yellow liquid. Dried 12 hr. over phosphoric anhydride, the liquid weighed 2.3661 g. Its infrared spectrum was identical to that of 1,3-propanesultam.

Acknowledgment.—We are indebted to Mr. P. Waszeciak, who prepared a sample of chromatographically pure propanesultam by fractional melting. We also acknowledge with thanks the assistance of Dr. Sidney Siggia, Director of the Olin Central Analytical Laboratories, and his staff for the microanalyses, infrared spectra, intrinsic viscosities, and v.p.c. results reported.

Notes

The Condensation of Acetone with Dimethylfulvene[1]

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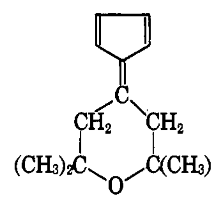
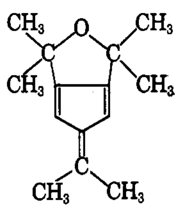
While it has been recognized for many years that cyclopentadiene will condense with more than one mole of acetone under basic conditions, it is noteworthy of the complexity of the chemistry of these compounds that no adequate proof of structure of the condensation product(s) has ever been given.[2] Thiele and Balhorn[3] reported that cyclopentadiene reacted with three equivalents of acetone and that dimethylfulvene reacted with two equivalents of acetone to give I, a structure assigned solely on the basis of elemental analysis.


I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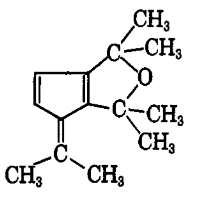

III

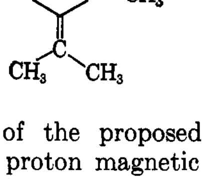
Subsequently, Ziegler and Crossman[4] modified the structure to either II or III on the basis of the related reaction of dimethylfulvene with anisaldehyde. Their argument rested on the observation that the condensation product of anisaldehyde with dimethylfulvene did not involve reaction with the methyl groups at the 6-position. Only one mole equivalent of anisaldehyde entered into the reaction.

The preparation of dimethylfulvene by the reaction of cyclopentadiene and acetone in the presence of alcoholic potassium hydroxide[5] always leads to the formation of a considerable amount of higher boiling material. Careful fractional distillation of the material at reduced pressures produced one main product (an orange oil) plus a large amount of tar. The same product was isolated when dimethylfulvene reacted with acetone in alcoholic potassium hydroxide. As will be seen subsequently, this product resulted from the addition of one mole of acetone to dimethylfulvene. Numerous repetitions of the preparation of dimethylfulvene and of the subsequent reaction of this with acetone failed to yield any evidence of a product corresponding to the condensation of two molecules of acetone per one molecule of dimethylfulvene.

The chemical analysis and hydrogenation equivalent of the condensation product from dimethylfulvene and acetone established the formula as $C_{11}H_{16}O$ with three double bonds in the molecule. The infrared spectrum indicated the presence of a hydroxyl group.

The hydrogenated product was a colorless oil, the analysis of which agrees with the formula $C_{11}H_{22}O$. This material also had a strong hydroxyl band in the infrared. The position of attachment was elucidated by subjecting the hydrogenated product to dehydration and ozonolysis yielding 3-isopropylcyclopentanone.

While these data locate the position of the acetone moiety at C-2 on the fulvene ring, the possible location of the three double bonds requires further information. The fact that the ultraviolet absorption spectra of the condensation product and of dimethylfulvene show maxima at 267 mμ (ϵ 1.8×10^4 and 2.2×10^4, respectively) suggests similar conjugated structures for both compounds. This would give structure IV as the correct formula for the condensation product.


IV

Confirmation of the proposed structure was obtained from the proton magnetic resonance spectrum of the condensation product. The following absorptions and their respective integrated proton values were observed in a 10% carbon tetrachloride solution: (1) the ring protons consisting of doublet at τ 3.61 (two protons) and a triplet at τ 3.86 (one proton); (2) a broad weak peak at τ 7.15 which was variable in position with dilution was attributed to the hydroxyl hydrogen; (3) a sharp band at τ 7.91 (6 protons); and (4) a similar band at τ 8.61 (6 protons). A detailed examination of the ring-H resonances revealed a typical AB_2 spectrum where $\sigma_A < \sigma_B$; $\nu_0\delta = -13.5$ c.p.s. The observed spectrum was analyzed by means

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[1] Presented at the Southwest Regional Meeting of the American Chemical Society, Dallas, Tex., December 7, 1962.

[2] J. H. Day, *Chem. Rev.*, **53**, 167 (1953).

[3] J. Thiele and H. Balhorn, *Ann.*, **348**, 1 (1906).

[4] K. Ziegler and F. Crossman, *ibid.*, **511**, 89 (1934).

[5] G. Crane, C. E. Boord, and A. L. Henne, *J. Org. Chem.*, **67**, 1237 (1945).

of Corio's tables.[6] A good fit for the AB_2 case for both line position and intensity was found for $J_{AB}/\nu_0\delta$ equal to 0.15. On this basis, the value of J_{AB} = 2.0 c.p.s. These data are all consistent with the structure of the condensation product as 2-(1-hydroxy-1-methylethyl)-6,6-dimethylfulvene (IV).[7]

Experimental

Reaction of Acetone with Cyclopentadiene.—The reaction of 181 g. of freshly prepared cyclopentadiene, 160 g. of acetone, and 69 ml. of 20% potassium hydroxide in ethanol was carried out as directed by Crane, Boord, and Henne.[5] After standing overnight in an icebox, the mixture was poured into a large volume of water. The total mixture was then extracted with several portions of ether. The combined extract was dried over magnesium sulfate, and, after filtration, the ether was removed by distillation through a 34-cm. Vigreux column. The residue was then distilled through the same column at 8 mm. yielding the following fractions: 124 g. of dimethylfulvene, b.p. 40–43°; and 9.7 g. of orange oil with $n^{25}D$ 1.5425, b.p. 118–120°. The remaining material was a nondistillable tar.

Reaction of Dimethylfulvene with Acetone.—Dimethylfulvene (123 g.), 102 g. of acetone, and 100 ml. of 11% potassium hydroxide in ethanol reacted with stirring at 0° overnight. The reaction mixture was worked up as described in the preceding reaction, and the product distilled (8 mm.) as follows: b.p. 110–124° (mostly 118–124°), 4.7 g. of orange oil with $n^{25}D$ 1.5438. The infrared spectra of this material was identical with that of the material reported in the previous reaction.

Characterization and Degradation of the Orange Oil.—The orange oil, b.p. 118–120° (8 mm.), $n^{25}D$ 1.5425, showed a strong hydroxyl band in the infrared at 2.98 μ. The hydrogenation equivalent was determined using Adam's platinum catalyst in ethanol: calcd. for $C_{11}H_{16}O$ with three double bonds, 54.8; found, 56.6. The compound in ethanol showed a maximum at 267 mμ (ϵ 2.2 × 10^4). The n.m.r. spectrum was determined in carbon tetrachloride solution (tetramethylsilane as an internal reference) with a Varian A-60 instrument, and the observed absorptions are given in the text.

Anal.[8] Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.59; H, 9.80.

A sample of this material was readily hydrogenated in ethanol using a 5% palladium-on-charcoal catalyst. Work-up of the product in the usual fashion and distillation through a semimicro column gave a colorless oil, b.p. 83–86° (6 mm.), $n^{25}D$ 1.4670, with a strong band in the infrared at 2.92 μ.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.74; H, 13.13.

The saturated alcohol (6 g. of alcohol mixed with 0.6 g. of piperadine) was dehydrated by slow passage in a stream of nitrogen through a vertical 18-cm. column of 8-mesh alumina heated to *ca.* 355°. The product condensed as a light yellow oil which was taken up in ether, washed with dilute hydrochloric acid, and dried over magnesium sulfate. After filtration, the ether was removed by distillation through a short Vigreux column. The residue was distilled through a semimicro Vigreux column to give a mixture of olefins (2.8 g.), b.p. 146–150°. The strong infrared band at 11.3 μ indicated that the major component contained a terminal double bond and, from subsequent data, was presumably 3-isopropenylisopropylcyclopentane. This component was isomerized to 3-isopropylideneisopropylcyclopentane by treating the olefin mixture on a steam bath for 2 hr. with 0.1 g. of *p*-toluenesulfonic acid. It was noted at this time that the 11.3-μ band had disappeared from the spectrum.

The crude olefin mixture was taken up in 25 ml. of methylene dichloride, washed with diluted sodium bicarbonate, and ozonized in a stream of ozonized air until saturated. Excess ozone was removed in a stream of nitrogen. The ozonide(s) was decomposed by stirring the solution with 3 ml. of 30% hydrogen peroxide in 22 ml. of 10% potassium hydroxide. Water (25 ml.) was added, and the organic layer was removed. The aqueous layer was further extracted with methylene dichloride. The methylene dichloride extracts were combined and dried, and the solvent was removed by distillation.

An authentic sample of 3-isopropylcyclopentanone was prepared by the hydrogenation of 3-isopropenylcyclopentanone[9] using Adam's platinum in ethyl acetate: b.p. 94–97° (34 mm.), $n^{22}D$ 1.4461; lit.[10] b.p. 183° (761 mm.), $n^{18}D$ 1.4443. The infrared spectrum of the compound indicated the absence of the unsaturated starting material. Analysis by v.p.c. indicated 95% purity.

The crude ozonization product was fractionated by v.p.c. using a 12-ft. silicone column. In this fashion, it was shown that the reaction mixture consisted of a major band corresponding in retention time to authentic 3-isopropylcyclopentanone plus several smaller bands. The band corresponding in retention time to authentic 3-isopropylcyclopentanone was trapped, $n^{18}D$ 1.4443. The infrared spectrum of this material was identical with that of the authentic sample; strong bands were observed at 1750, 1475, 1412, 1390, 1375, 1160, and 820 cm.$^{-1}$.

For comparison purposes an authentic sample of 2-isopropylcyclopentanone was prepared by the method of Cornubert and Borrel.[11] The retention time and infrared spectrum were decidedly different from the 3-isopropyl isomer (strong bands at 1750, 1475, 1412, 1390, 1375, 1275, 1195, 1160, 935, and 830 cm.$^{-1}$).

Acknowledgment.—This work was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is extended to the donors of this fund. We also would like to express our appreciation to the Robert A. Welch Foundation whose generosity made available the Varian A-60.

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[6] P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

[7] Recently, D. M. Fenton, and M. J. Hurwitz, *J. Org. Chem.*, **28**, 1646 (1963), established that, when dimethylfulvene and acetone are refluxed in methanolic potassium hydroxide, one obtains 3-isopropenyl-6,6-dimethylfulvene, a result in agreement with our findings.

[8] Microanalysis by Galbraith Laboratories, Knoxville, Tenn.

[9] C. Djerassi and B. Tursch, *J. Org. Chem.*, **83**, 4609 (1961).

[10] G. Burger and A. K. Macbeth, *J. Chem. Soc.*, 145 (1946).

[11] R. Cornubert and C. Borrel, *Bull. soc. chim. France*, 958 (1930).

Dipicolinoyl- and Di(6-acetylpicolinoyl)furoxans[1]

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The reaction of acetophenone and nitric acid has been known since 1887.[2] The formation of dibenzoylfuroxan as the main product by dimerization of benzoylnitrile N-oxide has been proposed,[3] and recently a minor product in this reaction has been assigned the structure of the dibenzoate ester of bis(benzoylformaldoximino)furoxan.[4] In similar work with thiophene derivatives, bis(3-thianaphthenoyl)furoxan[5] and di-(2-thenoyl)furoxan[6] have been prepared. The present work has been directed towards a study of the reaction of nitric acid with acetylpyridine isomers and 2,6-diacetylpyridine.

As weak bases, acetylpyridine isomers form salts with mineral acids. Experimental results indicate that the formation of acetylpyridine nitrates occurs along with nitrosation and oxidation. From either 3- or 4-acetylpyridine and nitric acid, both the formation of the corresponding nitrate salt and oxidation to the cor-

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[1] This work was supported by the Foundational Research Program of the Bureau of Naval Weapons.

[2] A. F. Holleman, *Ber.*, **20**, 3359 (1887).

[3] H. R. Snyder and N. E. Boyer, *J. Am. Chem. Soc.*, **77**, 4233 (1955).

[4] J. H. Boyer and M. S. Chang, *ibid.*, **82**, 2220 (1960).

[5] D. A. Shirley, B. H. Gross, and M. J. Danzig, *J. Org. Chem.*, **23**, 1024 (1958).

[6] M. S. Chang and A. J. Matuszko, *ibid.*, **26**, 5239 (1961).