

in equal molar quantities and isolated in a 81% yield: b.p. 125–126° (0.2 mm.); n_D^{20} 1.4586; $\nu_{\max}^{\text{CHCl}_3}$ 3000, 1640, 1380, 1310, 1210, 1150, 1040 cm^{-1} .

Anal. Calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_6$: C, 58.73; H, 7.75. Found: C, 58.69; H, 7.72.

Benzyl acetoacetate ethylene ketal was obtained in 64% yield from equal molar quantities of ethylene glycol and benzyl acetoacetate⁸: b.p. 115–120° (0.2 mm.); n_D^{20} 1.5064; ν_{\max} 1630, 1180, 1045 cm^{-1} (liquid film).

Anal. Calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_4$: C, 66.08; H, 6.83. Found: C, 65.93; H, 6.69.

4-Hydroxy-3-(3-oxocyclopentyl)-2-butanone Bisethylene Ketal (VIII).—A solution of 15 g. (0.05 mole) of the diketal ester VII in 75 ml. of ether was added dropwise to a stirred suspension of 4 g. (0.1 mole) of lithium aluminum hydride in 200 ml. of ether. The mixture was refluxed for 15 hr., stirred at room temperature for 12 hr., and then cooled in an ice bath. To the cooled mixture was added dropwise 12.5 ml. of water, and the mixture was stirred at room temperature for 12 hr. After filtration of the ether extract through Celite, the filtrate was distilled. The product weighed 12.6 g. (97% yield): b.p. 142–145° (0.1 mm.); n_D^{20} 1.4902; $\nu_{\max}^{\text{CHCl}_3}$ 3040, 2950, 1210, 1125, 1045, 750 cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_5$: C, 60.44; H, 8.59. Found: C, 60.13; H, 8.51.

α -(3-Oxocyclopentyl)acetoacetanilide Bisethylene Ketal (IX).—To an ice-cold, ethereal solution of ethylmagnesium bromide prepared from 2.4 g. (0.1 g.-atom) of magnesium, 10.9 g. (0.1 mole) of ethyl bromide, and 75 ml. of ether was added dropwise a solution of 9.2 g. (0.1 mole) of aniline in 10 ml. of ether. The mixture was stirred at room temperature for 1 hr.; then a solution of 15 g. (0.5 mole) of diketal ester VII in 25 ml. of ether was added dropwise. The mixture was stirred at room temperature for 1 hr. before being hydrolyzed with 10% ammonium chloride solution. Removal of the solvent from the organic layer left a gummy residue which was repeatedly extracted with petroleum ether (30–40°). The residue yielded 9.5 g. of gummy crystals. After repeated recrystallization from carbon tetrachloride, the material weighed 2.0 g. (11% yield): m.p. 135–136°; $\nu_{\max}^{\text{CHCl}_3}$ 1675, 1600, 1520, 1430, 1040 cm^{-1} .

Anal. Calcd. for $\text{C}_{19}\text{H}_{25}\text{NO}_5$: C, 65.69; H, 7.25; N, 4.03. Found: C, 65.77; H, 7.32; N, 4.14.

Acetoacetanilide Ethylene Ketal (X).—A solution of 10 g. (0.06 mole) of ethyl acetoacetate ethylene ketal¹⁰ and 3.4 g. (0.06 mole) of potassium hydroxide in 140 ml. of ethanol was stirred for 12 hr. The solvent was removed under reduced pressure leaving a white solid. This residue was suspended in 300 ml. of chloroform, and the suspension was cooled in an ice bath. A solution of 6.5 g. (0.06 mole) of ethyl chloroformate in 20 ml. of chloroform was added. After being stirred for 30 min. in an ice bath, the suspension was filtered. The filtrate was again cooled and a solution of 5.6 g. (0.06 mole) of aniline was added. The suspension was stirred for 4 hr. in an ice bath before being allowed to warm to room temperature over a period of 18 hr. The solution was extracted with water, 10% sodium bicarbonate solution, and water. Distillation of the ethereal layer yielded 8.5 g. of starting material and 2.3 g. (16% yield) of the ketal anilide, b.p. 150–155° (0.15 mm.), which solidified on standing, m.p. 72–73° (after recrystallization from cyclohexane).

Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{NO}_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.39; H, 6.74; N, 6.36.

Conversion of Benzyl Acetoacetate Ethylene Ketal to Acetoacetanilide (XI).—A solution of 9.4 g. (0.04 mole) of benzyl acetoacetate ethylene ketal in 30 ml. of ethanol was hydrogenated under an initial pressure of 50 lb. in the presence of 0.3 g. of 10% palladium on carbon for 48 hr. After filtration the solvent was removed from the filtrate at reduced pressure. The crude product, 5.5 g., was dissolved in 50 ml. of chloroform and cooled in an ice-salt bath. To the solution was added 3.8 g. (0.04 mole) of triethylamine followed 15 min. later by a chloroform solution of 4.1 g. (0.04 mole) of ethyl chloroformate. After the mixture had cooled for 30 min., 4.6 g. (0.05 mole) of aniline was added. The solution was allowed to warm to room temperature over a 12-hr. period and was then extracted with hydrochloric acid solution, potassium bicarbonate solution, and water. The solvent was removed at reduced pressure and the residue on cooling solidified; yield 2.3 g. (32%), m.p. 84–85° (after recrystallization from alcohol). A mixture melting point with an authentic sample of acetoacetanilide was not depressed.

(10) E. J. Salmi, *Ber.*, **71**, 1803 (1938).

Attempted Alkylation of Ethyl α -(3-Oxocyclopentyl)acetoacetate.—In a nitrogen atmosphere 21.4 g. (0.19 mole) of potassium *t*-butoxide¹¹ was dissolved in 150 ml. of tetrahydrofuran which had been distilled from lithium aluminum hydride. To this solution was added dropwise 40.5 g. (0.19 mole) of ethyl α -(3-oxocyclopentyl)acetoacetate (I). The dark brown solution was stirred for 2 hr.; then 41.2 g. (0.19 mole) of *m*-methoxyphenylethyl bromide⁴ was added dropwise. The mixture was stirred at room temperature for 36 hr. before being filtered. Tetrahydrofuran was removed with an aspirator leaving a residue from which a gummy precipitate was obtained by the addition of ether. This precipitate which contained some inorganic material could not be purified. The ether solution was extracted first with water and then with a 10% solution of hydrochloric acid. Removal of the solvent and distillation of the residue from the organic layer yielded 23.9 g. (0.1 mole) of *m*-methoxyphenylethyl bromide and 3.8 g. (0.014 mole) of ethyl 4-(*m*-methoxyphenyl)-2-acetobutyrate (XIII), b.p. 135–145° (0.4 mm.), lit.⁸ b.p. 180° (2 mm.). Compound XIII was converted to the semicarbazone of 5-(*m*-methoxyphenyl)-2-pentanone, m.p. 107–109°, lit.⁸ m.p. 109°. The first aqueous extract was acidified and extracted with ether. From distillation of this solution, 2.2 g. (0.02 mole) of ethyl acetoacetate was obtained. When potassium was employed to form the anion of I, a yield of 47% of XIII was obtained.

(11) A special alcohol free potassium *t*-butoxide from M. S. A. Research Corp., Callery, Pa.

1(9)-Octal-2,7-dione

JAMES A. MARSHALL AND NIELS H. ANDERSEN¹

Department of Chemistry, Northwestern University,
Evanston, Illinois

Received November 4, 1964

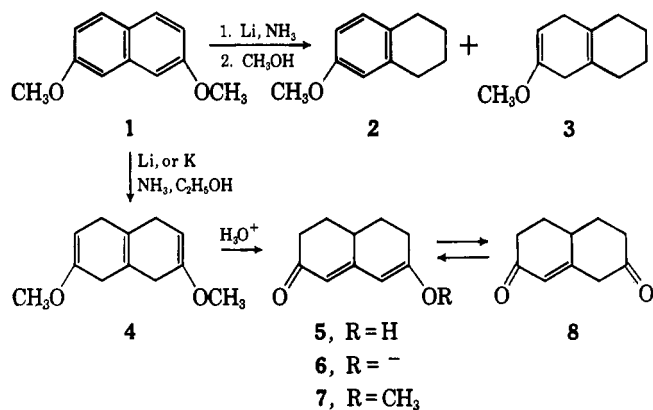
In connection with synthetic studies currently underway in our laboratory, we required 1(9)-octal-2,7-dione (8). A direct route to this dione through Birch reduction² of 2,7-dimethoxynaphthalene (1) followed by hydrolysis of the anticipated bisenol ether 4 seemed feasible. However, shortly after conception of this plan, a report appeared which described the reduction of 1 with lithium in ammonia giving only hydrogenolysis products identified as 6-methoxy-1,2,3,4-tetrahydronaphthalene (2) and 2-methoxy-1,4,5,6,7,8-hexahydronaphthalene (3).³ None of the expected product, 2,7-dimethoxy-1,4,5,8-tetrahydronaphthalene, was found.³ Therefore, investigation of the Birch reduction of 2,7-dimethoxynaphthalene appeared prerequisite to our future studies. The present paper describes the successful reduction of 1 to the bisenol ether 4 and reveals some properties of the vinylogous β -diketone 8 obtained *via* hydrolysis of 4.

Addition of a 17-fold excess of lithium to a solution of 2,7-dimethoxynaphthalene (1) in ammonia-ether-ethanol gave 2,7-dimethoxy-1,4,5,8-tetrahydronaphthalene (4), m.p. 64–66.5°, in 38% yield. Reduction of 1 in the identical manner using potassium afforded 4, m.p. 68.5–69.5°, in 72% yield. When the excess of lithium was decreased to 8-fold, the yield of enol ether 4, m.p. 66.5–69°, increased to 76%, whereas this material was obtained in 82% yield when the same excess of potassium was employed as the reducing agent under identical reaction conditions. The struc-

(1) National Science Foundation Predoctoral Fellow, 1964–1965.

(2) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); A. J. Birch and H. Smith, *ibid.*, **12**, 17 (1958).

(3) B. Weinstein and A. H. Fenselau, *J. Org. Chem.*, **29**, 2102 (1964).



ture of the bisenol ether **4** was ascertained from its elemental analysis, the absence of ultraviolet absorption, and the simplicity of its n.m.r. spectrum (resonance peaks at 4.53, 3.50, and 2.58 p.p.m. of intensity ratio 1:3:4).

The striking contrast between the results obtained in the initial absence of alcohol³ and those in which alcohol was initially present (Table I) clearly demonstrates the requirement of a proton source for effective suppression of hydrogenolysis reactions during Birch reduction of naphthalenic ethers. Birch² pointed out that the strongly basic amide produced during reduction of an aromatic ring with alkali metals in ammonia may catalyze isomerization of initially formed 1,4-dienes to 1,3-dienes. The latter can then undergo further reduction. Hydrogenolysis of aromatic ethers can thus occur through anionic elimination of alkoxide. In the present case, reduction of the naphthalene and subsequent isomerization of the 1,4-dihydronaphthalene to a 1,2-dihydronaphthalene occurs in the absence of alcohol.³ However, alcohol when initially present serves to reduce the basicity of the reaction medium thereby suppressing these undesired olefin isomerization.⁴ It is noteworthy that, even in the presence of alcohol, lithium (but not potassium) affords the normal reduction product **4** in poor yield when a large excess of metal is employed (Table I).

TABLE I
REDUCTION OF 2,7-DIMETHOXYNAPHTHALENE

Metal	G.-atoms of metal per mole of 1	Method	Product(s)	Yield, %
Lithium	40 ^a	I ^a	2	~40
			3	~40
			2	~5
	65	II ^b	3	~95
			4	38
			4	76
Potassium	68	II ^b	4	72
	32		4	82

^a Reduction in the initial absence of alcohol. ^b Reduction in the presence of alcohol.

(4) The Wilds-Nelson modification of the Birch reduction, whereby addition of alcohol follows addition of the metal, is most effective for aromatic ethers which are reduced with difficulty: A. L. Wilds and N. A. Nelson, *J. Am. Chem. Soc.*, **75**, 5360 (1953). However, in the present case (where reduction is facile) this method gives only hydrogenolysis products.³ Similar behavior has been observed for other naphthalenic ethers: W. Hüchel and E. Vevera, *Chem. Ber.*, **89**, 2105 (1956); E. L. Eliel and T. E. Hoover, *J. Org. Chem.*, **42**, 938 (1959). A useful modification for the reduction of substituted anisoles with lithium in the presence of alcohol and ammonia has been developed by W. S. Johnson, W. A. Vredenburg, and J. E. Pike [*J. Am. Chem. Soc.*, **84**, 3409 (1960), and preceding papers of the series].

Hydrolysis of bisenol ether **4** afforded a yellow solid, m.p. 174–176°, in 54% yield. The bands at 5.82, 6.00, and 6.22 μ in the infrared spectrum of a chloroform solution of this substance were concordant with the dione structure **8**. However, the infrared spectrum of the solid differed markedly and displayed bands at 2.9–3.7, 6.27, and 6.52 μ , indicative of the enolic form **5**.

Ultraviolet spectral data (Table II) supported these conclusions. A preference for the keto form **8** in chloroform is confirmed by absorption maxima at 242 and 300 m μ , but in 95% ethanol the enol form **5** is the sole species. Addition of alkali intensified the absorption at 385 m μ , whereas acidification caused disappearance of this absorption peak and a hypsochromic shift of the peak at 324 to 322 m μ . The observable dissociation of enol **5** (λ_{max} 324 m μ) to anion **6** (λ_{max} 385 m μ) suggests its formulation as a vinylogous carboxylic acid. A calculation based on the ultraviolet spectrum reveals a pK_a value of 6.6 for **5** in 95% ethanol.⁵ This value is consistent with the observed solubility of **5** in aqueous sodium bicarbonate and its re-formation upon acidification with acetic acid.

TABLE II
ULTRAVIOLET SPECTRA OF 1(9)-OCTAL-2,7-DIONE AND RELATED COMPOUNDS

Compd.	Solvent	λ_{max} , m μ (ϵ)
5	C ₂ H ₅ OH	324 (27, 100)
		385 (8, 090)
5	C ₂ H ₅ OH, H ⁺	322 (24, 900)
6	C ₂ H ₅ OH, OH ⁻	385 (89, 000)
7	C ₂ H ₅ OH	312 (28, 200)
8	CHCl ₃ ^a	242 (13, 100)
		300 (2, 100)
3,5-Cholestadien-3-ol-7-one ^b	C ₂ H ₅ OH	320 (24, 300)
3,5-Cholestadien-3-ol-7-one ^b	C ₂ H ₅ OH, OH ⁻	393 (62, 200)
3-Methoxy-3,5-cholestadien-7-one ^b	C ₂ H ₅ OH	308 (27, 600)
3-Acetoxy-3,5-cholestadien-7-one ^b	C ₂ H ₅ OH	283 (22, 500)
3,5-Pregnadiene-3,21-diol-7,20-dione ^c	C ₂ H ₅ OH	321 (23, 600)
		391 (3, 800)
3,5-Pregnadiene-3,21-diol-7,20-dione ^c	C ₂ H ₅ OH, OH ⁻	391 (74, 400)

^a Free of ethanol. ^b C. W. Greenhalgh, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 2375 (1952). ^c See ref. 7.

Alkylation of **5** with dimethyl sulfate in aqueous sodium hydroxide afforded enol ether **7** as the sole product. Further alkylation studies are in progress.

Experimental⁶

2,7-Dimethoxy-1,4,5,8-tetrahydronaphthalene (1). A. Using 68 G.-Atoms of Metal.—To a solution of 1.10 g. of 2,7-dimethoxynaphthalene (**1**)³ in 380 ml. of anhydrous liquid ammonia containing 16.7 ml. of absolute ethanol and 100 ml. of anhydrous

(5) Dihydroresorcinol and dimedone gave a pK_a of about 5.25 in water: G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1162 (1940), and following papers.

(6) (a) Melting points were determined on a calibrated Fisher-Johns hot stage. Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. N.m.r. spectra were determined on a Varian A-60 spectrometer. (b) The isolation procedure consisted of thorough extraction and back-extraction with the specified solvent, washing the combined extracts with saturated brine, and drying the extracts over anhydrous magnesium sulfate. The solvent was removed from the filtered extracts at 50° on a rotary evaporator under reduced pressure. (c) The apparatus described by W. S. Johnson and W. P. Schneider [*Org. Syn.*, **30**, 18 (1950)] was used to maintain a nitrogen atmosphere.

ether was added 2.76 g. of lithium wire in small pieces over 1.5 hr. After addition of half of the metal an additional 20 ml. of ethanol was added. The ammonia was allowed to evaporate, the residue was neutralized with solid ammonium chloride, and the product was isolated with ether^{6b} after the addition of 150 ml. of water. The semisolid residue was distilled affording 0.97 g., b.p. 100° (bath temp.) at 0.2 mm. Crystallization from pentane gave 0.43 g. (38%): m.p. 64–66.5°; $\lambda_{\text{max}}^{\text{CCl}_4}$ 5.83, 5.97 (C=C), 8.17 (C—O), 8.68, 9.00, 9.88, 14.91 μ ; $\delta_{\text{TMS}}^{\text{CCl}_4} = 4.53$ (C=C—H, singlet), 3.50 (O—CH₃, singlet), 2.58 p.p.m. (C=C—CH₂, singlet), in the ratio 1.8:6.0:7.9. The analytical sample, m.p. 69–69.5°, was obtained after several recrystallizations from hexane.

Anal. Calcd. for C₁₂H₁₆O₂: C, 74.96; H, 8.39. Found: C, 74.9; H, 8.6.

When 46.8 g. of potassium was utilized in the reduction of 3.31 g. of 1 as described above, the crude crystalline residue could be directly recrystallized to give 2.44 g. (72%) of material, m.p. 68.5–69.5°.

B. Using 32 G.—Atoms of Metal.—Reduction of 1.95 g. of 1 in 160 ml. of 1:4 ether–ammonia containing 25 ml. of absolute ethanol with 12.0 g. of potassium as described above gave 1.64 g. (82%) of product, m.p. 66.5–69°, on repeated trituration of the crude crystalline material with pentane. The noncrystalline residues (0.13 g.) displayed $\lambda_{\text{max}}^{\text{EtOH}}$ 235 μ (ϵ 1100; mol. wt. 188) and 280 (300; mol. wt. 162), indicating less than 0.1% recovery of starting material and formation of methoxytetralin 2 in about 1% yield.³

Repetition of this experiment using 2.13 g. of lithium afforded 1.52 g. (76%) of material, m.p. 66.5–69°. The noncrystalline material (0.28 g.) displayed $\lambda_{\text{max}}^{\text{EtOH}}$ 235 μ (ϵ 1330; mol. wt. 188) and 280 (660; mol. wt. 162), indicating less than 0.2% recovery of starting material and formation of methoxytetralin 2 in about 5% yield.

1(9)-Octal-2,7-dione (8)—A solution containing 11.7 g. of bisenol ether 4 in 100 ml. of ethyl acetate; 45 ml. of ethanol, and 30 ml. of 10% aqueous hydrochloric acid was refluxed under nitrogen^{6c} for 1.2 hr. The cooled solution was diluted with 200 ml. of water and the product was isolated with ethyl acetate^{6b} affording 5.4 g. (54%) of yellow solid: m.p. 170–172.5° after recrystallization from ethyl acetate; $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.82 (ketone CO), 6.00 (conj. ketone CO), 6.22 μ (conj. C=C); $\lambda_{\text{max}}^{\text{KBr}}$ 2.9–3.7 (OH), 6.27 (conj. CO), 6.52 (conj. C=C),⁷ 8.53 (C—O), 7.42, 7.84, 10.87, 11.04, 11.39 μ . An additional recrystallization from ethyl acetate gave the analytical sample, m.p. 174–176°.

Anal. Calcd. for C₁₀H₁₂O₂: C, 73.14; H, 7.37; neut. equiv., 164. Found: C, 73.2; H, 7.5; neut. equiv., 160.

The peak at 385 μ in the ultraviolet spectrum of enol 5 (Table II) was used to obtain the concentration of anion 6 which, in turn, was used to calculate the pK_a. A value of 6.6 was thus obtained for 5 in 95% ethanol (2.6 × 10⁻⁵ M solution).

Extraction with aqueous sodium bicarbonate removed 96% of 5 from solution in ethyl acetate. Extraction with water under identical conditions removed only 8% of 5. Acidification of the sodium bicarbonate extracts with acetic acid gave an essentially quantitative recovery of 5.

7-Methoxy-2,3,4,4a,5,6-hexahydro-2H-naphthalenone (7).—A solution of 1.14 g. of enol 5 in 6 ml. of 10% aqueous sodium hydroxide and 3 ml. of water was treated with 3 ml. of dimethyl sulfate.⁸ After 5 min., an additional 5 ml. of 10% aqueous sodium hydroxide was added and the solution was stirred for 1 hr. The reaction mixture was diluted with 20 ml. of water and the product was isolated with ethyl acetate^{6b} affording 0.48 g. (39%) of waxy solid: b.p. 130° (bath temp.) at 0.2 mm.; $\lambda_{\text{max}}^{\text{KBr}}$ 6.07 (conj. ketone CO), 6.21, 6.32 (conj. C=C), 8.50 (C—O), 7.21, 7.50, 7.90, 7.98, 8.28, 11.32 μ . The analytical sample, m.p. 94–95°, was obtained by recrystallization from heptane.

Anal. Calcd. for C₁₁H₁₄O₂: C, 74.13; H, 7.92. Found: C, 74.0; H, 7.9.

Acidification of the aqueous alkaline portion of the reaction mixture with acetic acid afforded 0.63 g. (55% recovery) of enol 5, m.p. 167–172°, which was isolated with ethyl acetate.^{6b}

(7) R. H. Lenhard and S. Bernstein [*J. Am. Chem. Soc.*, **78**, 989 (1956)] report 2.90, 3.19, 5.87, 6.25 and 6.47 μ for 3,5-pregnadiene-3,21-diol-7,20-dione.

(8) The procedure of J. Cornforth and R. Robinson [*J. Chem. Soc.*, 1855 (1959)].

Acknowledgment.—We thank the Public Health Service (R.G. AI-04965) and the National Science Foundation for support of this work. The A-60 spectrometer was purchased with funds awarded Northwestern University by the National Science Foundation.

Pyrolysis of

2-Acetoxy-2-(3-oxobutyl)cyclohexane-1,3-dione

THOMAS A. SPENCER, STEVEN W. BALDWIN,
AND KLAUS K. SCHMIEGEL

Department of Chemistry, Dartmouth College,
Hanover, New Hampshire

Received November 18, 1964

Pyrolysis of 2-acetoxy-2-(3-oxobutyl)cyclohexane-1,3-dione¹ (I) over a Pyrex glass packed column in a recycling apparatus² at 350° and 0.5 mm. affords 2-(3-oxobutyl)- Δ^2 -cyclopentenone (II) in 70% yield. The other products of this remarkably efficient thermal ring contraction are acetic acid (79% yield), identified by infrared spectrum, v.p.c. retention time, and conversion to piperazonium diacetate,³ and carbon monoxide, identified by v.p.c. retention time.

The 2-(3-oxobutyl)- Δ^2 -cyclopentenone (II), b.p. 81–82° (0.1 mm.), had λ_{max} 5.85–5.88 and 6.10 μ , $\lambda_{\text{max}}^{\text{EtOH}}$ 227 μ (ϵ 12,400), $\delta_{\text{TMS}}^{\text{CS}_2} = 2.02$ (3H) and 7.22 p.p.m. (1H), and formed (at room temperature) a monosemicarbazone, m.p. 180–182° dec. Upon hydrogenation over palladium on carbon, II was converted exclusively to 2-(3-oxobutyl)cyclopentanone⁴ (III), which yielded a bissemicarbazone, m.p. 228–229° (lit.⁴ m.p. 229°). Cyclization of III with pyrrolidine and acetic acid afforded 5,6,7,8-tetrahydroindanone-5⁵ (IV) in 71% yield. The IV thus obtained, and its semicarbazone and 2,4-dinitrophenylhydrazone derivatives, were identical with authentic samples.⁵

The alternate structure V for the pyrolysis product can be ruled out for the following reasons. The expected ultraviolet absorption maximum for II in ethanol is 227 μ ⁶; for V it is 242 μ .⁷ The n.m.r. spectrum shows no peaks between 2.65 and 7.22 p.p.m.; the absorption due to the side-chain methylene protons of V should be found at ca. 3.1 p.p.m.⁸ Treatment of

(1) T. A. Spencer, K. K. Schmiegel, and K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 3785 (1963).

(2) K. L. Williamson, R. T. Keller, G. S. Fonken, J. Szmuskovicz, and W. S. Johnson, *J. Org. Chem.*, **27**, 1612 (1962).

(3) C. B. Pollard, D. E. Adelson, and J. P. Bain, *J. Am. Chem. Soc.*, **56**, 1759 (1934).

(4) N. S. Gill, K. B. James, F. Lions, and K. T. Potts, *ibid.*, **74**, 4923 (1952).

(5) G. Stork, A. Brizzolara, H. Landesman, J. Szmuskovicz, and R. Terrell, *ibid.*, **85**, 207 (1963). We wish to thank Professor Stork for kindly providing us with a sample of IV.

(6) (a) Calculated according to the tabulation of L. M. Fieser and M. Fieser ["Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 19], including the 10- μ hypsochromic shift noted for cyclopentenones by A. E. Gillam and E. S. Stern ["Electronic Absorption Spectroscopy," Arnold Publishers Ltd., London, 1954, p. 96]; (b) M. F. Ansell and S. S. Brown [*J. Chem. Soc.*, 2955 (1958)] report λ_{max} 226 μ (ϵ 8300) for 2-methylcyclopentenone.

(7) H. S. French and L. Wiley [*J. Am. Chem. Soc.*, **71**, 3702 (1949)] discuss the ultraviolet spectra of exocyclically α,β -unsaturated cyclopentenones.

(8) See, for example, spectrum no. 545 in "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963.