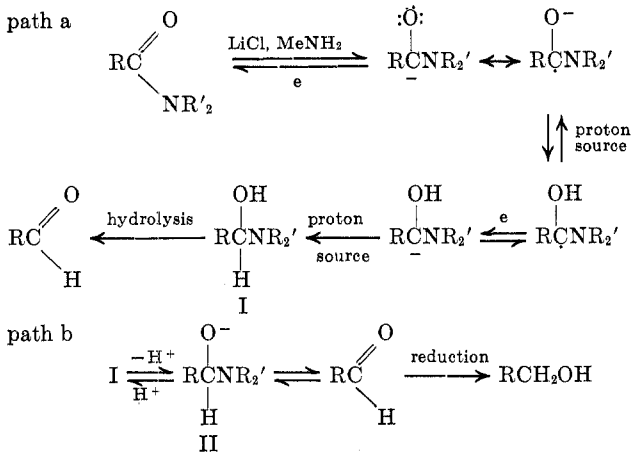
SCHEME I



would likely favor II because of the relative acid–base strengths involved. Hence the alcohol products observed would arise from II *via* path b as shown. It is necessary to assume that the aldehyde formed by path b undergoes rapid reduction to alcohol in the immediate vicinity of the cathode; otherwise it may well have sufficient opportunity to react with solvent to form the N-methylimine, which upon further reduction would yield amine.[6] The fact that amines were not obtained as reaction products excludes the formation of such N-methylimines, since we have shown that imines are converted into amines under the reaction conditions employed.

Electrolysis in the presence of a proton donor such as ethanol causes the reaction to proceed by path a, the equilibrium between I and II now favoring I. Since in the presence of ethanol the yields of alcohols were greatly reduced and amine products were not observed, one might conjecture that intermediate I effectively resists further reduction. Hydrolysis of I with aqueous acid yields the corresponding aldehyde.

To determine the effect of increased reaction times, a fiftyfold excess of current was passed through a solution of decanamide containing ethanol. It was found (entry 15, Table I) that decanol was the major product, with the yield of aldehyde being significantly decreased. This would be the predicted result if intermediates I and II were in equilibrium as depicted in Scheme I. Longer reaction times would increase the opportunity for intermediate II to follow path b, leading to aldehyde and ultimately alcohol.

Experimental Section

Preparation of Amides.—All amides were prepared by bubbling ammonia, methylamine, or dimethylamine through the corresponding carboxylic acids at reflux temperature followed by vacuum distillation of the product.

Electrolytic Reduction of Amides to Alcohols.—Primary, secondary, and tertiary amides were reduced to alcohols in an undivided electrolytic cell[5] consisting of a three-neck flask fitted with a Dry Ice condenser and two platinum electrodes. The flask was charged with lithium chloride (34 g, 0.8 mol), anhydrous monomethylamine (350–700 cc) and the amide (0.008–0.05 mol). A current of 2 A was passed through the solution, after which solvent was allowed to evaporate through a condenser maintained at −5°. The resulting residue was hydrolyzed with water (30–200 cc) and the aqueous solution was extracted with ether. The latter was dried with $MgSO_4$. Table I summarizes the results.

Electrolytic Reduction of Amides to Aldehydes.—Primary, secondary, and tertiary aliphatic amides were reduced to aliphatic aldehydes as described above except that the flask was charged with lithium chloride (17 g, 0.4 mol), anhydrous monomethylamine (300–600 cc), absolute ethanol (5 g, 0.1 mol), and the amide (0.005–0.05 mol). A current of 2 A was passed through the solution for *ca.* 2 hr (*ca.* 14,400 C). At the end of this time, solvent was allowed to evaporate through a condenser which was maintained at −5°. The resulting residue was hydrolyzed with water (20–30 cc) and the aqueous solution was extracted with ether. After removal of ether at room temperature under reduced pressure, the residue was acidified with 10% HCl at 0° and extracted with ether. Drying of the ether layer and removal of solvent at room temperature yielded products which were identified by their 2,4-dinitrophenylhydrazones, glpc, and ir. Table I summarizes the results.

Electrolytic Reduction of the N-Methylimine of Hexanal.—The reduction was carried out in a three-neck flask fitted with a Dry Ice condenser and two platinum electrodes. A current of 0.6 A was passed through a solution of anhydrous monomethylamine containing lithium chloride (4 g, 0.1 mol) and the N-methylimine of hexanal (1.1 g, 0.01 mol) for a period of 2 hr. The usual work-up gave 0.8 g of residue following hydrolysis with water (10 cc). Analysis by glpc showed the residue to consist of starting imine (56%) and N-hexylmethylamine (44%). The yield of amine was 32%.

Registry No.—$CH_3(CH_2)_4CONH_2$, 628-02-4; $CH_3(CH_2)_6CONH_2$, 629-01-6; $CH_3(CH_2)_8CONH_2$, 2319-29-1; $CH_3(CH_2)_{12}CONH_2$, 638-58-4; $CH_3(CH_2)_{14}CONH_2$, 629-54-9; $CH_3(CH_2)_{16}CONH_2$, 124-26-5; $CH_3(CH_2)_4CONHCH_3$, 3418-05-1; $CH_3(CH_2)_8CONHCH_3$, 23220-25-9; $CH_3(CH_2)_8CON(CH_3)_2$, 14433-76-2; $CH_3(CH_2)_{14}CON(CH_3)_2$, 3886-91-7.

Acknowledgment.—This research was sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under AFOSR Grant 822-67.

(6) R. A. Benkeser and S. Mels, *J. Org. Chem.*, **34**, 3970 (1969).

Reactions of α-Dichloromethylene Ketones[1a]

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β-Chlorovinyl ketones are readily prepared and their high reactivity has led to their use as intermediates in the synthesis of a variety of aliphatic, aromatic, and heterocyclic compounds.[2] Techniques for the preparation of β-β-dichlorovinyl ketones are rather limited and studies of their reactions have been restricted to acyclic analogs.[2-4] We recently described a convenient route to β,β-dichlorovinyl ketones involving the reaction of enamines and carbon tetrachloride[5] which makes available a variety of acyclic and cyclic derivatives. With the ready accessibility of the

(1) (a) Abstracted from part of the thesis submitted by R. V. K. in partial fulfillment of the requirements for the Ph.D. degree, Purdue University, August 1966; (b) David Ross Research Fellow, Purdue University, 1964–1966.

(2) A. Pohland and W. Benson, *Chem. Rev.*, **66**, 161 (1966).

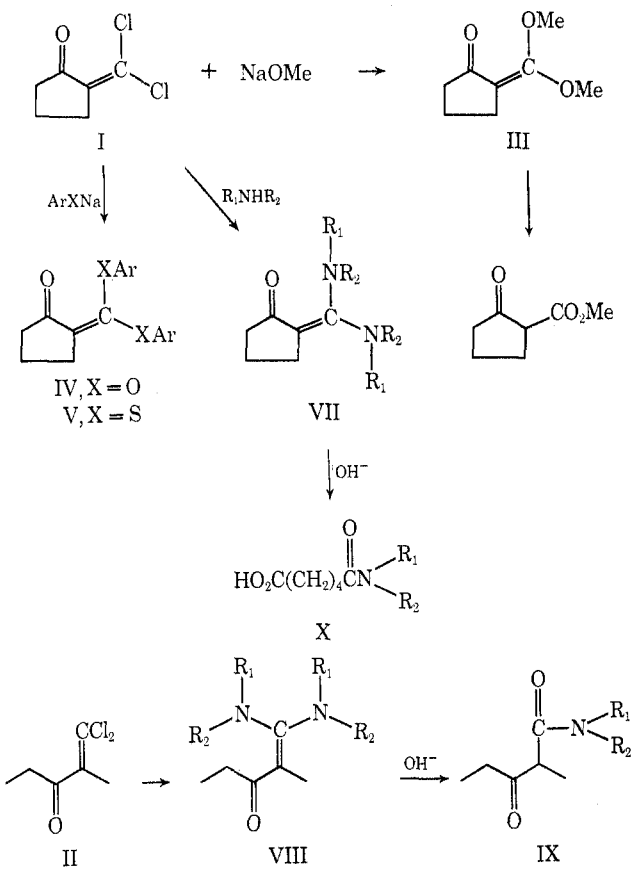
(3) S. Searles, R. A. Sanchez, R. L. Soulen, and D. G. Kundiger, *J. Org. Chem.*, **32**, 2655 (1967).

(4) R. L. Soulen, D. G. Kundiger, S. Searles, and R. A. Sanchez, *ibid.*, **32**, 2661 (1967).

(5) J. Wolinsky and D. Chan, *Chem. Commun.*, 567 (1966).

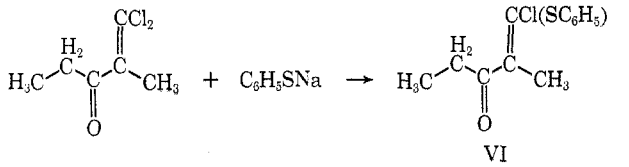
cyclic derivatives, it became of interest to examine their reactions, and, in particular, to compare their behavior with that of acyclic analogs. In this study we have focussed our attention on the reactions of nucleophiles with 2-dichloromethylenecyclopentanone (I) and 2-dichloromethylene-3-pentanone (II).

Reaction at the β-carbon atom with concomitant replacement of chlorine atoms occurs with alkoxides, thiolates, and primary and secondary amines. The addition of I to sodium methoxide in methanol gave a mixture of 2-dimethoxymethylenecyclopentanone (III) and 2-carbomethoxycyclopentanone. The dimethoxyvinyl ether III is easily hydrolyzed, even by atmospheric moisture, and was difficult to isolate in a high state of purity. On standing in contact with air it was converted into 2-carbomethoxycyclopentanone.



The reaction of I with sodium phenoxide and thiophenoxide gave IV and V in low yield. These aromatic derivatives were quite stable to atmospheric moisture.

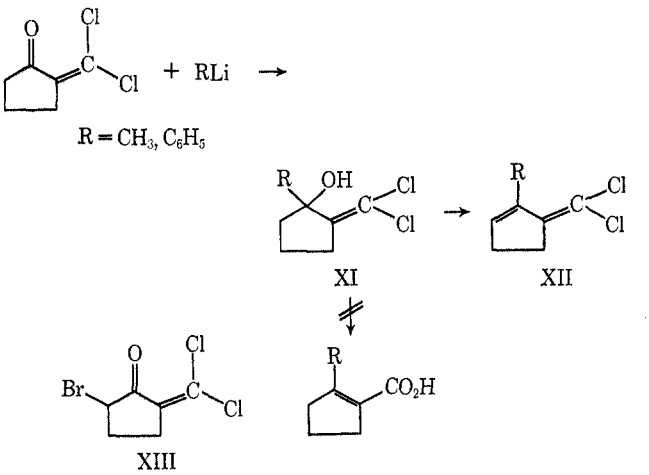
In contrast with the reactivity of I, the acyclic analog II gave an 83% yield of monosubstituted product VI when reacted with sodium thiophenoxides.



The reactions of I and II with amines were best conducted employing the amine as a solvent. Primary and secondary amines reacted smoothly to afford enamine derivatives VII and VIII in good yield. The enamines VII and VIII were quite stable and even after prolonged treatment with dilute acid were recovered unchanged. Dilute base, on the other hand, rapidly transformed enamines VIII into the corresponding amide IX. The hydrolysis of VII proved to be anamolous, since the cyclopentane ring was ruptured and afforded the monoamide derivative of adipic acid X.

Weaker bases such as phenylhydrazine, 2,4-dinitrophenylhydrazine, and hydroxylamine reacted exclusively with the carbonyl group of I and II to yield stable hydrazides and oximes. Various attempts to convert these derivatives into isooxazoles met with no success. For example, stirring the oxime of II with a slurry of sodium hydride and benzene gave a quantitative yield of a sodium salt. Attempts to cyclize the salt by heating in solvents such as acetonitrile, dimethylformamide, or dimethyl sulfoxide led to recovery of oxime or complete degradation of the starting material.

Organolithium reagents also reacted exclusively with the carbonyl group to give unsaturated tertiary alcohols XI. Dehydration of these alcohols gave only dienes XII and no unsaturated acid.[6]



The double bond in I proved to be inert to electrophillic reagents. Thus bromine or pyridinium hydrobromide perbromide transformed I into the rather unstable bromo derivative XIII.

Experimental Section[7]

2-Dichloromethylene-3-pentanone (II).—A stirred mixture of 100 ml of carbon tetrachloride, 20 g (0.13 mol) of 3-pentanone piperidine enamine, and 26.5 g (0.26 mol) of triethylamine was kept at 82° for 81 hr. Triethylamine hydrochloride, 19.77 g, was removed by filtration. The carbon tetrachloride was evaporated under diminished pressure and the residue was stirred at room temperature with water and then extracted with ether. The ether extracts were extracted with hydrochloric acid. The acid extracts were combined with the original aqueous phase and heated for 10–18 hr. The mixture was steam distilled and the distillate was saturated with salt and extracted with ether. The ether solution was dried and distilled to give 6.0 g (30%) of 2-dichloromethylene-3-pentanone (II), bp 40–44° (1.4 mm), $n^{25}D$ 1.4720, which was contaminated by *ca.* 2% 2-chloromethylene-3-pentanone.

A pure sample of II was isolated by vpc: $n^{25}D$ 1.4742; ir 5.90 and 6.20 μ; λ_{max}^{EtOH} 244 mμ (ε 3490); nmr (CCl_4) 1.08 (t, 3, CH_3-CH_2), 1.98 (s, 3, $CH_3C{=}C$), and 2.67 ppm (q, 2, CH_3CH_2).

Anal. Calcd for $C_6H_8Cl_2O$: C, 43.14; H, 4.83; Cl, 42.45. Found: C, 43.47; H, 5.09; Cl, 42.09.

(6) *Cf.* E. Jones and B. Weedon, *J. Chem. Soc.*, 937 (1946).

(7) All boiling and melting points are uncorrected. Nmr spectra were measured with a Varian Associates A-60 spectrometer. Microanalyses were performed by Dr. C. S. Yeh and associates.

The 2,4-dinitrophenylhydrazone derivative of II crystallized as glistening orange plates from dilute ethanol, mp 83–84.5°.

Anal. Calcd for $C_{12}H_{12}Cl_2N_4O_4$: C, 41.51; H, 3.49; N, 16.14; Cl, 20.43. Found: C, 41.17; H, 3.48; N, 15.84; Cl, 20.32.

The phenylhydrazone of 2-dichloromethylene-3-pentanone was crystallized from hexane: mp 64–65°; ir 2.90, 6.20, 6.62, and 6.70 μ; nmr 1.10 (t, 3), 2.08 (s, 3), 2.38 (q, 2), and 7.00 ppm (m, 6).

Anal. Calcd for $C_{12}H_{14}Cl_2N_2$: C, 56.03; H, 5.45. Found: C, 55.64; H, 5.30.

Heating the phenylhydrazone with pyrrolidine under mild conditions led to recovery of hydrazone, while more vigorous conditions (refluxing in benzene) gave a complex mixture from which a pure product could not be isolated.

The oxime of 2-dichloromethylene-3-pentanone was obtained as a colorless liquid: $n^{28}D$ 1.5034; ir 3.00, 3.29, 6.08, 6.15, and 11.0 μ; nmr 1.14 (t, 3), 2.01 (s, 3), 2.55 (q, 2), and 9.12 ppm (s, 1).

Anal. Calcd for $C_6H_9Cl_2NO$: C, 39.56; H, 4.94. Found: C, 40.42; H, 5.16.

2-Dichloromethylenecyclopentanone (I).—A stirred solution of 100 ml of carbon tetrachloride, 20 g of cyclopentanonone piperidine enamine, and 26.5 g of triethylamine was heated at 85° for 18 hr. The reaction mixture was worked up as described above to give 13.0 g of a colorless solid: mp 49–50° (from pentane); ir (CCl_4) 5.82, 6.37, and 11.20 μ; λ_{max}^{EtOH} 256 mμ (ϵ 13,820); nmr (CCl_4) multiplets at 2.00, 2.42, and 2.83 ppm.

Anal. Calcd for $C_6H_6OCl_2$: C, 43.67; H, 3.67; Cl, 42.97. Found: C, 43.71; H, 3.63; Cl, 43.26.

The 2,4-dinitrophenylhydrazone derivative of 2-dichloromethylenecyclopentanone was recrystallized from hot chloroform, mp 244–245°.

Anal. Calcd for $C_{12}H_{10}N_4O_4Cl_2$: C, 41.76; H, 2.92; N, 16.23; Cl, 20.54. Found: C, 41.61; H, 2.92; N, 16.17; Cl, 20.76.

The phenylhydrazone derivative of 2-dichloromethylenecyclopentanone was recrystallized from methanol: mp 111.5–113.5°; ir 2.95, 6.24, 6.45, 6.63, and 6.70 μ; nmr 1.80 (m, 2), 2.50 (m, 4), and 7.00 ppm (m, 6).

Anal. Calcd for $C_{12}H_{12}Cl_2N_2$: C, 56.47; H, 4.72. Found: C, 56.73; H, 4.81.

The oxime of 2-dichloromethylenecyclopentanone was purified by sublimation *in vacuo:* mp 147°; ir 2.85, 3.1, and 6.1 μ; nmr 1.8 (m, 2), 2.17 (m, 4), and 9.7 ppm (broad s, 1).

Anal. Calcd for $C_6H_7NOCl_2$: C, 40.01; H, 3.88; N, 7.88; Cl, 39.44. Found: C, 40.36; H, 4.14; N, 7.73; Cl, 39.58.

To a slurry of 450 mg (10 mmol) of sodium hydride in 20 ml of benzene was added a solution of 2-dichloromethylenecyclopentanone oxime in 4 ml of benzene and the resulting mixture was refluxed for 3 days. The sodium salt of the oxime was collected and dried: yield 2.0 g (100%); ir 3.4, 6.2, and 11.25 μ.

2-Dichloromethylenecyclohexanone.—A mixture of 1 l. of carbon tetrachloride, 200 g of cyclohexanone piperidine enamine, and 243 g of triethylamine was refluxed for 48 hr. The usual work-up and distillation of the organic phase gave 66 g of cyclohexanone and 14 g of a mixture of cyclohexanone and 2-chloromethylenecyclohexanone, bp 60–75° (1 mm).[5] The aqueous phase was distilled and the distillate was extracted with ether. The ether extract was distilled to give 25.5 g of 2-dichloromethylenecyclohexanone, bp 86–88° (2 mm), $n^{26}D$ 1.5252.

Anal. Calcd for $C_7H_8OCl_2$: C, 46.95; G, 5.50; Cl, 39.61. Found: C, 47.26; H, 4.72; Cl, 39.82.

The oxime of 2-dichloromethylenecyclohexanone was crystallized from hexane: mp 86–100°; ir 3.0, 6.20, and 11.21 μ; nmr 1.75 (m, 4), 2.68 (m, 4), and 9.75 (s, 1) ppm.

Anal. Calcd for $C_7H_9Cl_2NO$: C, 43.35; H, 4.64; Cl, 36.60. Found: C, 43.76; H, 5.11; Cl, 36.20.

A solution of 200 mg of the oxime was stirred in 20 ml of pyrollidine at ambient temperature for 4 hr. Evaporation of pyrollidine gave a quantitative recovery of oxime.

The phenylhydrazone derivative of 2-dichloromethylenecyclohexanone was purified by recrystallization from pentane: mp 72.5–73°; ir 2.95, 6.23, and 11.20 μ; nmr 1.65 (m, 4), 2.43 (m, 4), and 7.0 ppm (m, 6).

Anal. Calcd for $C_{13}H_{14}Cl_2N_2$: C, 57.99; H, 5.20; Cl, 26.38. Found: C, 57.32; H, 5.02; Cl, 26.50.

2-Dithiophenoxymethylenecyclopentanone (V).—To a slurry of sodium thiophenoxide, prepared from 450 mg of sodium hydride and 1.1 g of thiophenol, in ether was added 830 mg of 2-dichloromethylenecyclopentanone over a period of 1 hr. The resulting deep purple mixture was filtered and the ether was evaporated. The residue was taken up in 3% chloroform in hexane and a small amount of solid was removed. On cooling there was obtained 578 mg of yellow crystals: mp 94–95°; ir 5.95 μ; λ_{max}^{EtOH} 214 mμ (ϵ 19,500), 260 (7800), and 336 (14,000); nmr ($CDCl_3$) 2.0 (q, 2), 2.4 (t, 2), 2.8 (t, 2), and 7.1 ppm (s, 10).

Anal. Calcd for $C_{18}H_{16}OS_2$: C, 69.23; H, 5.12; S, 20.52. Found: C, 69.01; H, 5.32; S, 20.74.

2-Diphenoxymethylenecyclopentanone (IV).—2-Dichloromethylenecyclopentanone, 830 mg, was treated with 1.16 g of sodium phenoxide as described above to give 754 mg of crude product. Recrystallization from 2:1 hexane–chloroform, with Darco KB treatment, afforded 342 mg of solid: mp 95–95.5°; ir 5.85, 6.15, 6.35, and 6.8 μ; λ_{max}^{EtOH} 272 mμ (ϵ 17,800) and 310 (11,900); nmr ($CDCl_3$) 2.05 (m, 4), 2.68 (t, 2), and 7.02 ppm (d, 10).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.14; H, 5.71. Found: C, 77.09; H, 5.56.

1-Chloro-2-methyl-1-thiophenoxy-1-penten-3-one (VI).—To a slurry of 1.32 g (10 mmol) of sodium thiophenolate in 20 ml of ether was slowly added 835 mg (5 mmol) of 2-dichloromethylene-3-pentanone. After stirring for 1 hr at room temperature the solids were removed by filtration. Distillation of the filtrate gave 1.3 g of a yellow oil. A sample was redistilled: bp 116–116.5° (1 mm); $n^{23}D$ 1.5800; ir 3.22, 5.90, 6.35, and 6.68 μ; λ_{max}^{EtOH} 211 mμ (ϵ 14,100) and 252 (6670); nmr (CCl_4) 1.10 (t, 3), 2.05 (s, 3) 2.65 (q, 2), and 7.35 ppm (s, 5).

Anal. Calcd for $C_{12}H_{13}ClOS$: C, 59.87; H, 5.40. Found: C, 60.35; H, 5.27.

2-Diisopropylaminomethylenecyclopentanone.—A solution of 1.0 g of 2-dichloromethylenecyclopentanone in 15 ml of isopropylamine was stirred at room temperature for 15 min. Ether was added and the solid was removed by filtration. The ether and excess amine were removed under diminished pressure and the residue was extracted with hot hexane. The hexane was evaporated, leaving 980 mg (76.6%) of an oil which solidified on standing. Recrystallization from pentane gave yellow crystals: mp 81.82°; ir 3.00, 3.35, 6.18, and 6.40 μ; nmr ($CDCl_3$) 1.20 (d, 12), 1.80 and 2.35 (m, 8), and 3.75 ppm (m, 2).

Anal. Calcd for $C_{12}H_{22}N_2O$: C, 68.57; H, 10.47; N, 13.32. Found: C, 68.38; H, 10.41; N, 13.24.

2-Di-*n*-butylaminomethylenecyclopentanone was obtained from the reaction of 2-dichloromethylenecyclopentanone and *n*-butylamine. A sample was purified by preparative thin layer chromatography: ir 3.05, 3.2, and 6.4 μ; λ_{max}^{EtOH} 219 mμ (ϵ 6060) and 309 (12,700); nmr ($CDCl_3$) 0.95 (m, 7), 1.50 (m, 11), 2.40 (m, 4), and 3.25 ppm (m, 4).

Anal. Calcd for $C_{14}H_{26}N_2O$: C, 70.59; H, 11.92; N, 12.84. Found: C, 70.71; H, 11.97; N, 12.50.

2-Dipyrrolidinomethylenecyclopentanone was isolated in 34% yield from the reaction of pyrrolidine and 2-dichloromethylenecyclopentanone carried out as described above. A pure sample of this amino ketone was obtained by sublimation *in vacuo:* mp 96–100°; ir 6.20 and 6.75 μ; λ_{max}^{EtOH} 255 mμ (ϵ 3240) and 330 (7140); nmr ($CDCl_3$) 1.9 (m, 12), 2.3 (t, 2), and 3.3 ppm (m, 12).

Anal. Calcd for $C_{14}H_{22}N_2O$: C, 71.76; H, 9.41; N, 11.98. Found: C, 71.80; H, 9.66; N, 11.76.

2-Dipyrrolidinomethyllenecyclopentanone was recovered after treatment with 20% sulfuric acid at 100° for 6 hr. Heating 500 mg of the amino ketone for 45 min at 100° with 5 ml of 10% sodium hydroxide gave a homogeneous solution. The solution was cooled and extracted with chloroform to give 80 mg of unaltered amino ketone. Acidification of the aqueous solution and extraction with chloroform gave 229 mg of an oil which slowly solidified. Recrystallization from ethyl acetate gave a pure sample of X: mp 84–85°; ir 3.35, 5.8, and 6.25 μ; nmr 1.8 (m, 8), 2.4 (m, 4), 3.5 (m, 4), and 11.50 ppm (s, 1).

Anal. Calcd for $C_{10}H_{17}NO_3$: C, 60.30; H, 8.54. Found: C, 60.72; H, 8.45.

2-Dipyrrolidinomethylene-3-pentanone (VIII) was obtained in 93% yield as a viscous, straw-yellow oil, $n^{25}D$ 1.554, from the reaction of excess pyrrolidine with 2-dichloromethylene-3-pentanone. The amino ketone was heated for 15 min at 100° with 10 ml of 10% sodium hydroxide. The mixture was worked up as described above to give 50% of an oil. A pure sample of keto amide IX was obtained by evaporative distillation: $n^{25}D$ 1.4796; ir 2.90, 3.32, 5.79, and 6.08 μ; nmr 1.15 (t, 3), 1.35 (d, 3), 1.95 (m, 4), 2.42 (q, 2), and 3.50 ppm (m, 5).

Anal. Calcd for $C_{10}H_{17}NO_2$: C, 65.49; H, 9.29. Found: C, 65.57; H, 9.56.

5-Bromo-2-dichloromethylenecyclopentanone (XIII).—Pyridinium bromide perbromide, 1.9 g(5 mmol) was added to a solution of 830 mg (5 mmol) of 2-dichloromethylenecyclopentanone in 15 ml of carbon tetrachloride. The mixture was stirred at ambient temperature for 15 min and filtered. The filtrate was treated with anhydrous sodium carbonate. Evaporation of the solvent left 1.2 g of an oil which solidified on cooling. Recrystallization from pentane gave white crystals: mp 63–64°; ir 5.80 and 6.30 μ; nmr 2.32 (m, 2), 2.95 (m, 2), and 4.40 ppm (q, 1, CHBr).

Anal. Calcd for $C_6H_5BrCl_2O$: C, 29.50; H, 2.05. Found: C, 29.01; H, 2.13.

2-Dichloromethylene-1-hydroxy-1-methylcyclopentane.—A mixture of 830 mg (5 mmol) of 2-dichloromethylenecyclopentanone and 8 mmol of methyllithium in ether was prepared at −70° and then kept at ambient temperature for 10 hr. After the addition of 10 ml of 3.7% hydrochloric acid, the mixture was extracted with methylene chloride. The solution was dried and the solvents were removed, leaving an oil. The oil was triturated with four 10-ml portions of pentane. The pentane solution was treated with Darco KB and the volume was reduced to *ca.* 3 ml. On cooling to −70° unreacted 2-dichloromethylenecyclopentanone crystallized. The solid was removed and the remaining solvent was evaporated, leaving 390 mg (43%) of an oil which solidified on standing. Sublimation *in vacuo* gave a pure sample of the alcohol: mp 45.5–46°; ir 2.98, 6.15, and 6.31 μ; nmr 1.52 (s, 3, CH_3CO) ,1.87 (m, 4), and 2.50 ppm (m, 3).

Anal. Calcd for $C_7H_{10}Cl_2O$: C, 46.45; H, 5.50; Cl, 39.25. Found: C, 46.50; H, 5.58; Cl, 39.24.

3-Dichloromethylene-2-methylcyclopentene.—A mixture of 300 mg of 2-dichloromethylene-1-hydroxy-1-methylcyclopentane, 10 ml of 10% sulfuric acid, and 10 ml of methanol was stirred for 4 hr. The mixture was made basic with 10% sodium hydroxide solution and extracted with methylene chloride. After drying, the solvent was evaporated to leave 284 mg of an oil. Purification by vpc gave a colorless liquid: ir 5.80 (w), 6.17, 6.22, and 11.30 μ; λ_{max}^{EtOH} 230 mμ (ϵ 7280); nmr 2.08 (m, 3), 2.35 (m, 2), 2.70 (m, 2), and 5.98 ppm (br s, 1).

Anal. Calcd for $C_7H_8Cl_2$: C, 51.55; H, 4.90. Found: C, 51.50; H, 4.91.

3-Dichloromethylene-2-phenylcyclopentene.—A solution of phenylithium in ether, prepared from 1.18 g of bromobenzene and 105 mg of lithium, was added to a Dry Ice cooled solution of 2-dichloromethylenecyclopentanone in tetrahydrofuran. The reaction was worked up in the usual manner to give 1.08 g of an oil whose ir spectrum indicated the presence of a mixture of alcohol and starting ketone. A 243-mg portion of this oil was stirred for 2 hr at 25° with 0.5 ml of boron trifluoride etherate in 10 ml of ether. The ether solution was washed with sodium bicarbonate solution, dried, and evaporated to leave 201 mg of an oil. The oil was placed on a short alumina column and eluted with hexane to give 150 mg of diene. An analytical sample was prepared by evaporative distillation: ir 3.20, 6.24, 6.70, and 11.20 μ; nmr 2.60 (m, 2), 2.90 (m, 2), 6.15 (t, 1, HC=C), and 7.22 ppm (s, 5, ArH).

Anal. Calcd for $C_{12}H_{10}Cl_2$: C, 64.00; H, 4.44. Found: C, 64.20; H, 4.38.

Registry No.—I, 10412-35-8; II, 13017-26-0; 2,4-dinitrophenylhydrazone derivative of II, 23231-13-2; phenylhydrazone of 2-dichloromethylene-3-pentanone, 23231-14-3; oxime of 2-dichloromethylene-3-pentanone, 23231-15-4; 2,4-dinitrophenylhydrazone derivative of 2-dichloromethylenecyclopentanone, 23231-16-5; phenylhydrazone derivative of 2-dichloromethylenecyclopentanone, 23231-17-6; oxime of 2-dichloromethylenecyclopentanone, 23231-18-7; 2-dichloromethylenecyclohexanone, 10412-36-9; oxime of 2-dichloromethylenecyclohexanone, 23231-20-1; phenylhydrazone derivative of 2-dichloromethylenecyclohexanone, 23231-21-2; IV, 23231-22-3; V, 23231-23-4; VI, 23231-24-5; 2-diisopropylaminomethylenecyclopentanone, 23231-25-6; 2-di-*n*-butylaminomethylenecyclopentanone, 23231-26-7; 2-dipyrrolidinomethylenecyclopentanone, 23263-81-2; IX, 23231-27-8; X, 23231-28-9; XIII, 23240-69-9; 2-dichloromethylene-1-hydroxy-1-methylcyclopentane, 23240-70-2; 3-dichloromethylene-2-methylcyclopentene, 23240-71-3; 3-dichloromethylene-2-phenylcyclopentene, 23240-72-4.

Intermediates in Nucleophilic Aromatic Substitution. III.[1] Visible Absorption Spectra of the Acid and Basic Form of the 1,3,5-Trinitrobenzene–Piperidine Meisenheimer Complex in 10% Dioxane–90% Water

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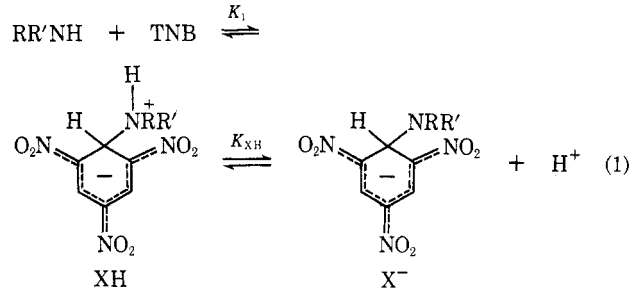
There exist a number of reports on the absorption spectra of the Meisenheimer complexes produced by the interaction of 1,3,5-trinitrobenzene (TNB) with aliphatic amines in a variety of solvents.[2–7] With primary and secondary amines, equilibrium 1 has



R′ = Alkyl or H

consistently been found to strongly favor X^- over XH, so that the spectra always referred to the basic form X^-. We wish now to report the spectrum of the zwitterionic form XH of the piperidine–TNB complex in 10% dioxane–90% water at 25°.

Figure 1 shows spectra of TNB in two different piperidine–piperidine hydrochloride buffer solutions, at different pH[8] but equal ionic strength. Knowledge of the equlibrium constants K_1 and K_{XH} and of the easily obtained spectrum of pure X^- would allow one to dissect the respective contributions of both species to the overall spectrum and thus to find the spectrum of pure XH by difference. The matter is, however, more complex for two reasons. (1) TNB and piperidine undergo another interaction to form the oxyhydroxylamine YH and its conjugate anion Y^-;[1] though YH and Y^- do not contribute to the visible spectrum, they appreciably reduce the equilibrium concentrations of XH and X^-. (2) There is also some concurrent for-

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