uct, obtained in a 63.5% yield, boiled at 196° (0.15 mm.), $n^{25}D$ 1.6050.[12]

A mixture of 65.6 g. (0.2 mole) of this mercaptol, 500 ml. of liquid ammonia and 200 ml. of dry ether was stirred and treated with small pieces of sodium until a blue color persisted for one hour. The solution became a bright yellow with the addition of the first piece of sodium and gradually changed to a pastel red as more sodium was added. A total of 25 g. of sodium was added with excess being neutralized with 3.5 g. of ammonium chloride. After the ammonia had evaporated, the residue was treated cautiously with 250 ml. of ether and 150 ml. of water. The layers were separated after all of the solid had dissolved and the ether layer extracted with 10% sodium hydroxide solution. The combined aqueous layers were extracted with ether. The ether layer was dried over anhydrous magnesium sulfate and distilled. From this first distillation, 16.3 g. of toluene was recovered as well as three other fractions. Redistillation of these fractions yielded 2.6 g. of crude cyclohexanethiol, b.p. 155–165°, $n^{25}D$ 1.4738 and 11.0 g. of cyclohexylphenylmethane, b.p. 250–255°, 113–115° (5 mm.), $n^{25}D$ 1.5210, d^{25}_4 0.9330. The values of these physical properties vary somewhat in the literature.[13] Oxidation of this material with alkaline permanganate yielded benzoic acid.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59; H, 10.41; MR_D, 56.45. Found: C, 89.48; H, 10.51; MR_D, 56.85.

The aqueous layer was acidified with 20% sulfuric acid. Considerable gas evolution was noted. Distillation of the liberated oil yielded 1.5 g. of the mercaptan, $n^{25}D$ 1.4747. The total yield of mercaptan amounted to about 18% of the theoretically possible amount. Cyclohexyl 2,4-dinitrophenyl sulfide was prepared from this compound in good yields, m.p. 145–146°. This melting point was not depressed when the substance was mixed with the sulfide prepared in the usual manner[14] from authentic cyclohexanethiol.[15]

Acknowledgment.—We are indebted to Messrs. W. L. Brown, H. L. Hunter and G. M. Maciak for the microanalyses reported and to Dolores M. Rolandson for technical assistance.

(12) This material was prepared by H. R. Sullivan.

(13) *Cf.* R. C. Huston and K. Goodemoot, THIS JOURNAL, **56**, 2433 (1934); N. G. Sidorova and I. P. Tsukervanik, *J. Gen. Chem. (U.S.S.R.)*, **10**, 2073 (1940).

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(15) J. Staněk, *Chem. Listy*, **46**, 383 (1952); *C. A.*, **47**, 4296*i* (1953).

INDIANAPOLIS, INDIANA

CONTRIBUTION FROM THE LABORATORY OF PHARMACEUTICAL CHEMISTRY, UNIVERSITY OF KANSAS SCHOOL OF PHARMACY]

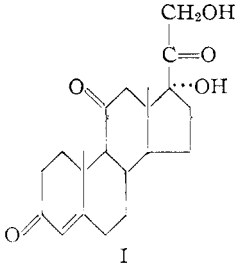
Steroidal Hormone Relatives. II.[1] The Synthesis of 4-(*m*-Carboxyphenyl)-3-(*p*-hydroxyphenyl)-2-hexanone

BY J. H. BURCKHALTER, PETER H. JACKSON, JOSEPH SAM AND HANS R. MEYER

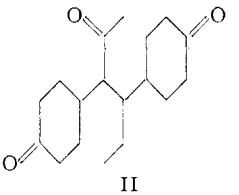
RECEIVED OCTOBER 10, 1953

4-(*m*-Carboxyphenyl)-3-(*p*-hydroxyphenyl)-2-hexanone (IIIa) and 4-(*m*-acetoxyacetylphenyl)-3-(*p*-methoxyphenyl)-2-hexanone (IV), designed as intermediates in the synthesis of open chain models of cortisone (*e.g.*, V), have been prepared in good yields. Attempts to reduce the benzene rings of IIIa to alicyclic rings have not yet been successful, as in the preparation of II. Compound IIIa showed considerable estrogenic effect, while IV lacked the effects of cortisone.

A previous report describes the synthesis of 3,4-bis-(4-oxocyclohexyl)-2-hexanone (II),[1] which is an open chain triketone holding carbonyl groups in positions corresponding to 3 and 11 of cortisone (I). We wish now to describe the preparation of



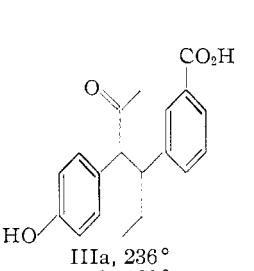
I



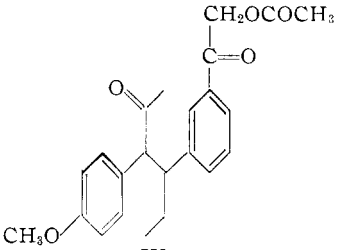
II

other open model compounds (III and IV) which may be considered to bear a closer structural relationship to the hormones of the adrenal cortex and which might serve as intermediates leading to V.

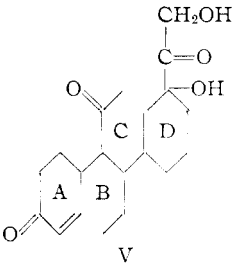
It can be seen that these structures contain a six-membered ring in a position corresponding to the five-membered D ring of the steroids. The observation that the androgenic effect of 17α-methyltestosterone is doubled by an enlargement of ring D[2] offers encouragement to the incorporation of a 6-membered D ring in the cortical steroids. Further, it is apparent that proposed compound V would not possess angular methyl groups. That the C-19 methyl between rings A and B of testosterone, progesterone and desoxycorticosterone can be omitted without loss of the specific activities of these hormones has recently been demonstrated.[3,4] An



IIIa, 236°
b, 160°



IV



V

(1) Paper I: J. H. Burckhalter and J. Sam, THIS JOURNAL, **74**, 187 (1952).

(2) L. Ruzicka, N. Wahba, P. T. Herzig and H. Heusser, *Chem. Ber.*, **85**, 491 (1952).

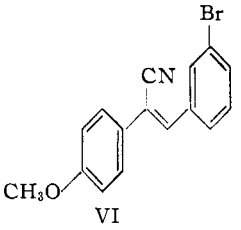
(3) A. J. Birch and H. Smith, *J. Chem. Soc.*, 1882 (1951).

(4) (a) L. Miramontes, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 3540 (1951); (b) A. Sandoval, L. Miramontes, G. Rosenkranz, C. Djerassi and F. Sondheimer, *ibid.*, **75**, 4117 (1953).

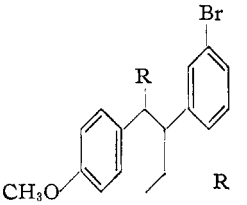
attempt already has been made to justify the open structure of rings B and C of compounds such as V by reference to the potent hexestrol as an open chain relative of estradiol.[1]

It is realized that the proposed extensive tampering with the structures of the cortical steroids, despite the justification of each variation, may fail to produce the desired results. But the realization that related structures may possess effects antagonistic if not similar to the natural hormones has offered further encouragement to the present studies.

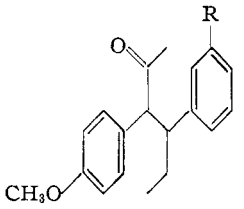
p-Methoxyphenylacetonitrile, the starting material used in the synthesis of III and IV, may be obtained more readily than formerly and in 80% yield, from *p*-methoxybenzyl alcohol, by alteration of the method of Rorig.[5] It was condensed with *m*-bromobenzaldehyde by the general method of Frost[6] to give *m*-bromo-α-(*p*-methoxyphenyl)-cinnamonitrile (VI) in 92% yield. By means of



VI



VII, CN
VIII, COOH
IX, $COCH_3$



R
X, CN
XI, COOH

the ethyl Grignard reagent, VI was converted to equal amounts (total yield 77%) of the diastereoisomeric forms of β-(*m*-bromophenyl)-α-(*p*-methoxyphenyl)-valeronitrile (VII).[7]

Basic hydrolysis of nitrile VII to the acid VIII was carried out by the general method of Hunter and Korman.[7] Using either the solid or liquid diastereoisomeric nitrile, only about 22% yield of a pure diastereoisomeric acid (VIIIa) was obtained, while none of the second diastereoisomer could be isolated in pure form. However, a solid mixture of the acids VIII, melting over a rather narrow range, was readily obtained in 90% yield from either the solid or liquid nitrile VII. Failure to obtain the second diastereoisomer in pure condition was of little consequence, since either the pure VIIIa or the mixture VIII gave both of the possible diastereoisomeric ketones IX. Each form was converted through the acid chloride and diethyl ethoxymagnesium malonate, by means of the procedure of Walker and Hauser,[8] to both of the ketones IX in about 84% total yield.

The diastereoisomeric ketones IX were also made in good total yield by treatment of either solid or liquid nitrile VII with the methyl Grignard reaction.[1,7]

The conversion of either the solid or liquid bromo ketone IX to the ketonitrile X was effected in 83% yield by use of a procedure involving cuprous cyanide in boiling quinoline.[9] Since X is a liquid it cannot be definitely stated that it is a single diastereoisomer. A single keto acid XI, a crystalline substance, was obtained in 75% yield by basic hydrolysis of the keto nitrile X. However, both a solid and a liquid form of the phenolic keto acid III were produced in 92% total yield when XI was demethylated with pyridine hydrochloride.

When it was observed in several of the steps that either of the diastereoisomers gave rise to the same product or mixture of products, the possibility of using crude mixtures of diastereoisomers was investigated. As expected, it was found that all the reactions could be carried out with the crude mixtures without decreasing the over-all yield and without rendering more difficult the isolation and purification of compound III. However, there was a considerable saving of time.

4-(*m*-Acetoxyacetylphenyl)-3-(*p*-methoxyphenyl)-2-hexanone (IV) was prepared from acid XI *via* the acid chloride and diazo ketone. The ketol acetate IV was obtained directly from the diazo ketone by reaction with acetic acid.

As described in a prior publication,[1] triketone II has been prepared through high pressure hydrogenation of the corresponding aromatic compound followed by chromic acid oxidation. However, similar preliminary experiments applied to IIIa and its ethyl ester have thus far failed to yield analogous alicyclic compounds which might be used in the synthesis of V.

Compound IV, while partially aromatic in structure, bears the ketol group characteristic of the cortical hormones. Also, it possesses oxygen functions in positions which may be related to 3 and 11 of cortisone. It is well known that cortisone (I) is unreactive to carbonyl reagents.[10] While it may be a dubious point of comparison, we wish to record the fact that IIIa, IX, X and XI are likewise unreactive toward these reagents.

Biological Results.—Dr. Charles A. Winter, Merck Institute for Therapeutic Research, has made preliminary tests of compounds IIIa and IV for estrogenic and cortisone-like effects. In ovariectomized rats, IIIa "would seem to have considerable estrogenic activity," while IV was inactive. Using 17 rats and a dose of 10 micrograms of IIIa per rat on each of two consecutive days, there were 9 positive, 4 negative and 4 doubtful vaginal smears. Neither IIIa or IV exhibited any anti-inflammatory action against cotton pellet implantations in rats; they failed to inhibit granuloma formation or to produce atropy of adrenals or thymus, effects which are produced by cortisone.

Acknowledgments.—The authors are grateful to Research Corporation for financial support of the

(5) K. Rorig, THIS JOURNAL, **73**, 1290 (1951).

(6) H. V. Frost, *Ann.*, **250**, 156 (1889). *Cf.* S. Wawzonek and E. M. Smolin, *Org. Syntheses*, **29**, 83 (1949).

(7) *Cf.* E. P. Kohler, *Am. Chem. J.*, **35**, 399 (1906), and J. H. Hunter and J. Korman, THIS JOURNAL, **70**, 3426 (1948).

(8) H. G. Walker and C. R. Hauser, *ibid.*, **68**, 1386 (1946).

(9) *Cf.* L. Long and A. Burger, *J. Org. Chem.*, **6**, 852 (1941); G. P. Hager and R. H. Burgison, *J. Am. Pharm. Assoc.*, **39**, 7 (1950).

(10) *Cf.* L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," 3rd Ed., Reinhold Publ. Corp., New York, N. Y., 1949, p. 409.

project, and to Dr. C. A. Winter of Merck Institute for the biological studies.

Experimental[11]

p-Methoxyphenylacetonitrile.—A simplified modification of the procedure of Rorig[5] was used. The method was shortened by keeping the chloride in the benzene solution for the next step. Consistent results in avoiding polymerization of the chloride were obtained by means of a bicarbonate wash. A solution of the chloride treated in this way may be stored for a long period.

Anhydrous hydrogen chloride was bubbled rapidly for an hour into a solution of 330 g. (2.4 moles) of *p*-methoxybenzyl alcohol (Givaudan-Delawanna) in a liter of benzene contained in a two-liter separatory funnel. The concentrated hydrochloric acid which separated was drawn off, and the benzene solution was washed once with water and then with a saturated sodium bicarbonate solution until the washings were no longer acidic.

The benzene solution, without further treatment, was then added during a 40-minute period to a boiling, stirred solution of 453 g. of sodium cyanide in 830 ml. of water. Stirring by means of a Hershberg stirrer was rapid enough to cause emulsification. After five hours of stirring and refluxing, the layers were separated. The aqueous layer was washed with benzene and the benzene layers combined. The solvent was removed by distillation, and the residue was distilled to give 280–289 g. (80–83% yield) of *p*-methoxyphenylacetonitrile, b.p. 92–95° (0.2 mm.) or 119–124° (0.8 mm.).

m-Bromobenzaldehyde.—The procedure of Buck and Ide, as modified by the private communication of F. T. Tyson,[12] was followed except that 500 ml. of 48% hydrobromic acid was added after the reduction of the *m*-nitrobenzoic acid, and that the diazotization was carried out at 5° instead of 0°. The yield was thereby increased from 67 to 80%, b.p. 66–68° (0.2 mm.); $n^{24}D$ 1.5646. (Diazotization at −10° gave less than 20% yield; at 0°, 68% yield or the same as reported.[12])

m-Bromo-α-(p-methoxyphenyl)-cinnamonitrile (VI).—The general method of Frost[6] was followed. To a well-stirred solution of 66.5 g. (0.45 mole) of *p*-methoxyphenylacetonitrile and 84 g. (0.45 mole) of *m*-bromobenzaldehyde in 800 ml. of absolute alcohol, there was added a cold solution of 10.6 g. (0.46 mole) of sodium in 300 ml. of absolute alcohol. An additional 200 ml. of alcohol was added and the resultant precipitate was dissolved by heating the mixture on a steam-bath. Rapid cooling yielded a yellow crystalline product. Recrystallization from alcohol gave 131.5 g. (92% yield) of VI, m.p. 96–98°.

Anal. Calcd. for $C_{16}H_{12}BrNO$: C, 61.16; H, 3.85. Found: C, 61.12; H, 3.88.

β-(m-Bromophenyl)-α-(p-methoxyphenyl)-valeronitrile (VII).—The procedure followed is that of Kohler[7] for the preparation of α,β-diphenylvaleronitrile. Hydrolysis of the complex made from 159.1 g. of *m*-bromo-α-(*p*-methoxyphenyl)-cinnamonitrile (VI) and the ethyl Grignard reagent gave a mixture of diastereoisomers, one a solid and the other a liquid. After recrystallization from alcohol, 68 g. of solid isomer (VIIa) was obtained, m.p. 111–113°.

Anal. Calcd. for $C_{18}H_{16}BrNO$: C, 62.80; H, 5.27; Br, 23.21. Found: C, 62.85; H, 5.32; Br, 23.42.

Removal of the alcohol from the filtrate of the solid isomer and distillation of the residue gave 67 g. of liquid isomer VIIb, b.p. 215° (2 mm.); total yield 135 g. (77%). Total yields as high as 89% have been obtained.

Anal. Found: C, 63.05; H, 5.43.

β-(m-Bromophenyl)-α-(p-methoxyphenyl)-valeric Acid (VIII).—The general method of Hunter and Korman was followed.[7]

A mixture of 34.4 g. (0.1 mole) of VIIa, 26 g. of sodium hydroxide, 43 ml. of water and 500 ml. of ethylene glycol was heated at reflux temperature for about 72 hours after which no more ammonia was evolved. The solution was diluted with a liter of water and then filtered. The filtrate was acidified by pouring it in a thin stream into a mixture of excess hydrochloric acid and ice. The precipitated oily solid was removed by filtration, treated with animal charcoal and recrystallized from dilute alcohol. There was obtained 8 g. (22% yield) of acid VIIIa, m.p. 149–151°. Further recrystallization from the same solvent did not change the melting point. From the liquid nitrile VIIb, VIIIa was obtained in the same yield.

Anal. Calcd. for $C_{18}H_{19}BrO_3$: C, 59.51; H, 5.27. Found: C, 59.83; H, 5.39.

Removal of the solvent from the filtrate of VIIIa left an oil which could not be crystallized to give the second diastereoisomer of VIII. Also, attempts through fractionation and hydrolysis of the esters, after the plan of Hunter and Korman,[7] resulted in failure.

In other preparative experiments, after water had been added to the basic hydrolysate, the mixture was extracted with ether to remove any unchanged nitrile or other neutral material. Then, after treatment of the basic solution with mineral acid, the acidic material was extracted with ether, the extracts dried first over saturated sodium chloride solution and then over sodium sulfate. Removal of the ether left an oil which was treated with alcohol to give from 88 to 91% of a mixture of diastereoisomers of VIII, m.p. 113–116°. Both the solid and liquid nitrile VII gave the same results. Single recrystallizations from either 80% alcohol or Skellysolve B failed to elevate the m.p. beyond 118°.

Anal. Found: C, 59.82; H, 5.73.

4-(m-Bromophenyl)-3-(p-methoxyphenyl)-2-hexanone (IX). Method A.—The procedure used is that of Walker and Hauser[8] for the preparation of methyl ketones. The method was modified in that all the absolute alcohol was added at once.

From 23 g. (0.075 mole) of VIIIa, 21.5 g. of crude ketone IX was obtained. Recrystallization from alcohol gave 10 g. (46%) of solid diastereoisomer IXa, m.p. 95–98°. A second recrystallization from the same solvent gave a maximum melting point of 105–106°.

Anal. Calcd. for $C_{19}H_{21}BrO_2$: C, 63.16; H, 5.86. Found: C, 63.08; H, 5.92.

Evaporation of the solvent from the mother liquor and distillation of the residue gave 9 g. (38%) of liquid diastereoisomer IXb, b.p. 175° (0.5 mm.), $n^{20}D$ 1.5709.

Anal. Found: C, 63.39; H, 5.97.

When the diastereoisomeric mixture of acids VIII was subjected to the same series of reactions, both isomeric ketones IX were obtained as with VIIIa.

Method B.—A general procedure involving the Grignard reagent was followed.[1,7] From 8.5 g. (0.025 mole) of solid nitrile VIIa, 2.4 g. (0.1 mole) of magnesium turnings and 14.1 g. (0.1 mole) of methyl iodide, there was obtained 4 g. (45% yield) of solid ketone isomer IXa, m.p. 107–108°, and 2.4 g. (27% yield) of liquid ketone IXb, b.p. 156–158° (0.03 mm.). The latter was redistilled at 170–172° (0.2 mm.); $n^{23}D$ 1.5690.

The procedure[1,7] was altered by heating the Grignard complex for at least 15 hours. Also, a chloroform rather than an ether extraction of the hydrolyzed complex was made.

The reaction was repeated using 8.5 g. of liquid nitrile VIIb. When the solid isomer failed to crystallize from the oily product, it was distilled to give 4.4 g. (50% yield) of liquid ketone IXb, b.p. 176–178° (0.2 mm.), $n^{20}D$ 1.5698, and 2.7 g. (21% yield) of IXa, b.p. 180° (0.1 mm.), which solidified upon standing, m.p. 98–104°.

4-(m-Cyanophenyl)-3-(p-methoxyphenyl)-2-hexanone (X).—The general method of Hager and Burgison[9] was followed. A mixture of 10 g. (0.028 mole) of IXa, 8 g. of cuprous cyanide and 50 ml. of quinoline was heated at reflux temperature for six hours. The hot liquid was then poured slowly with stirring into 600 ml. of concentrated hydrochloric acid. Three hundred ml. of chloroform was added and the mixture allowed to stand overnight. The layers were separated and the acid layer was further extracted with four 100-ml. portions of chloroform. The combined extracts were washed with water and the chloroform was removed by distillation. The residue gave 7.0 g. (83% yield) of X, b.p. 167° (0.02 mm.), $n^{20}D$ 1.5590.

From isomer IXb, the same product X was produced in equal yield.

Anal. Calcd. for $C_{20}H_{21}NO_2$: C, 78.14; H, 6.88. Found: C, 77.93; H, 7.00.

(11) Microanalyses by Mr. C. W. Beazley, Skokie, Illinois.

(12) J. S. Buck and W. S. Ide, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 132.

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.

(13) F. Arndt, ref. 12, p. 165.

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

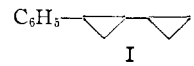
Conjugative Effects of Cyclopropane Rings. I. Synthesis and Properties of 1-Methyl-4-isopropyltricyclo[4,1,0^{1,6},0^{2,4}]heptanon-5

BY RICHARD H. EASTMAN

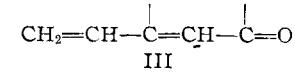
RECEIVED DECEMBER 4, 1953

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.

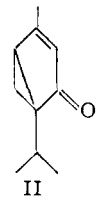
The investigations of Smith and Rogier[1] have demonstrated that the central cyclopropane ring in the non-polar system, 2-phenylbicyclopropyl (I), is incapable of transmitting the conjugative effect[2] of the distal cyclopropane ring in the system to the benzene nucleus. The cyclopropane ring in umbellulone (II) exerts a pronounced conjugative effect upon the ultraviolet absorption of the substance in that the spectrum of umbellulone [$\lambda_{max}^{alc.}$ 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.



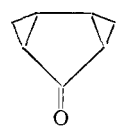
I



III



II



IV

(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.