4-(*m*-Carboxyphenyl)-3-(*p*-methoxyphenyl)-2-hexanone (XI).—A solution of 11.2 g. (0.0365 mole) of X, 11.2 g. of potassium hydroxide, in 12 ml. of water and 45 ml. of alcohol was heated at reflux for 20 hours. The basic solution was added to 500 ml. of water and extracted with ether to remove any unchanged nitrile. The basic solution was acidified with concentrated hydrochloric acid and the precipitate extracted with ether. Drying of the extract over magnesium sulfate and removal of the ether left an oil, which when dissolved in a minimum of hot alcohol and allowed to stand in an ice-chest, gave 8.9 g. (75% yield) of acid XI, m.p. 178–180°. Several recrystallizations of a small sample elevated the melting point to 185–185.5°.

Anal. Calcd. for $C_{20}H_{22}O_4$: C, 73.59; H, 6.79. Found: C, 73.31; H, 6.76.

In certain runs only a portion of the crystalline XI was obtained from the alcoholic solution. However, removal of solvent from the filtrate and distillation of the residue at 212–216° (0.04 mm.) gave a liquid which when warmed with ether yielded additional crystalline XI. Infrared spectra of the distillate and the two solids were identical.

4-(*m*-Carboxyphenyl)-3-(*p*-hydroxyphenyl)-2-hexanone (III).—A mixture of 32.6 g. (0.1 mole) of XI and 100 g. (0.85 mole) of pyridine hydrochloride was heated at reflux for five hours. The contents of the reaction flask was stirred into an excess of dilute hydrochloric acid. The mixture was extracted with ether and the ether removed from the dried extracts. The residue was crystallized by the addition of Skellysolve B; 15.2 g. (49%) of IIIa, m.p. 221–228°. Recrystallization from alcohol or acetone raised the m.p. to 234–236°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.94; H, 6.67.

Concentration of the filtrate from IIIa gave an oily residue which crystallized; 13.4 g. (43%) of IIIb, m.p. 159–160°. Recrystallization of the latter from Skelly C–ethyl acetate raised the m.p. to 172–173°. IIIa and IIIb each gave a distinct depression with the starting material XI.

Anal. Found: C, 72.85; H, 6.48.

4-(*m*-Carbethoxyphenyl)-3-(*p*-hydroxyphenyl)-2-hexanone.—A solution of 14 g. (0.045 mole) of IIIa, 200 ml. of absolute alcohol and 10 ml. of concentrated sulfuric acid was heated at reflux temperature for eight hours. About 150 ml. of alcohol was then removed by distillation and the residue was diluted with water and extracted with ether. Successive washings of the extract with water, saturated sodium bicarbonate solution and water, drying over sodium sulfate and evaporation of the solvent left 14 g. of crude product. Recrystallization from alcohol gave 10 g. (65% yield) of ester, m.p. 155–156°.

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.10. Found: C, 73.69; H, 7.30.

4-(*m*-Acetoxyacetylphenyl)-3-(*p*-methoxyphenyl)-2-hexanone (IV).—A benzene solution of the acid chloride of XI (prepared from 5 g. of the acid by reaction with 5 ml. of thionyl chloride in benzene and catalyzed by a drop of pyridine) was added to a cold solution of diazomethane in ether (prepared from 10 g. of nitrosomethylurea[13]) and the mixture allowed to stand overnight at room temperature. The solvents were evaporated without heating at the water pump to leave 6.5 g. of viscous oil. To this oil was added 7.7 ml. of glacial acetic acid, and the solution was warmed on the steam-bath until the vigorous evolution of nitrogen had slackened, whereupon it was allowed to heat at reflux temperature for one-half hour. The acetic acid was removed *in vacuo* at steam-bath temperature, and the residue was taken up in ether and washed with water and 10% sodium hydroxide solution. The ether layer was dried and evaporation of the ether left 5.5 g. of viscous oil. Distillation gave 3.0 g. (57% yield) of IV, b.p. 162–165° (0.01 mm.). Crystallized from alcohol, the ester melted at 98–100°.

Anal. Calcd. for $C_{22}H_{26}O_5$: C, 72.23; H, 6.85. Found: C, 72.35; H, 7.05.

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[13] F. Arndt, ref. 12, p. 165.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Conjugative Effects of Cyclopropane Rings. I. Synthesis and Properties of 1-Methyl-4-isopropyltricyclo[4,1,$0^{1,6}$,$0^{2,4}$]heptanon-5

BY RICHARD H. EASTMAN

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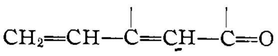
The synthesis of a tricyclic ketone which is an analog of cyclopentadienone with cyclopropane rings replacing the double bonds is described. The spectroscopic properties of the tricyclic ketone show that the cyclopropane rings do not establish a conjugated system. The nature of the unsaturation of the cyclopropane system is discussed, and it is proposed that a cyclopropane ring can extend a chain of conjugation but cannot transmit conjugation effects of contiguous unsaturated groups.

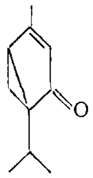
The investigations of Smith and Rogier[1] have demonstrated that the central cyclopropane ring in the non-polar system, 2-phenylbicyclopropyl (I), is incapable of transmitting the conjugative effect[2] of the distal cyclopropane ring in the system to the benzene nucleus. The cyclopropane ring in umbellulone (II) exerts a pronounced conjugative effect upon the ultraviolet absorption of the substance in that the spectrum of umbellulone [$\lambda_{\max}^{\text{alc.}}$ 220 (ϵ 5,900), 265 (ϵ 3,290)][3] is approximately that calculated for the system III.[4] We have synthesized a tricyclic ketone having the chromophoric system IV to determine whether the cyclopropane rings in the rigid, *polar* system establish a chain of conjugation to the carbonyl group.

I

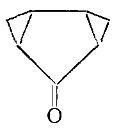


$$CH_2{=}CH{-}\overset{|}{C}{=}CH{-}\overset{|}{C}{=}O$$

III



II



IV

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[1] L. I. Smith and E. R. Rogier, THIS JOURNAL, **73**, 3840 (1951).

[2] For leading references on the conjugative effects of the cyclopropane ring see: ref. 1; C. E. Boord, *et al.*, *ibid.*, **71**, 172, 2483, 3595 (1949); R. P. Mariella and R. R. Raube, *ibid.*, **74**, 518, 521 (1952); V. A. Slabey, *ibid.*, **74**, 4930 (1952).

[3] The spectrum was first observed by A. E. Gillam and T. F. West [*J. Chem. Soc.*, 98 (1945)] who attributed the anomaly to cross conjugation of the cyclopropane ring and double bond with the carbonyl group.

[4] R. B. Woodward, THIS JOURNAL, **64**, 76 (1942); L. F. and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1949, p. 192.

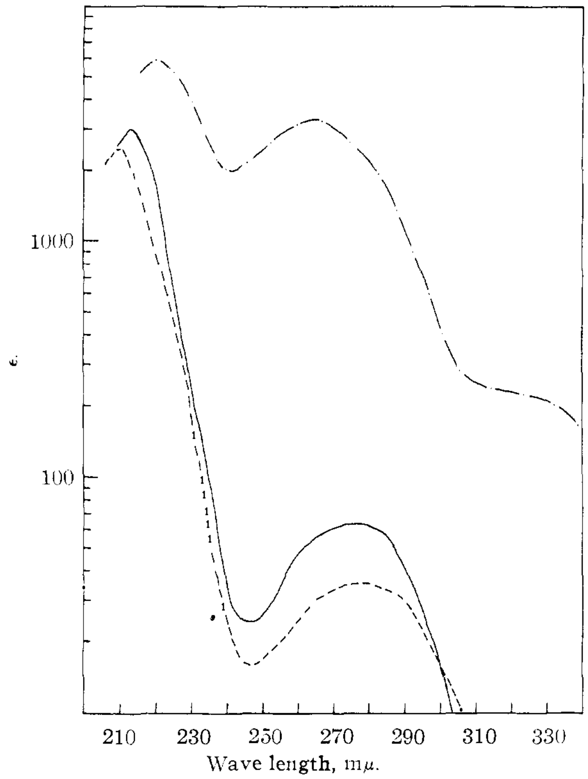
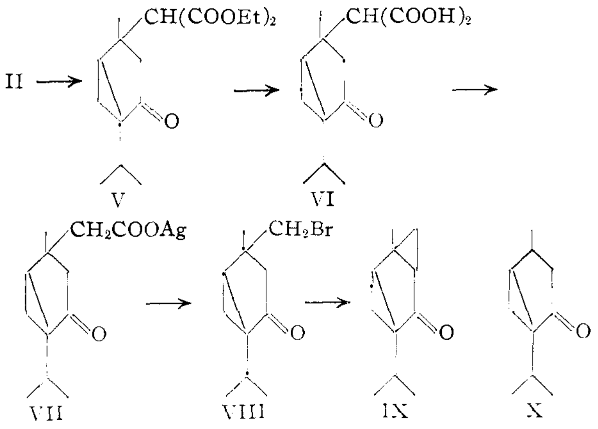


Fig. 1.—Ultraviolet absorption spectra in alcohol: -·-· umbellulone II; ---, dihydroumbellulone (X); —, tricyclic ketone (IX).

Umbellulone (II) participated smoothly in a Michael condensation with malonic ester to yield the diester V which was judged to be stereochemically homogeneous on the basis of the identity of the infrared spectra of early and late cuts in its distillation. Hydrolysis of the ester with alcoholic potassium hydroxide yielded a single malonic acid VI, isolated conveniently from the hydrolysis mixture as its beautifully crystalline potassium salt. Decarboxylation of the malonic acid (VI) proceeded smoothly at 150° and the liquid acid product was converted directly to the silver salt VII which was in turn treated with bromine in dry carbon tetrachloride solution in the Hunsdiecker reaction[5] to produce the bromide VIII in 16% yield.



The bromide VIII did not react with boiling alcoholic silver nitrate, a behavior characteristic of its neopentyl halide structure and shown by the similarly constituted umbellulone dibromide.[6] Treatment of the bromide VIII with warm alcoholic alkali-free halide ion gave the saturated tricyclic ketone IX in excellent yield. The structure assigned to the tricyclic ketone is based upon its mode of preparation, the behavior of its bromide precursor VIII toward alcoholic silver nitrate, and its saturated character as evidenced by resistance to oxidation by alkaline permanganate and the absence of bands in the 6.0–6.7 μ region in its infrared spectrum.

The stereochemical disposition of the cyclopropane rings in this tricyclic ketone remains unknown, molecular models providing no basis for prediction. The evidence is strong, however, that only one of the stereoisomeric pairs has been prepared in that the malonic ester and acid precursors (V and VI) were apparently homogeneous.

The ultraviolet absorption spectrum (Fig. 1) of the tricyclic ketone shows $\lambda_{\max}^{\text{alc.}}$ 214 (ϵ 2990), 275 (ϵ 62) and is not significantly different from that of β-dihydroumbellulone (X) which shows $\lambda_{\max}^{\text{alc.}}$ 210 (ϵ 2470), 280 (ϵ 35). Thus, in this rigid, tricyclic analog of the cyclopentadienone system no chain of conjugation exists involving both cyclopropane rings.[7] The absence of such conjugation provides direct experimental evidence that the unsaturation of the cyclopropane system is different in kind from that of the olefinic linkage. The spectroscopic properties of umbellulone (II) demonstrate that the unsaturation of a cyclopropane ring can exert a conjugative effect when the ring is at the end of a chain of conjugation; but the properties of the tricyclic ketone IX equally demonstrate that a cyclopropane ring does not conduct conjugative effects from one contiguous unsaturated group to another.

A satisfactory theoretical explanation of these observations and conclusions can be based upon the non-classical structure proposed by Roberts and Mazur[8] for the cyclopropylmethylcarbonium ion. The bathochromic effect of the cyclopropane ring in umbellulone finds expression in the contributing structure XIV wherein the unsaturation electrons of the cyclopropane ring enter the α,β-unsaturated carbonyl system.

In the case of the tricyclic ketone[9] two structures of the type XV contribute separately but the un-

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[5] *Cf.* W. E. Doering and M. Farber, THIS JOURNAL, **71**, 1514 (1949).

[6] R. H. Eastman and A. Oken, *ibid.*, **75**, 1029 (1953).

[7] Superficial examination of the spectra (Fig. 1) could lead to the conclusion that a chain of conjugation involving both cyclopropane rings does exist in the tricyclic ketone inasmuch as the high intensity maximum in that compound is displaced toward the high intensity maximum of umbellulone, and the low intensity band is shifted hyper- and hypsochromically in the direction of the band at 265 mμ shown by umbellulone. However, such an interpretation involves ascribing *both* a hypsochromic *and* a bathochromic effect to the establishment of a chain of conjugation. The anomaly arises because of the error in associating the weak carbonyl band at 275 mμ in the tricyclic ketone with the strong, unsaturated ketone band at 265 mμ in umbellulone while in fact it should be associated with the shoulder at 320 mμ in the latter substance. If there were a chain of conjugation through the cyclopropane rings to the carbonyl group of the tricyclic ketone both the high and low intensity bands should be bathochromically shifted relative to those of dihydroumbellulone.

[8] J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 3542 (1951).

[9] The choice of the *cis* isomer is arbitrary.