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THE STRUCTURE OF THE BASE CATALYZED CONDENSATION PRODUCT OF DIMETHYLFULVENE WITH ACETONE

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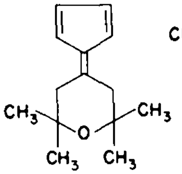
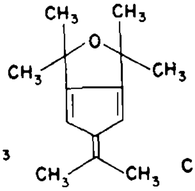
Abstract—The structure of the sodium ethoxide catalyzed condensation product of dimethylfulvene with acetone is shown to be 3-(dimethylethoxy)methyl-6,6-dimethylfulvene (V).

IN the course of his classical work on fulvenes, Thiele[1] found that the condensation of dimethylfulvene with acetone in the presence of sodium ethoxide yielded a reddish-orange oil which analyzed roughly for $C_{14}H_{20}O$. Thiele did not enter into a rigorous structural determination of this product, but assigned to it tentatively structure I.

In 1934 Ziegler and Crossman[2] made the logical suggestion that such structures as II and III should also be considered as possibilities for the reddish-orange oil. Fairly recently, however, structure IV has also been put forward as a possibility,[3] although such an expression clearly violates Bredt's rule.



I



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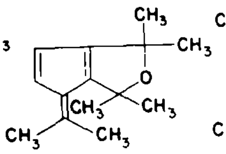

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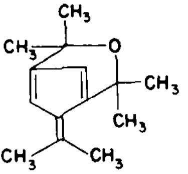

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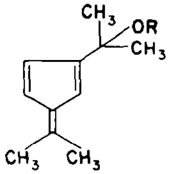
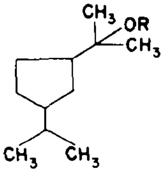
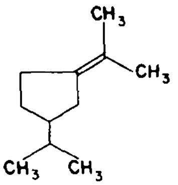


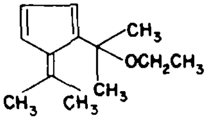
V, R = O–CH₂–CH₃
VI, R = O–CH₃



VII, R = O–CH₂–CH₃
VIII, R = O–CH₃



IX



X

The condensation product was isolated as a rather unstable reddish-orange oil which tended to polymerize on standing and had to be kept under nitrogen at near 0°. Repeated elemental analyses on the compound indicated that it analyzed best not

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

[2] K. Ziegler and F. Crossmann, *Liebigs Ann.* **511**, 89 (1934).

[3] E. D. Bergmann, *Progress in Organic Chemistry.* 3 pp. 109–110. Academic Press, New York (1955).

for the expected $C_{14}H_{20}O$, but rather for $C_{13}H_{20}O$, thus eliminating structures I to IV as possibilities. A Rast molecular weight determination confirmed this new molecular formula.

The U.V. spectrum of the condensation product, $\lambda_{\max}^{\mathrm{EtOH}}$ 267 mμ (log ϵ 4·10), was found to be very similar to that of dimethylfulvene itself, $\lambda_{\max}^{\mathrm{EtOH}}$ 266 mμ (log ϵ 4·25), indicating that the conjugated system in the two compounds was essentially the same. The I.R. spectrum exhibited no hydroxyl or carbonyl absorption, but showed peaks at 6·1 μ (C=C), and 8·65 μ (aliphatic ether). Furthermore, the condensation product was found to absorb three moles of hydrogen, two rapidly and a third slowly, on catalytic hydrogenation at room temperature to yield a saturated hexahydro derivative. Ozonization of the condensation product gave a 67% yield of acetone isolated as the 2,4-dinitrophenylhydrazone derivative.

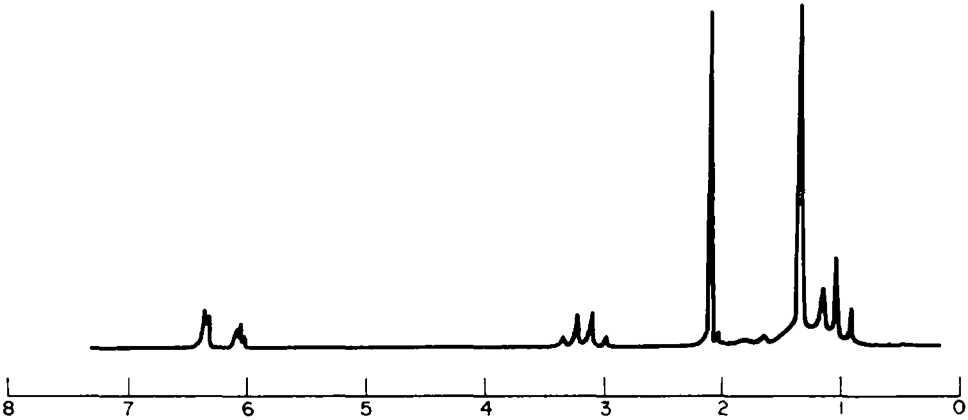

FIG. 1

It was also found that the N.M.R. spectrum of the condensation product V (Fig. 1) showed the characteristic triplet and quadruplet peaks of an ethoxy group centered at 1·05 and 3·17 p.p.m. respectively (T.M.S., internal standard, taken as 0). In addition two singlets, each representing six protons at 1·38 and 2·12 p.p.m., indicated the presence of two C-methyls and one isopropylidene function respectively. The presence of the ethoxyl group in the condensation product was also confirmed by an ethoxyl determination on the hexahydro compound VII. The N.M.R. spectrum of V, when compared to that of the hexahydro derivative VII, clearly indicated the presence of an ethyl-t-butyl type ether in both compounds since the number of protons on the carbons *alpha* to the ether oxygen did not increase upon hydrogenation, but remained constant at two. On the basis of the above data structure V became a possibility for the condensation product, while the hexahydro derivative could be represented by VII.

In an effort to further simplify the N.M.R. spectrum, the condensation reaction was run using sodium methoxide instead of ethoxide. Again a reddish-orange oil was obtained which this time analyzed for $C_{12}H_{18}O$ and which was tentatively assigned structure VI. The N.M.R. spectrum of this new condensation product showed three peaks in the high field region. The six isopropyl protons were represented by a singlet corresponding to six protons at 1·35 p.p.m., the six isopropylidene protons showed up at 2·12 p.p.m., and the three methoxyl protons were found at 2·98 p.p.m. The absorption in the vinylic region was identical to that obtained for compound V. In analogy to V, the condensation product VI could also be catalytically reduced to the hexahydro derivative VIII.

To ascertain the correctness of expressions V and VI for the condensation products, the two hexahydro derivatives VII and VIII were treated separately first with hydrogen iodide, and then with potassium t-butoxide in t-butyl alcohol. The products resulting from this identical treatment gave practically superimposable I.R. spectra as expected, showing that both samples are identical and represented by structure IX. The 3-isopropylideneisopropylcyclopentane (IX) was characterized by means of a mass spectrographic analysis which showed (in terms of m/e) a parent peak at 152 corresponding to the total mass of the assigned structure, a large peak at 109 corresponding to the loss of the isopropyl group (M-43), and another large peak at 43 corresponding to the isopropyl group itself. The N.M.R. spectrum of IX showed the six isopropylidene protons at 1·70 p.p.m. However, because of the lack of symmetry in the molecule and the somewhat restricted rotation of the isopropyl function, this last group was not represented by a clear doublet, but showed an unsymmetrical doublet centered at 1·00 p.p.m. ($J = 10$ cps) which integrated for six protons.

Ozonization of IX followed by distillation of the product through a spinning band column gave a colourless liquid which appeared to be 3-isopropylcyclopentanone. The I.R. spectrum of this compound showed a carbonyl peak at 5·73 μ characteristic of a five membered ring ketone. Furthermore, the compound had a refractive index and gave a semicarbazone derivative that checked with the corresponding values for authentic 3-isopropylcyclopentanone recorded in the literature.

However, since the physical properties of 3-isopropylcyclopentanone and its semicarbazone derivative are very close to those for the isomeric 2-isopropylcyclopentanone (see Table), it was necessary to differentiate between these two possibilities Authentic 2-isopropylcyclopentanone was synthesized therefore via the base catalyzed. condensation of acetone with cyclopentanone followed by catalytic hydrogenation of the product. The 2-isopropylcyclopentanone thus obtained had an I.R. spectrum identical to that already recorded for it in the literature,[4] but different from that of the 3-isopropylcyclopentanone obtained in this study. Furthermore, the two ketones had different retention times in a gas chromatographic analysis, and their respective semicarbazone derivatives exhibited a definite depression in a mixture melting point

TABLE 1. PHYSICAL CONSTANTS OF 2-ISOPROPYL AND 3-ISOPROPYL-CYCLOPENTANONE AND DERIVATIVES

	n_D		b.p.		m.p. Semicarbazone	
	Found	Lit.	Found	Lit.	Found	Lit.
2-Isopropyl-cyclopentanone	1·4423 at 24°	1·4438[5] at 20°	59–60°/10 mm	62–64/11 mm[5]	188·5–189·5	190°–191° [4]
3-Isopropyl-cyclopentanone	1·4405 at 26°	1·4428[6] at 21°	68–69°/14 mm	78/17 mm[7]	189°	192° [7]

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[4] T. Onogaki, *J. Chem. Soc. Japan* **83**, 206 (1962).

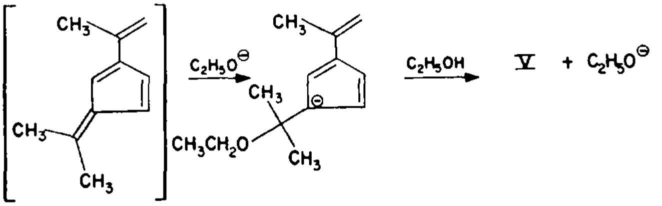
[5] W. Hückel and G. Näher, *Ber. Dtsch. Chem. Ges.* **91**, 792 (1958).

[6] O. Wallach, *Liebigs Ann.* **388**, 59 (1912).

[7] O. Wallach, *Liebigs Ann.* **384**, 204 (1911).

determination. Thus the characterization of 3-isopropylcyclopentanone as a degradation product conclusively proves the correctness of expression V for the condensation product first obtained by Thiele, and eliminates the alternate possibility X.

Mechanistically, the formation of V can be explained in terms of 3-isopropenyldimethylfulvene (XI) as a reaction intermediate which adds the elements of ethyl alcohol in accordance with the following sequence:



EXPERIMENTAL

The I.R. spectra of the pure liquids were taken as films and the solids as KBr discs on a Beckmann I.R.-5A spectrometer; the U.V. spectra were measured in 95% ethanol on a Cary-14 spectrometer; the N.M.R. spectra were taken on the pure liquids on a Varian A-60; and the mass spectrometer measurements were obtained using a Bendix 14-101. All m.p.s are uncorrected.

Preparation of 3-(*dimethylethoxy*)*methyl*-6,6-*dimethylfulvene* (V)

To 330 g of dimethylfulvene[8] was added 180 g of distilled acetone, and to this mixture was added 200 ml of a 5% solution of sodium ethoxide in ethyl alcohol. The mixture was allowed to stand overnight under nitrogen. The product was extracted with 200 ml ether and sufficient water was added to dissolve the base. After extraction the product was dried over sodium sulfate. It was always necessary to store the product under nitrogen near 0° to preclude polymerization. The product was filtered and vacuum distilled on a spinning band column (b.p. 120° at 15 mm). The yield was 41 g or 6·9%. (Found: C, 81·24; H, 10·27; Rast mol. wt. 194. $C_{13}H_{20}O$ requires: C, 81·20; H, 10·41%; mol. wt. 192). I.R. peaks at 6·10, and 8·65 μ. $n_D^{26} = 1{\cdot}5277$.

Preparation of 3-(*dimethylmethoxy*)*methyl*-6,6-*dimethylfulvene* (VI)

The above procedure was followed except that a 5% solution of sodium methoxide in methanol was used. The product had b.p. 110–112° at 15 mm. The yield was 8·5%. (Found: C, 80·45; H, 9·82; Rast mol. wt. 181. $C_{12}H_{18}O$ requires: C, 80·85; H, 10·18%; mol. wt. 178). I.R. peaks at: 6·1, 6·95, and 8·60 μ; $n_D^{26} = 1{\cdot}5256$.

Ozonolysis of V

The following procedure is a modification of the method of Halsall *et al.*[9] Into the sample tube of the ozonizer was placed 3·60 g condensation product V and 60 ml purified chloroform. Ozone was passed through for a period of 2 hr during which time it was necessary to add an additional 15 ml chloroform. The ozonized mixture was placed in a 1 l., three necked, round bottomed flask equipped with an upright condenser. There was added 250 ml water containing 10 g zinc dust and the system was refluxed for 30 min. The flask was then connected to a horizontal condenser and the mixture steam distilled into a 2 l. Erlenmeyer flask. The vapors were allowed to bubble directly through a dimedone solution. Both the chloroform layer and the formaldehyde dimedone (40 mg, equivalent to a 0·7% yield) which separated from the aqueous phase were discarded, and a 2,4-dinitrophenylhydrazine solution added to the aqueous phase. A yellowish precipitate appeared. This material was collected and recrystallized from hot 95% ethanol. The crystalline material (3·2 g, equivalent to a 67% yield) which separated from the solution was collected and dried in *vacuo* at room temp for 12 hr. A mixture m.p. of this compound and known acetone 2,4-dinitrophenylhydrazone was taken and found to be 125–126°, identical with that of the authentic material.

[8] J. Thiele, *Ber. Dtsch. Chem. Ges.* 33, 671 (1900).

[9] T. G. Halsall, H. R. Arthur and R. D. Smith, *J. Chem. Soc.* 2605 (1958).

Preparation of 3-*(dimethylethoxy)methylisopropylcyclopentane* (VII)

To 6·9 g V was added 0·17 g platinum dioxide and the mixture placed in a Parr hydrogenator using ethyl alcohol as solvent. The hydrogenation was allowed to run for 48 hr. The uptake of the first two moles of hydrogen occurred during the first 2 hr. The product was filtered, and distilled on a spinning band column (b.p. 104 at 15 mm). The yield was 4·8 g or 67·5%. (Found: C, 78·93; H, 12·87; Rast mol. wt. 201; —OCH_2CH_3, 20·8. $C_{13}H_{26}O$ requires: C, 78·72; H, 13·21%; mol. wt. 198; —OCH_2CH_3, 22·6). I.R. peaks at 3·40, 6·82, and 8·88 μ; n_D^{24} = 1·4420.

Preparation of 3-*(dimethylmethoxy)methylisopropylcyclopentane* (VIII)

The above procedure was followed using the methoxy compound VI. The product distilled at 96° at 15 mm. The yield was 68%. (Found: C, 78·43; H, 13·04. $C_{12}H_{24}O$ requires: C, 78·19; H, 13·13%). I.R. peaks at 3·40, 6·82, and 8·90 μ; n_D^{26} = 1·4585.

Preparation of 3-*isopropylideneisopropylcyclopentane* (IX)

(a) Two grams of the saturated product VII was refluxed with 10 ml of 57% hydrogen iodide for 24 hr. The heterogeneous mixture was stirred continuously during the refluxing. At the end of this period the alkyl iodide was drawn off with a pipette and washed with water. It was then heated with 10 ml of 1·86N potassium t-butoxide in 30 ml of t-butyl alcohol for 3 hr. Sufficient water was then added to dissolve the potassium iodide which had formed, and the hydrocarbon extracted with 50 ml of ether. The ether solvent was removed on a flash evaporator and the residue distilled through a spinning band column at red press (b.p. 75° at 15 mm). The yield was 0·9 g or 58·5%.

(b) Starting with the saturated methoxy compound VIII essentially the same procedure as outlined above was followed. The yield was 75·5%. The I.R. spectra of the products of these two procedures, (a) and (b), were identical. (Found: C, 86·62; H, 13·26. $C_{11}H_{20}$ requires: C, 86·76; H, 13·24). I.R. peaks at 3·50, 6·95, 7·37, and 9·05 μ; n_D^{26} = 1·455C.

Ozonolysis of IX *to* 3-*isopropylcyclopentanone*

Five grams of the olefin IX was dissolved in 50 ml spectrograde chloroform and ozonized for 4 hr. Completion of the ozonization was determined with potassium iodide starch paper. Water was then added to destroy the ozonide, the organic layer separated, and the choroform removed on a flash evaporator. The residue was distilled using an 18 in spinning band column at red press.

Preparation of 2-*isopropylcyclopentanone*

The following modified procedure of Hückel and Näher[5] was used. To 12 g 2-isopropylidenecyclopentanone[10] in ethanol was added 600 mg 5% Pd on carbon. The mixture was placed in a Parr hydrogenator and hydrogenated for 3 hr at an initial pressure of 30 lbs/in². After filtration and evaporation of the solvent, the product was purified by distillation through an 18 in. spinning band column at red press. The yield was 8·9 g or 73%.

Gas chromatography of isomeric isopropylcyclopentanones

An F & M. Model 202 gas chromatograph was used. The column packing was 80/100 mesh Gas Chrom S with 15% Carbowax 1000. The column length was 5 ft, the column temp 100°, and the injection point temp 200°. The helium flow rate was 90 ml/min, the 2-isopropylcyclopentanone peak appeared after 13·6 min, and the 3-isopropylcyclopentanone peak after 20·6 min.

Acknowledgements—We wish to express our appreciation to the National Science Foundation for a research grant (NSF-G10032), and to the United States Army Civil Schooling for the support of Captain R. B. Henry.

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[10] G. Vavon and A. Apchié, *Bull. Soc. Chim. Fr.* **43**, 667 (1928).