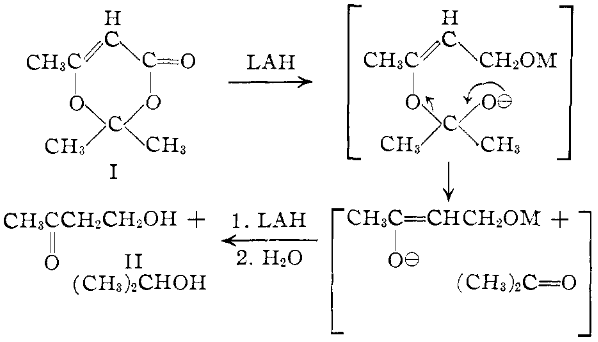
the reduction of the adduct with lithium aluminum hydride was carried out in order to obtain further evidence relating to the structure.

It has been shown[1,4] that the reduction of a dioxolanone with lithium aluminum hydride yields cleavage products, *i.e.*, a glycol and an alcohol. Since structure I is analogous to that of a dioxolanone the following reduction mechanism was postulated



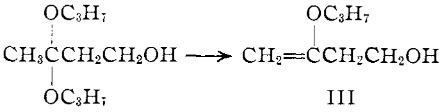
The reaction between the diketene–acetone adduct and lithium aluminum hydride gave two fractions: (a) b.p. 82–84°, and (b) b.p. 42–48° (30 mm.), $n^{25}\text{D}$ 1.419. The lower boiling fraction (a) was identified as the expected propanol-2 by its physical properties and the identity of its phenylurethan with an authentic sample.

The higher boiling fraction (b) was shown not to be the expected 3-keto-1-butanol (II) but was identified as 3-isopropoxy-3-buten-1-ol (III) by its analysis, infrared absorption spectrum and its physical and chemical properties. The absorption spectrum contained a band characteristic of a hydroxy group and bands characteristic of a vinyloxy group.[5]

The reactions between fraction (b) and the appropriate reagents gave an α-naphthylurethan and a 2,4-dinitrophenylhydrazone whose analyses were in agreement with those of the corresponding derivatives of II. The preparation of the carbonyl derivative is of interest in view of the report that the reaction of II with phenylhydrazine yields 2-phenyl-5-methylpyrazoline rather than the phenylhydrazone.[6] Fraction b gives a positive haloform reaction.

The vinyl ether structure III for fraction b is supported by the fact that vinyl alkyl ethers react with reagents for determining carbonyl groups and, in fact, these reactions are the basis for the analytical determination of such compounds.[7]

It has been reported that the dimethyl ketal of II is unstable and upon distillation reverts to 3-methoxy-3-buten-1-ol.[8] It is therefore logical to postulate that the expected reduction products, isopropyl alcohol and 3-keto-1-butanol (II), react to form the diisopropyl ketal of II which undergoes thermal decomposition to yield III.



$$CH_3\overset{OC_3H_7}{\underset{OC_3H_7}{C}}CH_2CH_2OH \longrightarrow \underset{III}{CH_2{=}\overset{OC_3H_7}{C}CH_2CH_2OH}$$

Since none of the other structures postulated for the diketene–acetone adduct[3] would be expected to yield the indicated reduction products, structure I appears to be correct for the adduct.

Experimental

A solution of 50 g. (0.35 mole) of the diketene–acetone adduct[9] in 50 ml. of ether was added over one hour to 15 g. (0.39 mole) of lithium aluminum hydride in 500 ml. of ether. The mixture was refluxed for an additional 1.5 hours and decomposed by the successive addition of 15 ml. of water, 15 ml. of 15% sodium hydroxide and 45 ml. of water. The mixture was filtered, the filter cake extracted with ether and the ether layers combined. The filter cake contained a white crystalline solid, not further identified, intermixed with the inorganic salts. The combined ether extracts were dried over magnesium sulfate and distilled through a Vigreux column to yield two fractions: (a) 10 g. (48% yield) of isopropyl alcohol, b.p. 82–84°, identified through the phenylurethan, and (b) 11 g., b.p. 42–48° (30 mm.), $n^{25}\text{D}$ 1.419.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.61; H, 10.77. Found: C, 65.01; H, 11.11.

The α-**naphthylurethan** of fraction b was the derivative of 3-keto-1-butanol.

Anal. Calcd. for $C_{15}H_{15}NO_3$: C, 70.04; H, 5.84. Found: C, 69.96; H, 5.69.

The **2,4-dinitrophenylhydrazone** of fraction b was the derivative of 3-keto-1-butanol.

Anal. Calcd. for $C_{10}H_{12}N_4O_5$: C, 44.78; H, 4.48. Found: C, 45.18; H, 4.22.

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[4] N. G. Gaylord and J. A. Snyder, *Chemistry & Industry*, 1234 (1954).

[5] R. L. Adelman, This Journal, **77**, 1669 (1955).

[6] K. von Auwers and H. Broche, *Chem. Ber.*, **55**, 3907 (1922).

[7] M. G. Voronkov, *Zhur. Anal. Khim.*, **1**, 218 (1946); *C. A.*, **41**, 3714 (1947); M. F. Shostakovskiĭ and E. N. Prilezhaeva, *J. Gen. Chem.* (*U.S.S.R.*), **17**, 1129 (1947); *C. A.*, **42**, 3633 (1948); M. F. Shostakovskiĭ and N. I. Uvarova, *Zhur. Anal. Khim.*, **6**, 348 (1951); *C. A.*, **46**, 2963 (1952).

[8] G. F. Hennion and W. S. Murray, This Journal, **64**, 1220 (1942).

[9] Aldrich Chemical Company, Inc., Milwaukee, Wis.

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Conjugative Effects of Cyclopropane Rings. III. Spectroscopic Properties of 1-Acetyl-2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropane[1]

By Richard H. Eastman[1] and Stanley K. Freeman[2]

Received September 6, 1955

Attachment of a cyclopropane ring to a carbonyl group modifies the ultraviolet absorption characteristics in two ways: the intensity of the weak $n \rightarrow \pi$ band[3] near 280 mμ is increased about twofold and the position of maximum absorption of the N_1, V_1 band[3] is shifted from its position at *ca.* 190 mμ in simple ketones to 210–215 mμ. Attachment of a vinyl group to the carbonyl group produces similar modifications in the spectrum of the carbonyl group and the electronic effect of the cyclopropane ring has been likened[4] to that of the vinyl group on this basis. It has been of interest to inquire to what extent the unsaturation electrons of the cyclopropane ring[5] partake of the character of π-electrons

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[1] Work done in the Department of Chemistry and Chemical Engineering, Stanford University, Stanford, California.

[2] Benzol Products Company, Newark 5, N. J.

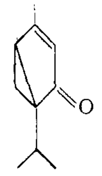
[3] Harden McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

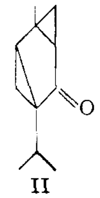
[4] For references to earlier work see Papers I and II of this series: R. H. Eastman, This Journal, **76**, 4115 (1954), and R. H. Eastman and J. C. Selover, *ibid.*, **76**, 4118 (1954).

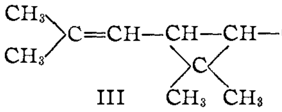
[5] The unsaturation electrons of the cyclopropane ring share the property of π-electrons in general of forming complexes with metal ions; C. F. H. Tipper, *J. Chem. Soc.*, 2045 (1955).

in polar systems in general. The ultraviolet absorption of umbellulone (I) has been taken as evidence[4] that a cyclopropane ring partakes of the character of a vinyl group when the ring is at the *end* of a chain of conjugation,[6] but the spectrum of the tricyclic ketone II indicated that the cyclopropane ring does not function as a central transmitting group analogous to a vinyl group in a chain of conjugation.[4]

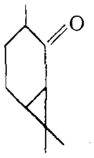
We have now prepared the ketone III to determine whether in this system the cyclopropane ring might function as a vinyl group in connecting the olefinic and carbonyl chromophores.[7]

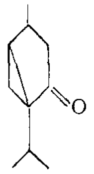

I


II


$\mathrm{(CH_3)_2C{=}CH{-}\underset{\overbrace{C(CH_3)_2}}{CH{-}CH}{-}COCH_3}$

III


IV


V

In order to assess the extent to which the unsaturation electrons of the cyclopropane ring partake of the character of the π-electrons in the vinyl group we compare first the ultraviolet absorption of the semicarbazone of the ketone III (Fig. 1) ($\lambda_{\max}^{\text{alc}}$ 237, ϵ 13,600) with that calculated[8] for the system $\mathrm{(C)_2C{=}C{-}C{=}C{-}C{=}NNHCONH_2}$, $\lambda_{\max}^{\text{alc}}$ *ca.* 300 mμ, and with the nearly identical absorption maximum reported for carone (IV) semicarbazone ($\lambda_{\max}^{\text{alc}}$ 235.5, ϵ 13,500)[9] and that found for β-dihydroumbellulone (V) semicarbazone (Fig. 1). The comparison shows that the cyclopropane ring bears little chromophoric similarity to the vinyl group when placed as a connecting link between chromophores.

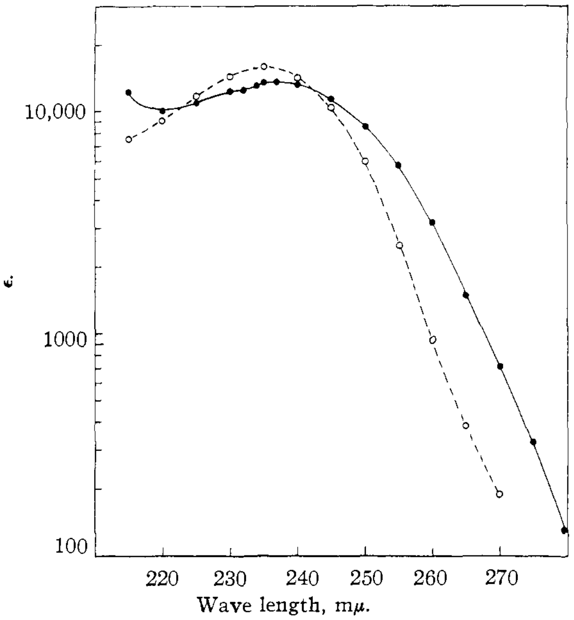
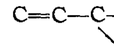
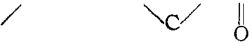
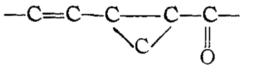
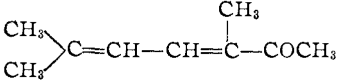


Fig. 1.—Ultraviolet absorption spectra in 95% ethanol: open circles, β-dihydroumbellulone semicarbazone; closed circles, semicarbazone of 1-acetyl-2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropane (III).

On the other hand, the spectrum of the ketone III (Fig. 2) appears to involve three band systems with maxima at about 280, 235 and 210 mμ, and is not simply the sum of the independent chromophores,  $\mathrm{C{=}C{-}\underbrace{C{-}C}_{C}{-}}$ and  $\mathrm{{-}\underbrace{C{-}C}_{C}{-}\underset{\underset{O}{\|}}{C}{-}}$. These data are in accord with those of Kierstead, Linstead and Weedon,[7] taken by them as evidence of conjugation through the cyclopropane ring. One explanation of the dichotomy between conclusions drawn from the spectra of the semicarbazones and from the spectrum of the ketone is that the system  $\mathrm{{-}C{=}C{-}\underbrace{C{-}C}_{C}{-}\underset{\underset{O}{\|}}{C}{-}}$ has a set of rather weak bands which are partially obscured by the strong bands of the separate chromophores in the case of the ketone, and almost completely obscured by the much more intense absorption of the semicarbazone chromophore.[10] In any event it is apparent that the coupling by the cyclopropane ring in the ketone bears little resemblance to that of the vinyl group since the principal absorption band of the system  $\mathrm{(CH_3)_2C{=}CH{-}CH{=}\overset{\overset{CH_3}{|}}{C}{-}COCH_3}$ may be calculated to appear close to 290 mμ.[11]

We are of the opinion that these observations

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[6] Cross-conjugation of a double bond and a cyclopropane ring to a carbonyl group has been shown [E. J. Corey and H. J. Burke, THIS JOURNAL, **76**, 5258 (1954)] to have little effect on the α,β-unsaturated carbonyl chromophore, an observation which invalidates the suggestion of A. E. Gillam and T. F. West [*J. Chem. Soc.*, 98 (1945)] that the anomalous ultraviolet absorption of umbellulone is due to such a system.

[7] Prior to publication of Paper I of this series (ref. 4) R. W. Kierstead, R. P. Linstead and B. C. L. Weedon [*J. Chem. Soc.*, 3610 (1952)] had reported that the structurally similar 2-vinylcyclopropane-1,1-dicarboxylic acid showed no high intensity absorption in the ultraviolet at wave lengths longer than 210 mμ. Subsequently they [*ibid.*, 1799 (1953)] found evidence for electronic interaction between the double bond, cyclopropane ring and carbonyl group in the spectrum of 1-acetyl-1-carbomethoxy-2-vinylcyclopropane in which maxima of ϵ 1,150 at 251, 257 and 264 mμ were demonstrated. See also, S. H. Harper, K. C. Sleep and L. Chrombie, *Chemistry and Industry*, **50**, 1538 (1954).

[8] (a) "Electronic Absorption Spectroscopy," A. E. Gillam and E. S. Stern, Edward Arnold, Ltd., London, 1954, pp. 102, 113. (b) The semicarbazone of heptadiene-3,5-one-2 (which lacks one γ-substituent relative to the model) is reported by L. K. Evans and A. E. Gillam [*J. Chem. Soc.*, 432 (1945)] to show $\lambda_{\max}^{\text{alc}}$ 290 mμ ϵ 37,000.

[9] A. E. Gillam and T. F. West, *ibid.*, 95 (1945).

[10] This explanation was suggested in correspondence by B. C. L. Weedon.[7]

[11] "Natural Products Related to Phenanthrene," L. F. and M. Fieser, 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1949, p. 192. Heptadiene-3,5-one-2 (which lacks, relative to the model, one γ-substituent which would be responsible for a *ca.* 18 mμ bathochromic shift) shows $\lambda_{\max}^{\text{alc}}$ 271, ϵ 22,600; ref. 8b.

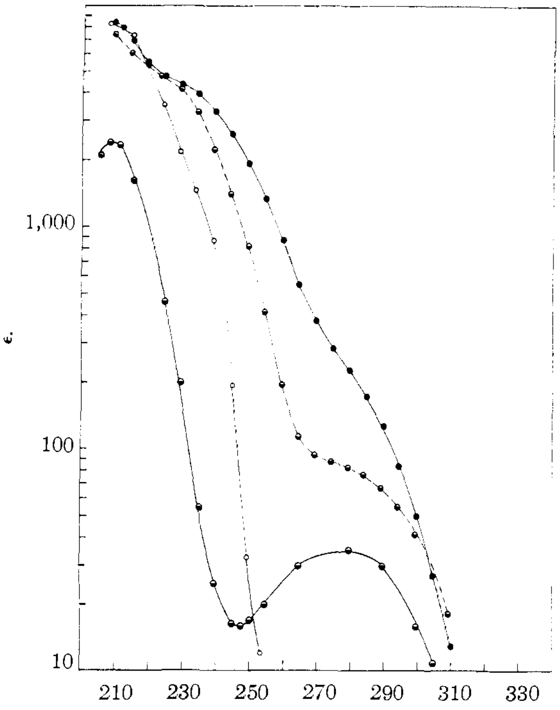

Fig. 2.—Ultraviolet absorption spectra of: 1-acetyl-2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropane (III): ●-●, in 95% ethanol; ◒--◒, in isoöctane; 1-(α-hydroxyethyl)-2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropane in 95% ethanol: ○-○; β-dihydroumbellulone (V) in 95% ethanol: ◒-◒.

support the essential features of the hypothesis that the unsaturation electrons of the cyclopropane ring lack the property of π-electrons in general of functioning centrally in a chain of conjugation.

Experimental

1-Acetyl-2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropane.—Following the procedure of Cason, Sumrell and Mitchell[12] the cadmium Grignard reagent was prepared using 33.5 g. of magnesium, 200 g. of methyl iodide and 200 g. of anhydrous cadmium chloride, with 400 ml. of dry benzene to displace by distillation the 1 liter of ether used in preparation of the methyl Grignard. To the cadmium Grignard reagent thus prepared was added during one hour, while maintaining a reaction temperature of 40–50°, 130 g. of *dl-trans*-chrysanthemumic acid chloride[13] (b.p. 98.3° at 15 mm. in a 14 TP helices-packed column, $n^{25}\text{D}$ 1.4830) in 170 ml. of benzene. When the addition was complete the reaction mixture was brought to the boiling point (70°) and held there for an additional hour. The reaction mixture was decomposed first with 400 ml. of water, then by the addition of 68.5 ml. of concentrated hydrochloric acid in 100 ml. of water, and the product was steam distilled along with the solvent. The steam distillate was freed of solvent in a 13 TP glass-helices packed column and the product fractionated. After a small fore-run there was obtained 60 ml. of pale-yellow oil, b.p. 90–91° at 15 mm., $n^{20.5}\text{D}$ 1.4661–1.4670 first to last cut. A center cut of 35 ml. was refractionated in the same column giving, after a small fore-run, 30 ml. of colorless oil, $n^{23}\text{D}$ 1.4666, b.p. 90.8–91.2° at 15 mm.

Anal.[14] Calcd. for $C_{11}H_{18}O$: C, 79.46; H, 10.92. Found: C, 79.39, 79.49; H, 10.93, 10.89.

The semicarbazone was prepared from 3.0 g. of ketone using semicarbazide acetate in ethanol, and the crude material (3.9 g. m.p. 157–60°) was crystallized four times from ethanol to yield 2.0 g. of white crystalline solid, m.p. 162–163.5° (cor.).

Anal. Calcd. for $C_{12}H_{21}ON_3$: C, 64.54; H, 9.36; N, 18.82. Found: C, 64.52; H, 9.36; N, 18.64.

In view of the possible influence of impurities on the spectrum of such a weakly absorbing substance particular care was taken to obtain the purest sample of the ketone III possible. The ultraviolet and infrared spectra[15] (C=O, 5.91 μ) were invariant on samples purified by: (a) chromatography on alumina, (b) regeneration from the semicarbazone by oxalic acid hydrolysis, and (c) passage through a 12 ft. by 10 mm. liquid–vapor partition column of the type described by James and Martin.[16] In particular the liquid–vapor partitionogram provided no evidence for the existence of a mixture of *cis* and *trans* isomers. It is not known with which isomer we were dealing.

The carbinol, 1-(α-hydroxyethyl)-2,2-dimethyl-3-(2-methyl-1-propenyl) cyclopropane, corresponding to the ketone was prepared from 0.8 g. of the ketone by reduction with 1 g. of sodium borohydride in 25 ml. of 50% methanol at 50° for 1 hr. The product was separated by dilution and ether extraction. Sublimation at 30 mm. and 100° gave 0.50 g. of colorless, viscous oil which showed no absorption in the region 5.0–5.6 μ, showing that reduction was complete. The ultraviolet absorption of this material is reported in Fig. 2.

Anal. Calcd. for $C_{11}H_{22}O$: C, 78.51; H, 11.98. Found: C, 78.52, 78.63; H, 11.94, 12.19.

Spectra.—Ultraviolet absorption spectra were obtained with a Beckman model DU instrument, using the photomultiplier attachment below 230 mμ; and infrared determinations were made with a Perkin–Elmer model 21 recording spectrophotometer.

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[12] T. Cason, G. Sumrell and R. S. Mitchell, *J. Org. Chem.*, **15**, 850 (1950).

[13] We wish to thank Benzol Products, Inc., for a generous gift of the acid chloride used in this work.

[14] Analyses by Microchemical Specialties, Berkeley, Calif.

[15] The small bathochromic shift in the C=O frequency from 5.88 μ shown by methyl cyclopropyl ketone is attributed to the effect of the *gem*-dimethyl substitution, not to coupling through the cyclopropane ring since it has been shown [E. R. Blout, M. Fields and R. Karplus, THIS JOURNAL, **70**, 194 (1948)] that a γ,δ-double bond produces an inappreciable shift in the C=O frequency of an α,β-unsaturated aldehyde.

[16] A. T. James and A. J. P. Martin, *Analyst*, **77**, 915 (1952). The column used contained G. E. Silicone Oil SF-96 on graded 545 Celite and gave substantial resolution of terpene ketones boiling within 3° near 200°.

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BENZOL PRODUCTS, INC.
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Some Substituted α-(Aryloxy)-isobutyric Acids and Amides[1]

BY HENRY GILMAN AND GENE R. WILDER

RECEIVED JULY 5, 1955

During the course of investigation of the formative activity of various plant hormones, it was found desirable to include in this work a series of α-disubstituted aryloxyacetic acids.[2]

It has been reported[3] that some compounds of this type have recently been studied as plant hormones, but no chemical details have yet been provided.

The compounds were prepared by treating a phenol with acetone, chloroform and sodium hydroxide, using acetone as the solvent.[4]

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[1] This work was supported by a contract with the Chemical Corps, Camp Detrick, Maryland.

[2] The results of the biological tests will be reported elsewhere.

[3] D. J. Osborne and R. L. Wain, *Science*, **114**, 92 (1951).

[4] (a) P. Galimberti and A. Defranceshi, *Gazz. chim. ital.*, **77**, 431 (1947) [*C. A.*, **42**, 3362 (1948)]; (b) G. Link, German Patent 80,986 [*Chem. Zentr.*, **66**, [II] 90 (1895)].