MAT CH-7 (at 70 eV).

1,1-Dicyano-2,2-dimethyl-7a-(*N*-pyrrolidinyl)perhydroindene (Adduct 12). A solution of 35.0 g (0.292 mol) of 1,1-dicyano-2,2-dimethylcyclopropane (**9**)[5] and 67.0 g (0.445 mol) of 1-*N*-pyrrolidinylcyclohexene (**5**) (freshly distilled) in 300 ml of dry xylene (distilled from calcium hydride) was refluxed for 31 hr under an atmosphere of nitrogen. The disappearance of the cyclopropane was followed by GLC.[8] The mixture was then fractionated, giving 60.2 g (76%) of viscous yellow oil, bp 118–152° (0.05–0.07 mm), which partially solidified. This was recrystallized from warm (<45°) 95% ethanol, giving 36.0 g (45.6%) of white prisms, mp 78–79°, of adduct **12**.[9] The ir ($CHCl_3$) of this material exhibited a nitrile band at 2232 cm^{-1}; the NMR ($CDCl_3$) showed two methyl singlets at δ 1.38 and 1.45 and the typically unresolved pyrrolidinyl A_2B_2 multiplet centered at δ 3.10; the MS gave a parent ion at *m/e* 271. Adduct **12** showed no uv absorption above 220 nm (EtOH).

In addition, 2.80 g (4.4%) of enaminonitrile **13**, mp 164–165°, was obtained from the mother liquor.

1-Amino-2-cyano-3,3-dimethylspiro[4.5]decen-1-one-6 (13). A solution of 1.00 g of adduct **12** in 20 ml of 95% ethanol was refluxed for 19 hr. Concentration under reduced pressure left 710 mg (91%) of **13**, as shown by mixture melting point and ir. Recrystallization of crude **13** from 95% ethanol gave white prisms of **13**, mp 167–168.5°.[9] The enaminonitrile showed an ultraviolet absorption maximum (95% EtOH) at λ 264 nm (ϵ 11900); ir ($CHCl_3$) 3472, 3367, 2188, 1701, 1645, 1597 cm^{-1}; ^1H NMR (acetone-d_6) δ 0.97, s, 3 H; 1.13, s, 3 H; 6.08, s, 2 H (D_2O labile); ^{13}C NMR[10] ($CDCl_3$) (downfield from Me_4Si) CH_3 20.6, 30.1; CH_2 21.6, 27.2, 38.3, 39.6, 48.4; CH, . . .; C 42.2, 63.3, 88.2, 117.4, 160.4, 219.4 ppm.

2-Oxo-4,4-dimethylcyclopentanepentanoic Acid (14). A mixture of 1.00 g (4.58 mmol) of enaminonitrile **13**, 25 ml of 85% phosphoric acid, and 25 ml of glacial acetic acid was refluxed (150°) for 71 hr, then poured onto 100 g of crushed ice. This mixture was extracted with four portions of ether which were combined, dried over magnesium sulfate, and concentrated under reduced pressure, leaving 1.60 g of brown oil. The oil was dissolved in benzene, washed with water, and again dried and concentrated, affording 801 mg (83%) of yellowish prisms, mp 80–83°. Recrystallization of the crude keto acid from benzene–hexane or ether gave white prisms of **14**, mp 84–85°.[9] The ir ($CHCl_3$) of **14** showed bands at 1730, 1712,[11] 2500–3500 cm^{-1} (br); NMR ($CDCl_3$) δ 1.06, s, 3 H; 1.18, s, 3 H; 11.05, s, 1 H (D_2O labile); MS *m/e* 112 > 42 > 56 > 57 > 97 > 69 > 83 > 40 > 46 > 67 > 54 > 70 > 81 > 68, parent ion *m/e* 212 (7.4% of *m/e* 112). A sample of this keto acid was proved identical with the product of acid hydrolysis of keto diester **17** (Chart I) by mixture melting point and comparison of ir, NMR, and mass spectra.

Keto acid **14** was also isolated in 14% yield from a similar phosphoric–acetic acid hydrolysis of adduct **12** (8 days reflux).

Ethyl 2-Oxo-4,4-dimethylcyclopentanecarboxylate (16).[12] To a refluxing suspension of 5.98 g (0.142 mol) of a 57% dispersion of sodium hydride in mineral oil in 70 ml of dry benzene and 11.81 g (0.10 mol) of freshly distilled diethylcarbonate was added, with stirring under a nitrogen atmosphere during 4 hr, a solution of 5.61 g (0.050 mol) of 3,3-dimethylcyclopentanone.[13] The reaction mixture was refluxed for an additional 0.5 hr, then cooled and cautiously acidified with a solution of 10 ml of acetic acid in 10 ml of benzene, followed by 35 ml of water. The aqueous layer was extracted with three portions of benzene. The combined organic layers were washed with several small portions of water, then dried over magnesium sulfate and concentrated by distillation. The concentrate was fractionated, giving 5.80 g (63%) of keto ester **16**, bp 99° (13 mm)–122° (16 mm) (>95% pure by GLC estimate[14]).

A sample of this material which was purified by GLC[14,9] showed ir (CCl_4) 1762, 1731, 1663, 1620 cm^{-1};[15] NMR (CCl_4) δ 1.06, s; 1.23, s; 1.27, t (J = 7 Hz) (combined 9 H); 2.10, s; 1.97–2.28, m (combined 4 H); 3.21, t, 1 H (J = 10 Hz; D_2O labile); 4.11, q, 2 H (J = 7.5 Hz); MS *m/e* 29 > 44 > 42 > 55 > 33 > 101 > 56 > 73 > 123 > 156 > 32 > 69 > 83 >39 > 184 > 169; parent ion *m/e* 184 (6.2% of *m/e* 29). Keto ester **16** gave a positive ferric chloride test, but no enolic H showed in the NMR.

Ethyl 1-Carbethoxy-2-oxo-4,4-dimethylcyclopentanepentanoate (17). To a suspension of 1.10 g (0.026 mol) of a 57% dispersion of sodium hydride in mineral oil in 25 ml of dry benzene was added, with stirring under nitrogen during 15 min, a solution of 3.68 g (0.020 mol) of keto ester **16** in 10 ml of dry benzene. Stirring was continued until hydrogen evolution ceased (5 min). To the white suspension of enolate salt was then added, during 10 min, a solution of 5.12 g (0.020 mol) of ethyl 5-iodopentanoate[16] in 15 ml of dry benzene. The resulting mixture was refluxed for 18.5 hr, then cooled and quenched with a solution of 5 ml of acetic acid in 20 ml of benzene, followed by 15 ml of water. The aqueous layer was extracted with two portions of benzene; the combined organic layers were washed with saturated aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated by distillation. The concentrate was fractionated, affording 2.00 g (32%) of keto diester **17**, bp 139° (0.20 mm)–145° (0.28 mm) (>90% pure by GLC estimate[14]). A sample of **17** purified by GLC[9,14] showed ir (CCl_4) 1730, 1755 cm^{-1} (sh);[17] NMR (CCl_4) δ 1.11, s; 1.217, t (J = 7 Hz); 1.242, t (J = 7 Hz) (the upfield legs of both triplets are hidden under the *gem*-dimethyl singlet); 4.00 q (J = 7 Hz); 4.04, q (J = 7 Hz) (combined 4 H); MS *m/e* 184 > 41 > 55 > 81 > 56 > 43 > 109 > 83 > 67 > 39 > 138 = 95 = 42 > 137 = 45 > 53 > 69 = 77 = 79 > 123 > 193 (21% of *m/e* 184), parent ion *m/e* 312 (4% of *m/e* 184). Keto diester **17** gave a negative ferric chloride test.

Keto diester **17** (313 mg, 1.0 mmol) was hydrolyzed by refluxing with 18 ml of 20% hydrochloric acid for 27 hr. The mixture was then concentrated to dryness under reduced pressure. The residual oil was triturated with saturated aqueous sodium bicarbonate which was then extracted with ether and finally acidified with concentrated hydrochloric acid. The acid mixture was extracted with three portions of ether which were combined, dried over magnesium sulfate, and evaporated, leaving 104 mg of colorless oil which slowly crystallized. Recrystallization of this (benzene–hexane) gave 42 mg of keto acid **14**, mp 82–83.5°, which was identical with the keto acid isolated by hydrolysis of both adduct **12** and enaminonitrile **13** (mixture melting point, ir, MS, NMR).

1-Methylcyclohex-3-enecarboxaldehyde.[13] A practical improvement upon Pines' Diels–Alder procedure (autoclave, 150°) was obtained by the use of stannic chloride as a catalyst.[18]

To a solution of 77.88 g (1.00 mol) of methacrolein (90%, technical grade) in 500 ml of benzene at 3° was added a solution of 36.11 g (0.139 mol) of anhydrous stannic chloride in 50 ml of benzene. After the initial mild exotherm (the temperature rose to 18°), 1,3-butadiene was bubbled in subsurface with good stirring. The temperature was maintained at 20–30° with intermittent ice cooling (continuously at first) during 3 hr (cooling was rarely required after the first 1.5 hr). The reaction mixture (total volume 1 l.) was then poured into a mixture of 100 g of ice and 200 ml of water and shaken vigorously (much effervescence of dissolved butadiene). The organic layer was washed with dilute hydrochloric acid, 5% aqueous sodium chloride, and saturated aqueous sodium bicarbonate, then dried over magnesium sulfate and concentrated by distillation. The concentrate was fractionated (much foaming), affording 96.1 g (77%) of aldehyde: bp 74° (27 mm) (>99% pure by GLC estimate[19]); ir (CCl_4) 1732 cm^{-1} (no bands at 1600–1650 cm^{-1}); NMR (CCl_4) δ 1.03, s, 3 H; 1.33–2.65, m, 6 H; 5.57, s (crude triplet when expanded), 2 H; 9.30, s, 1 H; MS *m/e* 43 > 67 = 95 > 39 > 81 > 41 > 55 > 80 = 79 > 77 > 78, 91 = 109, parent ion *m/e* 124 (49% of *m/e* 43).

Semicarbazone: mp 173.5–174° (lit.[13] mp 170–172°).

The use of freshly distilled methacrolein or rigorously anhydrous conditions did not improve the yield of aldehyde. The use of anhydrous aluminum chloride as catalyst lowered the yield to 47%.

Acknowledgment. The authors gratefully thank the NIH for financial support of this project (NIH ROIAM11226).

Registry No.—**5**, 1125-99-1; **9**, 6904-09-2; **12**, 57091-01-7; **13**, 57091-02-8; **14**, 57091-03-9; **15**, 20500-49-6; **16**, 22773-08-6; **17**, 57091-04-0; diethyl carbonate, 105-58-8; 1-methylcyclohex-3-enecarboxaldehyde, 931-96-4.

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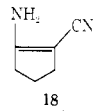

18

2189, 1645, 1605 cm^{-1}; uv λ 263 (ϵ 13000). **13**: ir ($CHCl_3$) 3472, 3367, 2188, 1645, 1597 cm^{-1}; uv λ 264 (ϵ 11900).
(8) A 10 ft × 0.38 in. column packed with Chromosorb coated with 20% by weight of SE-30 silicone gum was used.
(9) A satisfactory elemental analysis was obtained for this material.
(10) We are indebted to W. C. Jankowski of Varian for this spectrum.
(11) W. Herz, *J. Org. Chem.*, **22**, 630 (1957): 2-oxocyclopentanepentanoic acid ir 1730, 1710 cm^{-1}.
(12) (a) R. N. Chakravarti, *J. Chem. Soc.*, 1028 (1947); (b) S. Kagawa et al., *Tetrahedron Lett.*, 3913 (1969); neither reference reports physical data for **16**.
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(14) A 6 ft × 0.25 in. column packed with Chromosorb P coated with 30% by weight of SE-30 silicone gum was used.
(15) N. J. Leonard, H. S. Gutowsky, W. J. Middleton, and E. M. Petersen, *J. Am. Chem. Soc.*, **74**, 4070 (1952): 2-carbethoxycyclopentanone ir 1756, 1725, 1660, 1618 cm^{-1}.
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(17) W. Herz, *J. Am. Chem. Soc.*, **78**, 1485 (1956): ethyl 1-carbethoxy-2-oxocyclopentanepentanoate ir 1735, 1755 cm^{-1} (sh).
(18) A modification of the procedure of W. Kreiser, W. Haumesser, and A. Thomas, *Helv. Chim. Acta*, **57**, 164 (1974).
(19) A 4 ft × 0.25 in. column packed with Chromosorb W coated with 20% by weight of DC 200 silicone oil was used.

Mechanistic Studies on the Photochemical Reactions of Isoxazoles[1]

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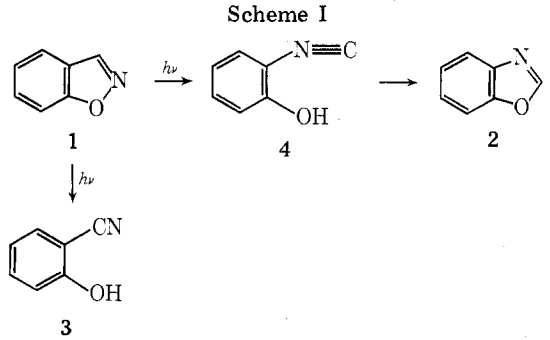
The mechanisms of the photochemical conversion of isoxazoles to oxazoles and ketoketenimines have been investigated. Isonitrile **14** was detected by an ir band at 2160 cm^{-1} in the photoconversion of **5** to **15** at −77°. Compound **14** was further identified by independent synthesis and by hydrolysis to formamide **17** in acid. Ir bands at 1690 and 1655 cm^{-1} are consistent with the hypothesis that azirine **13** is the precursor to isonitrile **14.** It is postulated that a vinyl nitrene is the immediate precursor to **13.** Photolysis of **10** at −77 or −196° resulted in the formation of an ir band at 2050 cm^{-1}. This band was assigned to ketoketenimine **23.** The structure of **23** was proved by independent synthesis and trapping with water. No intermediates in the photochemical conversion of **10** to **21** were detected by trapping or low-temperature ir studies. New syntheses of isoxazoles **5** and **10** were developed.

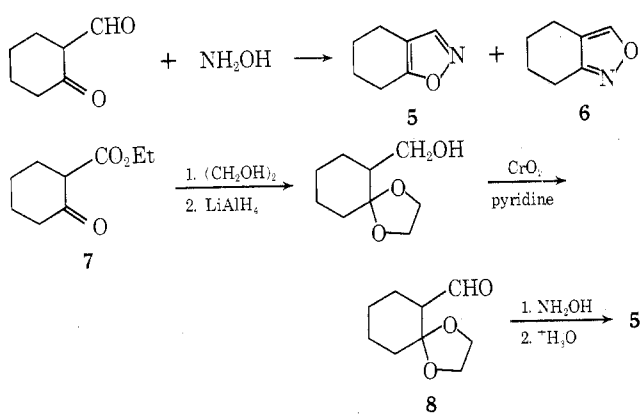
A study of the mechanisms of the photochemical rearrangement of indoxazene (**1**) to benzoxazole (**2**) and 2-cyanophenol (**3**) has been reported (Scheme I).[2] The isonitrile (**4**) was detected spectrally by trapping experiments and by independent synthesis. The present study was undertaken with the objective of learning more about the mechanism of the photochemical isomerization of isoxazoles to oxazoles.[3–5]

Scheme I



Results and Discussion

Synthesis of Isoxazoles. The reported synthesis of 4,5,6,7-tetrahydro-1,2-benzisoxazole (**5**) from 2-oxocyclohexanecarboxaldehyde was complicated by the formation of isomer **6,** which we were unable to separate from **5.**[6,7] A successful synthesis of pure **5** was devised starting from ethyl 2-oxocyclohexanecarboxylate (**7**) via aldehyde **8.**[8]



Attempted direct synthesis of 3-methyl-4,5,6,7-tetrahydro-1,2-benzisoxazole (**10**) from 2-acetylcyclohexanone (**9**) led to a 1:4 mixture of the desired isomer **10** and isomer **11,** respectively. A higher proportion (5:1) of **10** was obtained by preferential ketalization of the cyclohexanone carbonyl of **9** followed by its reaction with hydroxylamine and acid hydrolysis of the ketal. We succeeded in obtaining pure **10** starting from cyclohexanone and proceeding via 1-acetyl-2-chloro-1-cyclohexene.