3:1. These materials were separated with an Aerograph Autoprep Model A-700 (Wilkens Instrument and Research) and identified by comparison of their infrared spectra with those of authentic compounds.

Reduction of Ia with Lithium Aluminum Hydride.—A solution of 50 g. (0.36 mole) of Ia in 75 ml. of dry ether was added slowly to a stirred slurry of 9.5 g. (0.25 mole) of lithium aluminum hydride in 500 ml. of dry ether. The reaction temperature was controlled at 15–20° by an ice bath. The reaction mixture was stirred for 1 hr. after the addition was complete. Water (10 ml.) was added slowly, followed by 8 ml. of 20% sodium hydroxide solution and an additional 36 ml. of water. The alumina was removed by filtration and washed several times with ether. The combined filtrates were dried over anhydrous magnesium sulfate and low-boiling materials were removed at room temperature *in vacuo*. The n.m.r. spectrum of the residue (35 g.) was characteristic of VII. Distillation of this material through a 10-in. Vigreux column gave 28 g. of 3-ethoxy-4-methyl-2-pentenal (VIII), b.p. 70–72° (3 mm.).

Infrared absorptions (smear) for VII were at 2.98, 6.1, and 6.21 μ. The n.m.r. spectrum (neat) of VII showed singlets at 2.98, 6.1, and 6.21 μ. The n.m.r. spectrum (neat) of VII showed singlets at 4.42 (C=CH), 4.10 (OCH), and 3.23 (OH), a quartet at 3.73, a triplet at 1.10 (C_2H_5O), and a doublet at 1.22 p.p.m. (CH_3). Infrared absorptions (smear) for VIII were at 3.62, 6.02, and 6.22 μ. The n.m.r. spectrum (neat) of VIII showed doublets at 9.82 (CHO) and 5.45 (C=CH), a quartet at 3.75 and a triplet at 1.42 (C_2H_5O), and a septet at 2.88 and a doublet at 1.02 p.p.m. [$(CH_3)_2CH$].

Anal. Calcd. for $C_8H_{14}O_2$ (VIII): C, 67.6; H, 9.9. Found: C, 67.3; H, 9.9.

3-Amino-4,4-dimethyl-2-cyclobuten-1-one (IX).—A mixture of 20 g. (0.14 mole) of Ia and 40 ml. of 28% ammonium hydroxide was stirred at room temperature for 4 hr. The resulting solid was isolated by filtration, washed with water, and dried in air to give 13.9 g. (89%) of IX which melted at 213° with decomposition. An analytical sample, recrystallized from ethyl alcohol, had m.p. 213° with decomposition; infrared absorptions (KBr) at 3.16, 5.98, and 6.4 to 6.9 μ (broad). The n.m.r. spectrum of IX showed a broad peak at 8.50 (NH_2) and singlets at 4.22 (C=CH) and 1.15 p.p.m. (CH_3).

Anal. Calcd. for C_6H_9NO: C, 64.8; H, 8.2; N, 12.6. Found: C, 65.0; H, 8.3; N, 12.6.

3-Piperidino-4,4-dimethyl-2-cyclobuten-1-one (X).—A solution of 40 g. (0.28 mole) of 3-ethoxy-4,4-dimethyl-2-cyclobuten-1-one and 24.3 g. (0.28 mole) of piperidine in 100 ml. of benzene was refluxed for 5 hr. Most of the benzene was removed by distillation at atmospheric pressure. The residue crystallized on cooling to give 50.4 g. (98%) of crude X, m.p. 101.5–104°. A sample recrystallized twice from a mixture of benzene and hexane had m.p. 104–104.5°; infrared absorptions (KBr) at 5.75 and 6.28 μ. The n.m.r. spectrum showed singlets at 4.32 (C=CH) and 3.33 (methylenes attached to N of piperidine), a broad peak at 1.75 (remaining methylenes of piperidine), and a doublet at 1.22 p.p.m. (CH_3).

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.7; H, 9.6; N, 7.8. Found: C, 74.0; H, 9.8; N, 7.7.

3-(2-Anilinovinyl)-2,2-dimethyl-3-cyclobuten-1-one (XIV).—A mixture of 7.6 g. (0.05 mole) of II and 4.65 g. (0.05 mole) of aniline was allowed to stand for several days at room temperature. The crystalline product was washed with cold benzene and recrystallized from ethyl alcohol to give 6.3 g. of XIV, m.p. 169–170°. XIV showed significant infrared absorptions at 6.12, 6.3, 6.45, 6.55, and 6.9 μ. The n.m.r. spectrum (dimethylformamide) showed singlets at 1.38 (CH_3) and 4.50 (ring H), a doublet at 5.92 (C=CH), and a complex multiplet at 7.25 p.p.m. (C_6H_5NHCH=C).

Anal. Calcd. for $C_{14}H_{15}NO$: C, 78.8; H, 7.1; N, 6.6. Found: C, 79.1; H, 7.2; N, 6.7.

Reaction of Ia with Ethyl Alcohol (XVa).—A solution of 28.0 g. (0.2 mole) of Ia in 50 ml. of ethyl alcohol was refluxed for 36 hr. Periodic examinations of the reaction solution by infrared showed a steady decrease in the amount of starting material. Distillation of this solution through a 6-in. Vigreux column gave 27.1 g. (73%) of XVa, b.p. 80–81° (6 mm.), $n^{20}D$ 1.4468; infrared absorptions (smear) at 5.82, 6.08, 8.7, and 9.07 μ.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.5; H, 9.7. Found: C, 64.7; H, 10.1.

Reaction of Ia with Butyl Alcohol (XVb).—A solution of 28.0 g. (0.2 mole) of Ia in 59 g. (0.8 mole) of butyl alcohol was refluxed under a short, packed column for 3 hr. The temperature at the head of the column remained at 115° during this period. The solution was cooled and examination of its infrared spectrum indicated that all of Ia was gone. To this solution was added 0.1 g. of *p*-toluenesulfonic acid and refluxing was continued. The head temperature rose to 77° and 10 ml. of ethyl alcohol distilled at 77–81°. The excess butyl alcohol was removed *in vacuo* and the residue was taken up in ether, washed with sodium bicarbonate solution and then with water, and finally dried over anhydrous magnesium sulfate. Distillation of this solution through a 10-in. packed column gave 25.8 g. (53%) of XVb, b.p. 97–101° (0.7 mm.), $n^{20}D$ 1.4522; infrared absorptions (smear) at 5.87 and 6.21 μ. The n.m.r. spectrum (neat) showed a singlet at 4.82 (C=CH), a multiplet at 3.70 (two OCH_2's and CH), and a complex region between 1.55 and 0.95 p.p.m. (all remaining protons). These areas were in the proportions of 1:5:20.

Anal. Calcd. for $C_{14}H_{26}O_3$: C, 69.4; H, 10.8. Found: C, 69.6; H, 10.9.

Acknowledgment.—The authors thank V. Wilson Goodlett for interpretation of n.m.r. spectra, A. L. Thompson for interpretation of infrared spectra, and E. U. Elam for the experiment on the reduction of V over palladium.

Ketenes. IV. Reactions of Ketenes with Ketene O,N-Acetals and Ketene N,N-Acetals[1]

ROBERT H. HASEK, P. GLENN GOTT, AND JAMES C. MARTIN[2]

Research Laboratories, Tennessee Eastman Company, Division of Eastman Kodak Company, Kingsport, Tennessee

Received February 24, 1964

Ketene O,N-acetals and N,N-acetals having olefinic hydrogen atoms are converted by dimethylketene into isobutyryl O,N-acetals and N,N-acetals. However, reaction with ketene gives 2:1 adducts, 4-(dialkylamino)-2H-pyran-2-ones.

In view of the facile addition of ketenes to enamines and vinyl ethers to form cyclobutanones,[3,4] an investigation into the reactions of ketenes with such highly nucleophilic olefins as ketene O,N-acetals and ketene N,N-acetals seemed warranted. Ketene N,N-acetals I with hydrogen atoms on the olefinic carbon reacted vigorously with dimethylketene to form acylketene N,N-acetals II. No infrared spectral evidence of intermediate cyclobutanone formation could be found when a reaction was carried out below 0°.

As attempts to prepare a dimethylketene N,N-acetal were unsuccessful, the action of a "blocked" ketene

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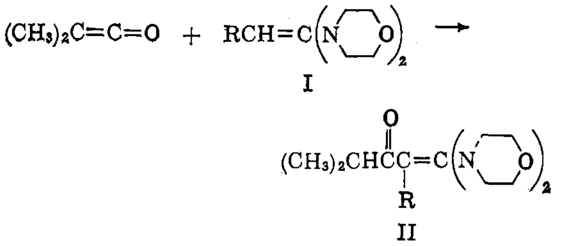
[1] Paper III in this series: R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, **29**, 2510 (1964).

[2] To whom all inquiries should be sent.

[3] R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

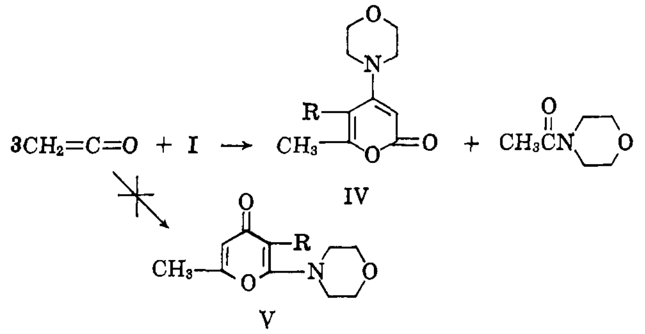
[4] R. H. Hasek, P. G. Gott, and J. C. Martin, *ibid.*, **29**, 1239 (1964).



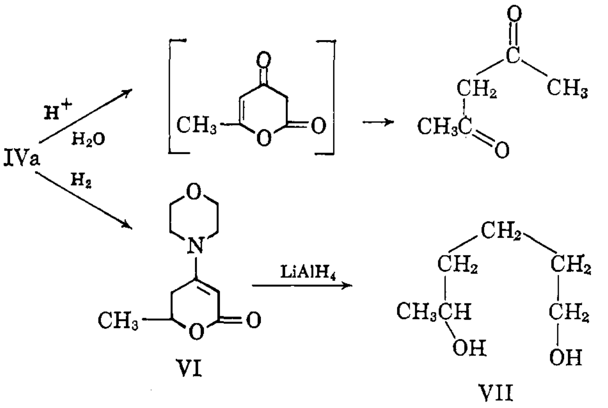
(a, R = H; b, R = CH_3)

N,N-acetal (no olefinic hydrogen atoms) was not checked.[5] Strangely enough, dimethylketene did not react with the blocked dimethylketene, O,N-acetal, 1-ethoxy-N,N-dimethylisobutenylamine; in this sense, the olefin behaved like an isobutenyl ether rather than an isobutenylamine.

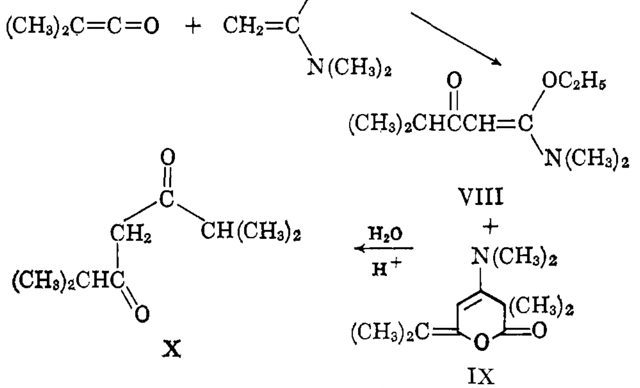
Ketene combined with the ketene N,N-acetals to form aminopyranones IV. The pyranone structure was supported by elemental analysis, infrared and n.m.r. spectra, and hydrolysis of the pyranone to 2,4-pentanedione. Proof that the 2-pyranone IV rather than the 4-pyranone V was formed was obtained by catalytic hydrogenation of IVa to the dihydro derivative VI and reduction of VI to 1,5-hexanediol (VII) with lithium aluminum hydride (see col. 2, top).



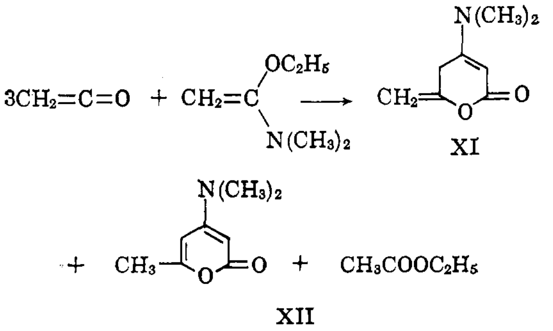
(a, R = H; b, R = CH_3)



Ketene O,N-acetals also exhibited a strong tendency to combine with ketenes. Dimethylketene and 1-ethoxy-N,N-dimethylvinylamine combined in benzene to give two products: 1-(dimethylamino)-1-ethoxy-4-methyl-1-penten-3-one (VIII) in 36% yield and 4-(dimethylamino)-3,6-dihydro-6-isopropylidene-3,3-dimethyl-2H-pyran-2-one (IX) in 49% yield. When this reaction was run at 0°, the infrared spectrum of the cold reaction solution showed no band characteristic of a cyclobutanone. The addition of 2 moles of dimethylketene per mole of 1-ethoxy-N,N-dimethylvinylamine in acetonitrile gave the pyranone IX in 71% yield. The formation of 2:1 adducts of ketenes with enamines is also favored in polar solvents.[3] The structural assignment for IX was based on elemental analysis, infrared and n.m.r. spectra, hydrolysis of the pyranone to 2,6-dimethyl-3,5-heptanedione (X), and analogy with other results obtained in this work.



Ketene and 1-ethoxy-N,N-dimethylvinylamine reacted vigorously to give a mixture, 4-(dimethylamino)-5,6-dihydro-6-methylene-2H-pyran-2-one (XI) and 4-(dimethylamino)-6-methyl-2H-pyran-2-one (XII).



The presence of these two products was detected by n.m.r. spectrum of the crude solid. The mixture was easily converted to pure XII by melting or by addition of a trace of acid to a tetrachloroethane solution of the mixture. The structure of XII was assigned on the basis of similarities between its infrared and n.m.r. spectra and those of the aminopyranone IVa.

We have observed that the reactions of ketenes and ketene O,O-acetals give anomalous results, and these will be reported in a later paper.

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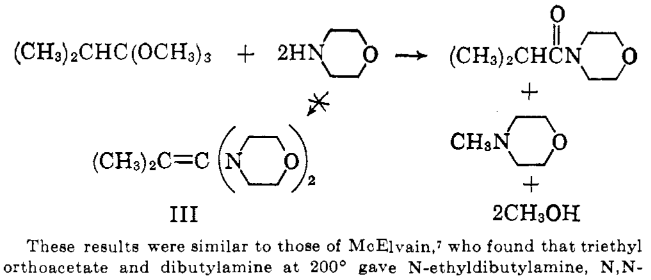
(5) An attempt to prepare 4,4,-isobutenylidenedimorpholine (III) from trimethyl orthoisobutyrate by the general method of Baganz and Domaschke[6] did not give III, but gave a 78% yield of 4-isobutyrylmorpholine. The reaction proceeded as shown.



These results were similar to those of McElvain,[7] who found that triethyl orthoacetate and dibutylamine at 200° gave N-ethyldibutylamine, N,N-dibutylacetamide, and 2 moles of ethyl alcohol.

(6) H. Baganz and L. Domaschke, *Ber.*, **95**, 2095 (1962).

(7) S. M. McElvain and B. E. Tate, *J. Am. Chem. Soc.*, **67**, 202 (1945).

Experimental

4,4′-Vinylidenedimorpholine,[6] 4,4′-propenylidenedimorpholine,[6] 1-ethoxy-N,N-dimethylvinylamine,[8] and 1-ethoxy-N,N-dimethylisobutenylamine[9] were prepared by methods described in the literature. Ketene was obtained from Tennessee Eastman Company, and dimethylketene was prepared by pyrolysis of isobutyric anhydride.[10]

4-Methyl-1,1-dimorpholino-1-penten-3-one (IIa).—Over a period of 10 min., 20.7 g. (0.3 mole) of dimethylketene was added to a stirred solution of 57 g. (0.29 mole) of 4,4′-vinylidenedimorpholine in 150 ml. of benzene under a nitrogen atmosphere. The reaction was quite exothermic and an ice bath was required to keep the reaction temperature at 20–35°. The solution was stirred at room temperature for 2 hr., and the solvent was then removed *in vacuo* to give a nearly quantitative yield of crude product. The solid was recrystallized from hexane to give 57 g. (74%) of IIa, m.p. 103.5–105°; infrared absorptions[11] (KBr) at 6.21, 6.67, and 6.91 μ. The n.m.r. spectrum (CCl_4)[12] showed a doublet at 0.96 and a septet at 2.34 (isopropyl group), multiplets at 3.12 and 3.61 (morpholine groups), and a singlet at 4.35 p.p.m. (olefinic proton).

Anal. Calcd. for $C_{14}H_{24}N_2O_3$: C, 62.7; H, 9.0; N, 10.4. Found: C, 62.4; H, 8.8; N, 10.4.

2,4-Dimethyl-1,1-dimorpholino-1-penten-3-one (IIb).—Dimethylketene (14.0 g., 0.2 mole) was added rapidly to a stirred solution of 42.4 g. (0.2 mole) of 4,4′-propenylidenedimorpholine in 150 ml. of benzene under a nitrogen atmosphere. The temperature of the exothermic reaction rose to 47° even with cooling by ice. After 1 hr., the solvent was removed *in vacuo* to give a viscous residue. This material was not distillable at 180° (0.2 mm.), but, when cooled, the viscous residue slowly crystallized. Recrystallization from a mixture of benzene and hexane gave 13 g. (23%) of IIb, m.p. 155–157°; infrared absorptions (KBr) at 6.28, 6.75, 6.90, and 6.95 μ. The n.m.r. spectrum (CH_2Cl_2) showed a doublet at 1.07 (methyl protons of isopropyl group), a singlet at 1.91 (methyl group attached to olefinic carbon), a septet at 2.38 (tertiary proton of isopropyl group), and multiplets at 3.25 and 3.82 p.p.m. (protons of morpholine groups).

Anal. Calcd. for $C_{15}H_{26}N_2O_3$: C, 63.8; H, 9.3; N, 9.9. Found: C, 63.7; H, 8.8; N, 10.1.

6-Methyl-4-morpholino-2H-pyran-2-one (IVa).—Ketene (35 g., 0.84 mole) was added to a stirred solution of 62.0 g. (0.31 mole) of 4,4′-vinylidenedimorpholine in 250 ml. of ether. The temperature of the exothermic reaction was kept at 15–25° by intermittent use of an ice bath. A large amount of solid precipitated and, after 1 hr., was isolated by filtration and dried in air. The yield of crude IVa, m.p. 173–177°, was 51 g. (85%). A sample for analysis, recrystallized twice from benzene, had m.p. 177–179°; infrared absorptions (KBr) at 5.9, 6.12, and 6.7 μ. The n.m.r. spectrum ($CHCl_3$) showed a singlet at 2.17 (methyl protons), multiplets at 3.30 and 3.74 (protons of morpholine group), and broad peaks at 5.08 and 5.84 p.p.m. (olefinic protons).

Anal. Calcd. for $C_{10}H_{13}NO_3$: C, 61.6; H, 6.7; N, 7.2. Found: C, 61.7; H, 6.6; N, 7.1.

Hydrolysis of IVa.—A solution of 10 g. (0.0515 mole) of IVa in 50 ml. of 10% hydrochloric acid was heated at 60–75° for 1 hr. The reaction mixture was extracted with ether and the organic layer was dried over anhydrous magnesium sulfate. Distillation in a microdistillation apparatus gave 1.7 g. (33%) of 2,4-pentanedione, b.p. 48° (35 mm.). The infrared spectrum of this material was identical with that of an authentic sample of 2,4-pentanedione.

5,6-Dimethyl-4-morpholino-2H-pyran-2-one (IVb).—Ketene (17 g., 0.41 mole) was added to a stirred solution of 30 g. (0.14 mole) of 4,4′-propenylidenedimorpholine in 100 ml. of ether. The temperature of the exothermic reaction was maintained at 10–25° by an ice bath. After 2 hr., the solvent was removed *in vacuo*, and the residue was distilled through a 6-in. packed column to give 11 g. of viscous material, b.p. 125–185° (1.3 mm.). A sample purified by g.l.c.[13] solidified; after being washed with ether, it had m.p. 94–97.5°; infrared absorptions (KBr) at 5.9, 6.18, and 6.5 μ. The n.m.r. spectrum ($CHCl_3$) showed singlets at 1.93 (methyl protons in the 5-position), 2.17 (methyl protons in the 6-position), and 5.32 (olefinic proton), and a multiplet at 2.99 p.p.m. (protons of morpholine group).

Anal. Calcd. for $C_{11}H_{15}NO_3$: C, 63.1; H, 7.2; N, 6.7. Found: C, 62.6; H, 7.1; N, 6.8.

6-Methyl-4-morpholino-5,6-dihydro-2H-pyran-2-one (VI).—A solution of 19.5 g. (0.1 mole) of IVa in 530 ml. of methanol was hydrogenated over 4 g. of 5% ruthenium on carbon in a magnetically stirred pressure bottle at room temperature for 8 hr. at 40 p.s.i. The catalyst was removed by filtration and the solvent was evaporated *in vacuo* to give a solid residue. Recrystallization of the solid from ethyl alcohol gave 14.0 g. (71%) of VI, m.p. 118–121°; infrared absorptions (KBr) at 6.03 and 6.35 μ. The n.m.r. spectrum ($CHCl_3$) showed a doublet at 1.38 (methyl protons), multiplets at 2.55 (methylene protons), 3.31 and 3.79 (protons of morpholine group), and 4.42 (methylidyne proton), and a broad single peak at 4.88 p.p.m. (olefinic proton).

Anal. Calcd. for $C_{10}H_{15}NO_3$: C, 60.9; H, 7.7; N, 7.1. Found: C, 61.1; H, 7.7; N, 6.9.

Reduction of VI with Lithium Aluminum Hydride.—A mixture of 5.0 g. (0.025 mole) of VI, 2.6 g. (0.07 mole) of lithium aluminum hydride, and 150 ml. of tetrahydrofuran was stirred for 15 hr. at 25°. The reaction was hydrolyzed by the successive addition of 2.6 ml. of water, 1.95 g. of 20% sodium hydroxide solution, and 9.1 ml. of water. The mixture was filtered and evaporated *in vacuo* to give 2.9 g. of a viscous oil. This material was a mixture rich in one component, which was isolated by g.l.c.[13] (195°, Carbowax) and identified as 1,5-hexanediol (VII), n^{20}_{D} 1.4535, lit.[14] n^{20}_{D} 1.4528; infrared absorptions (smear) at 3.0, 8.80, 8.92, 9.10, 9.30, and 9.49 μ. The n.m.r. spectrum (neat) showed a doublet at 1.15 (methyl protons), broad peaks at 1.46 (protons of three adjacent methylene groups) and 3.58 (methylidyne proton and protons of methylene group adjacent to oxygen), and a singlet at 5.12 p.p.m. (protons of hydroxy groups).

Anal. Calcd. for $C_6H_{14}O_2$: C, 61.0; H, 11.9. Found: C, 61.3; H, 12.0.

The bis(*p*-nitrobenzoate) prepared from VII melted at 89–90°[15] after recrystallization from ethyl alcohol.

Anal. Calcd. for $C_{20}H_{20}N_2O_8$: C, 57.7; H, 4.8; N, 6.7. Found: C, 57.4; H, 5.0; N, 6.7.

Preparation of 1,5-Hexanediol.—Over a 45-min. period, under a nitrogen atmosphere, ethyl alcohol (0.28 mole) was distilled from a stirred mixture of 40 g. (0.28 mole) of 2-ethoxy-3,4-dihydro-6-methyl-2H-pyran[18] and 200 ml. of 1% phosphoric acid. The resulting aqueous solution of 5-oxohexanal[19] was neutralized

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[8] H. Meerwin, W. Florian, N. Schön, and G. Stopp, *Ann. Chem.*, **641**, 1 (1961).

[9] K. C. Brannock, R. D. Burpitt, and J. G. Thweatt, *J. Org. Chem.*, **29**, 940 (1964).

[10] R. H. Hasek and E. U. Elam (to Eastman Kodak Co.), Canadian Patent 618,772 (1961).

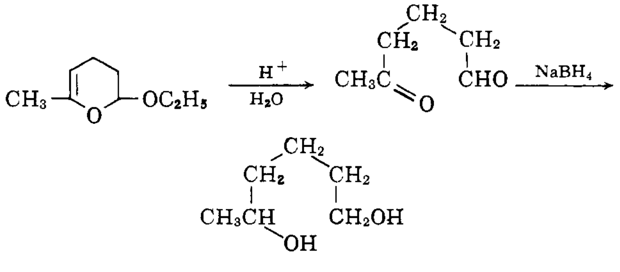
[11] Infrared spectra were determined on a Baird AB-2 instrument.

[12] N.m.r. spectra were recorded on a Varian A-60 instrument at 60 Mc. with tetramethylsilane as an internal standard.

[13] G.l.c. separations were made on an Aerograph Autoprep Model A-700 made by Wilkens Instrument and Research.

[14] C. Crisan, *Ann. chim.* (Paris), [13]**1**, 436 (1956).

[15] The melting point of this derivative was at variance with the melting points reported by von Rudloff[16] and Colonge.[17] This prompted us to prepare 1,5-hexanediol by an independent synthesis and compare the melting point of its derivative with that from VII. The following reaction sequence was used for the synthesis.



The diol made by this route had infrared and n.m.r. spectra identical with those of VII, and the melting point of the bis(*p*-nitrobenzoate) was 88.5–90°, identical with that found for VII. A closer examination of the data (infrared spectrum and melting point of derivative) of von Rudloff[16] showed that he had 1,5-*pentane*diol.

[16] E. von Rudloff, *Can. J. Chem.*, **36**, 486 (1958).

[17] J. Colonge, J. Dreux, and M. Thiers, *Bull. soc. chim. France*, 1459 (1959).

[18] R. I. Longely and W. S. Emerson, *J. Am. Chem. Soc.*, **72**, 3079 (1950).

and treated with 6 g. of sodium borohydride. After standing for 16 hr. at 25°, the mixture was heated to 60° for 1 hr. and continuously extracted with ether to give 20 g. (60%) of 1,5-hexanediol, b.p. 94–96° (0.6 mm.), $n^{20}\mathrm{D}$ 1.4535.

The bis(*p*-nitrobenzoate) melted at 89–90° and did not depress the melting point of the bis(*p*-nitrobenzoate) of VII prepared by reduction of VI.

1-(Dimethylamino)-1-ethoxy-4-methyl-1-penten-3-one (VIII).—Under a nitrogen atmosphere, 16.8 g. (0.24 mole) of dimethylketene was added over a period of 15 min. to a stirred solution of 27.3 g. (0.24 mole) of 1-ethoxy-N,N-dimethylvinylamine in 100 ml. of benzene. The temperature of the exothermic reaction was held in the range of 20 to 50° by an ice bath. Stirring was continued for 1 hr. at room temperature and the solution was then distilled through a 6-in. Vigreux column to give 30.2 g. of material, b.p. 106–121° (0.5 mm.). This mixture (shown to be two materials by g.l.c.) was redistilled through a 36-in. spinning-band column to give 16.1 g. (36%) of VIII, b.p. 80° (0.5 mm.), $n^{20}\mathrm{D}$ 1.5050, and 12.2 g. (49%) of 4-(dimethylamino)-3,6-dihydro-6-isopropylidene-3,3-dimethyl-2H-pyran-2-one (IX), b.p. 95–96° (0.5 mm.), $n^{20}\mathrm{D}$ 1.5450.

VIII showed infrared absorptions (smear) at 6.17, 6.50, 6.75 and 6.85 μ. The n.m.r. spectrum (neat) showed a doublet at 1.00 (methyl protons of isopropyl group), a triplet at 1.28 (methyl protons of ethoxy group), a septet at 2.38 (methylidyne proton of isopropyl group), singlets at 2.82 (methyl protons of dimethylamino group) and 4.40 (olefinic proton), and a quartet at 4.02 p.p.m. (methylene protons of ethoxy group).

Anal. Calcd. for $C_{10}H_{19}NO_2$ (VIII): C, 64.9; H, 10.3; N, 7.6. Found: C, 64.8; H, 10.4; N, 7.3.

IX showed infrared absorptions (smear) at 5.8, 6.06, and 6.3 μ. The n.m.r. spectrum (neat) showed singlets at 1.45 (protons of methyl groups attached to the ring), 1.75 and 1.82 (protons of methyl groups attached to a double bond), 2.70 (methyl protons of dimethylamino group), and 5.62 p.p.m. (olefinic proton).

Anal. Calcd. for $C_{12}H_{19}NO_2$ (IX): C, 68.8; H, 9.1; N, 6.7. Found: C, 68.5; H, 9.2; N, 6.9.

4-(Dimethylamino)-3,6-dihydro-6-isopropylidene-3,3-dimethyl-2H-pyran-2-one (IX).—Under a nitrogen atmosphere, 61.5 g. (0.88 mole) of dimethylketene was added to a stirred solution of 50.0 g. (0.435 mole) of 1-ethoxy-N,N-dimethylvinylamine in 300 ml. of acetonitrile. The temperature of the exothermic reaction was kept between −10 and +10° by intermittent use of a Dry Ice–acetone bath. Stirring was continued for 2 hr. The reaction mixture was filtered to remove some polymeric material, and the filtrate was distilled through a 12-in. packed column to give 64.5 g. (71%) of IX, b.p. 107–108° (0.95 mm.), $n^{20}\mathrm{D}$ 1.5452.

Hydrolysis of XIII.—A mixture of 5 g. of IX and 15 ml. of 10% hydrochloric acid solution was warmed on a steam bath for 1 hr. Carbon dioxide evolved and an oily layer separated. The mixture was extracted with 50 ml. of ether, and the organic layer was washed successively with water, sodium bicarbonate solution, and again with water, and then dried over anhydrous magnesium sulfate solution. The solvent was removed *in vacuo* to give 3.0 g. of residue which was shown by g.l.c. to be virtually pure 2,6-dimethyl-3,5-heptanedione (X). Infrared absorptions (smear) were at 5.86 and 6.22 μ. The n.m.r. spectrum (neat) showed a doublet at 1.12 (methyl protons of two isopropyl groups), a septet at 2.42 (methylidyne protons of two isopropyl groups), and singlets at 5.45 (olefinic proton) and 15.47 p.p.m. (enolic hydroxy proton).

4-(Dimethylamino)-5,6-dihydro-6-methylene-2H-pyran-2-one (XI) and 4-(Dimethylamino)-6-methyl-2H-pyran-2-one (XII).—Ketene (17.2 g., 0.42 mole) was passed into a stirred solution of 40.0 g. (0.35 mole) of 1-ethoxy-N,N-dimethylvinylamine in 200 ml. of ether at 0–5°. While the reaction mixture was stirred at room temperature for 2 hr., a solid slowly precipitated. This material weighed 15.2 g. (71% based on ketene) and melted at 129–131°. Recrystallization from toluene gave 12.2 g. of yellow solid. When the melting point was taken slowly, the compound melted at 129–131°, but when a sample was introduced into a melting point bath preheated to 120°, it melted, resolidified, and then melted again at 129–131°. The n.m.r. spectrum (CH_2Cl_2) showed the original material to be a mixture containing about 40% XI and 60% XII. The portion of the spectrum due to XI showed a singlet at 3.04 (methyl protons of dimethylamino group) and finely split singlets at 3.46 (protons of methylene group), 4.72 (protons of vinylidene group), and 4.48 p.p.m. (olefinic proton). The portion of the spectrum due to XII showed singlets at 2.20 (methyl protons) and 3.06 (methyl protons of dimethylamino group), and finely split singlets at 4.92 (olefinic proton) and 6.05 p.p.m. (olefinic proton). The infrared absorptions (KBr) for XI and XII were at 5.95, 6.10, 6.30, and 6.45 μ.

Anal. Calcd. for $C_8H_{11}NO_2$ (XI and XII): C, 62.7; H, 7.2; N, 9.2. Found: C, 62.9; H, 7.5; N, 9.2.

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Further Studies on 2,5-Cyclohexadienones Containing the Trichloromethyl Group[1]

MELVIN S. NEWMAN AND JOHN A. EBERWEIN[2]

The Evans Chemistry Laboratory, Columbus, Ohio 43210

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The products of reactions of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone with phenyl-, methyl-, and ethoxyethynylmagnesium bromide and of 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone with ethoxyethynylmagnesium bromide are described. In no case could the expected carbinol be isolated, since rearrangements occurred under mild conditions. In all cases 1,3- or 1,5-migration of the trichloromethyl groups occurred.

We have been interested in the rearrangements which 4-methyl-4-trichloromethyl-2,5-cyclohexadienols and the corresponding dienones undergo.[3-8] The work described herein was undertaken to gain further knowledge of the rearrangements which can occur in these types of compounds.

When 4-methyl-1-phenyl-4-trichloromethyl-2,5-cyclohexadienol was treated with formic acid, *p*-methylbiphenyl, 3-methyl-4-trichloromethylbiphenyl, and 2-methyl-4-phenylbenzoic acid were formed.[6] However, when 3,4-dimethyl-2,5-cyclohexadienone (I) was

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