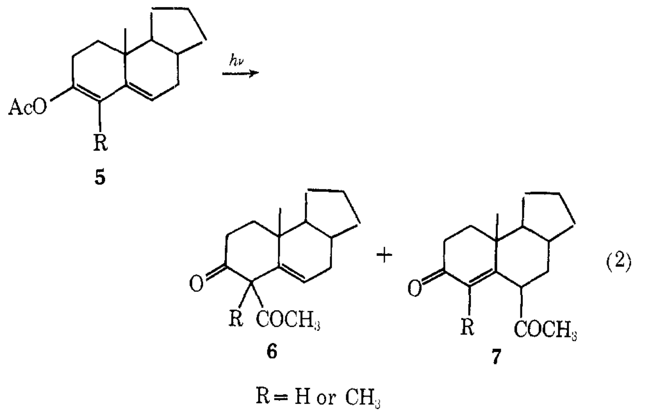
ride in carbon disulfide, whereupon the only volatile product was 2-phenylcyclohexanone.

Thus, under a variety of experimental conditions involving the use of light, heat, and acid treatment, β-phenyl vinyl acetates were found to resist 1,5-acyl migration to the aromatic ring. Two possible explanations are (1) an unfavorable stereochemical relationship for concerted 1,5-migration, and (2) the requisite loss of aromaticity along this pathway (eq 1). The reported occurrence of both 1,3- and 1,5-acyl migration in a steroidal dienyl acetate system (eq 2)[3] appears to minimize the importance of the former consideration. However, this conclusion would be invalid if **7** were actually derived from **6** by 1,3-acyl migration[8] rather than directly from **5** by 1,5 migration, a question that does not appear to be resolved.



Experimental Section

Irradiation of Phenylacetaldehyde Enol Acetate (1).—Irradiation of **1**, a mixture of the cis and trans isomers,[4] was carried out in solution at 254 nm with a low-pressure Hg immersion lamp (PCQ9G-1 lamp, supplied by Ultraviolet Products, Inc.). The solution, purged with N_2 prior to and during the irradiation, also contained an internal standard (*n*-tetradecane) for monitoring the reaction course by glc analysis.[9] Irradiation of **1**, 0.02 *M* in either benzene or acetonitrile, yielded a single product, which was photolabile and attained a maximum concentration of about 25%. The product, mp 69–70°, was obtained in 10% yield after silica gel chromatography and crystallization from ether–hexane, and was identified as 2-acetylphenylacetaldehyde (**2**), reported mp 67–68°,[5] on the basis of elemental and spectral analysis. The ultraviolet spectrum exhibited λ_{max}^{MeOH} at 310 nm (ϵ 6.65 × 10^3) and 242 (3.95 × 10^3). The infrared spectrum, obtained in chloroform, featured broad H-bonded OH absorption and strong bands at 1640, 1610, and 1605 cm^{-1}, indicative of the enolized β-dicarbonyl system. The nmr spectrum, obtained in deuteriochloroform, exhibited a sharp singlet at τ 7.85 (3 H, CH_3), a multiplet at τ 2.6 (5 H, aromatic hydrogens), a doublet at τ 1.70 (1 H, J = 6 Hz, vinyl H), and a doublet at τ −5.50 (1 H, J = 6 Hz, OH). Upon addition of D_2O, the OH resonance disappeared and the doublet at τ 1.70 was transformed into a singlet. The parent peak in the mass spectrum corresponded to the molecular ion (*m/e* 162) and the fragmentation pattern was consistent with the assignment.

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2. Found: C, 73.3; H, 6.0.[10]

Irradiation of 1-Acetoxy-2-phenylcyclohexene (3).—Irradiation of **3**,[7] prepared from 2-phenylcyclohexanone by treatment with acetic anhydride and *p*-toluenesulfonic acid,[11] was conducted as described above. In addition to small amounts of 2-phenylcyclohexanone, irradiation of **3** yielded a single product, mp 73–74°, which was obtained in 15% yield after silica gel chromatography and crystallization from ether–hexane. On the basis of elemental and spectral analysis, the product was formulated as the previously unknown compound, 2-acetyl-2-phenylcyclohexanone (**4**). The ultraviolet spectrum exhibited λ_{max}^{MeOH} at 285 nm (ϵ 340) and 260 (430), attributable to the β-phenyl carbonyl system. The infrared spectrum, obtained in chloroform, featured two closely spaced carbonyl bands at about 1710 cm^{-1}. The nmr spectrum, obtained in deuteriochloroform, exhibited a broad multiplet at τ 8.20 (4 H, C-4 and C-5 ring methylenes), a sharp singlet at τ 7.97 (3 H, CH_3), a broad multiplet at τ 7.44 (4 H, C-3 and C-6 ring methylenes), and a multiplet at τ 2.63 (5 H, aromatic hydrogens). In the mass spectrum, the base peak at *m/e* 174 is readily explicable in terms of the loss of ketene (McLafferty rearrangement) from the molecular ion (*m/e* 216), which was also present.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.8; H, 7.5. Found: C, 78.1; H, 7.5.

Pyrolysis Experiments.—On heating at 550° for 30 min in sealed Pyrex tubes, the enol acetates **1** and **3**, 0.05 *M* in benzene or acetonitrile which also contained an internal standard (*n*-hexadecane), were recovered unchanged as evidenced by glc and infrared analysis.

A solution of 100 mg of enol acetate **3** in 100 ml of cyclohexane was passed in a slow stream of N_2 over a period of 30 min through a vertical Vycor tube packed with glass helices (1 × 25 cm) and enclosed in an oven at 750°. The enol acetate suffered only slight decomposition under these conditions. However, when the helices were packed to a height of 50 cm, only trace amounts of starting material and volatile products were detected.

Treatment of 1-Acetoxy-2-Phenylcyclohexene (3) with Lewis Acids.—Treatment of **3** with $AlCl_3$ in CS_2 under standard conditions for the Fries rearrangement[12] led primarily to nonvolatile tarry material together with small amounts of 2-phenylcyclohexanone. On heating **3** with boron trifluoride etherate, both 0.1 *M* in benzene which also contained *n*-hexadecane (internal standard), in sealed Pyrex tubes at 210°, the enol acetate reacted slowly (50% in 1.5 hr) but only trace amounts of product could be detected by glc analysis, suggestive of a polymerization process.

Registry No.—**2**, 13055-49-7; **4**, 33777-04-7.

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[8] E. Baffiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969); also see D. I. Schuster, G. R. Underwood, and T. P. Knudsen, *J. Amer. Chem. Soc.*, **93**, 4304 (1971).

[9] Conducted on a Varian 1740 flame ionization instrument with a 5 ft × 1/8 in. column of 3% SE-30 on 100–120 Varaport.

[10] The relatively large discrepancy in carbon (0.8) is attributed to the instability of **2**, which underwent substantial decomposition on standing at room temperature in the dark over a period of 2 weeks.

[11] H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963).

[12] E. Miller and W. H. Hartung in "Organic Syntheses," Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N. Y., 1943, pp 543–545.

Photochemistry of 6-Propyl-2-cyclohexenone

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Received September 20, 1971

In extension of previous observations[2,3] on photolysis of cyclopentenones in dilute solution, we have examined the photochemistry of several alkylcyclohexenones.[4] The results indicate that photochemical reactions of the six-membered ring compounds are much less specific; complex mixtures of products result with no single component accounting for more than a fourth or fifth of the

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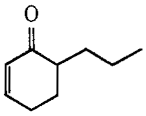
[1] Fellow of the Alfred P. Sloan Foundation and author to whom inquiries should be addressed.

[2] W. C. Agosta and A. B. Smith, III, *J. Amer. Chem. Soc.*, **93**, 5513 (1971).

[3] W. L. Schreiber and W. C. Agosta, *ibid.*, **93**, 3814 (1971).

[4] Earlier investigations in this general area, dealing largely with the lumirearrangement of 4,4-dialkyl-2-cyclohexenones, have been summarized and discussed by W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *J. Org. Chem.*, **33**, 4060 (1968).

total. A single example suffices, and we record here observations arising from photolysis of 6-propyl-2-cyclohexenone (**1**). Preparative experiments are described after the photochemical results.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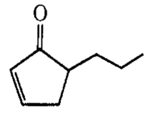
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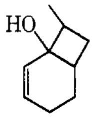
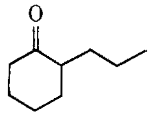


3

Under irradiation conditions[5] leading to about 75% destruction of 5-propyl-2-cyclopentenone (**2**) in 6 hr, photolysis of the homologous cyclohexenone (**1**) in *tert*-butyl alcohol required 2 weeks for similar conversion and furnished a host of volatile products. Of these we have identified four. The major component (23%[6]) was recognized from its ir and 220-MHz nmr spectra as cyclobutanol **3**. The photoreduction product, 2-propylcyclohexanone (**4**, 2%[6]), was identified by comparison with authentic material. A third component was a cyclization product, *exo*-5-methylbicyclo[2.2.2]-octan-2-one (**5**, 4%[6]), the structure of which was deduced from its spectroscopic properties and analogy with the formation (44%) of its lower homolog **6** from **2**.[2] As earlier with **6**,[2] the stereochemistry of the methyl substituent in **5** was confirmed by an independent synthesis which is detailed below. Also as before,[2] we found no sign (<1%) of the endo isomer of **5** among the photoproducts and ascribe this selectivity to steric control in cyclization of the type II[7] biradical **7**, which is the presumed precursor of both **5** and **3**.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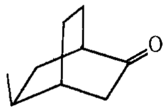
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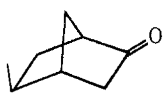
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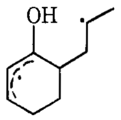

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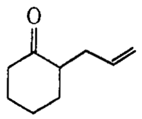
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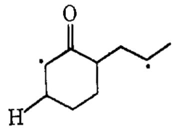
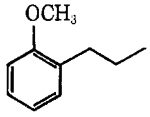


9

Finally we obtained a small amount of 2-allylcyclohexanone (**8**, 3%), a product representing transfer of unsaturation from ring to side chain. This may be the result of abstraction of hydrogen from the methyl group of **7** by the β carbon atom. Alternatively, the initial abstraction could be by the β carbon atom to form **9**, and this intermediate could then undergo hydrogen transfer from methyl to the α carbon atom. The former pathway seems more likely, since **7** is already implicated in formation of **3** and **6**, although there are known examples of direct hydrogen abstraction by the β carbon atom of unsaturated ketones.[2,3,8]

Starting ketone **1** was prepared from *o*-propylanisole (**10**) by Birch reduction followed by treatment with acid. The desired product was purified through the methiodide **11** of its Michael adduct with piperidine, all according to a procedure developed[9] earlier for closely related cyclohexenones. Pyridine-catalyzed elimination of *N*-methylpiperidine from **11** led to **1**. The corresponding saturated ketone **4** was available on catalytic hydrogenation of **1**.



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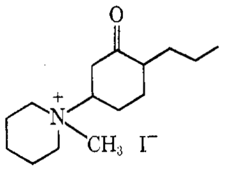
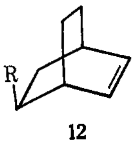


11

Synthesis of bicyclic ketone **5** began with the Diels–Alder adduct[10] of methyl acrylate and 1,3-cyclohexadiene. Methoxide-catalyzed equilibration of the adduct gave a 1:2 mixture of exo (**12a**) and endo (**13a**) esters, as reported.[10] Saponification then furnished a mixture of the carboxylic acids **12b** and **13b**, which were separated by selective formation from **13b** of the iodolactone.[11] This left unchanged the desired exo acid **12b**, which was isolated and purified. Diazomethane esterification of **12b** yielded only **12a**, the configuration of which had been previously assigned[10] on the basis of nmr arguments and the base-catalyzed equilibration mentioned above. Acid **12b** was now reduced with lithium aluminum hydride to alcohol **12c**, and this was converted to the tosylate **12d** and again reduced with hydride to form hydrocarbon **12e**. The overall yield from **12b** to **12e** was 85%. Hydroboration[12] of the double bond of **12e**, followed by dichromate oxidation, provided a mixture of **5** and **14**. This mixture was reduced directly to the related alcohols, which were partially separated by preparative vpc of the derived trimethylsilyl ethers.[13] A pure ether **15a** was isolated and converted on acid hydrolysis to a single alcohol **15b**.



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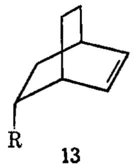
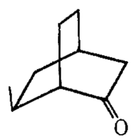


13

a, R = COOCH$_3$
b, R = COOH
c, R = CH$_2$OH
d, R = CH$_2$OTs
e, R = CH$_3$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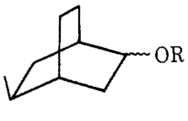

15

a, R = OSi(CH$_3$)$_3$
b, R = H

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[5] Complete details are given in ref 2; a uranium glass filter was used to prevent secondary photolysis of products which were saturated ketones.

[6] Yields are approximate only and are based on vpc analysis of the crude photolysate.

[7] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, Chapter 5; P. J. Wagner, *Accounts Chem. Res.*, **4**, 168 (1971).

[8] D. Belluš, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969), and references cited therein.

[9] G. Stork and W. N. White, *J. Amer. Chem. Soc.*, **78**, 4604 (1956).

[10] R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **30**, 423 (1965).

[11] W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, *J. Amer. Chem. Soc.*, **80**, 5488 (1958). In contrast to this earlier report, under our conditions the exo acid did not react in base with iodine.

[12] G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963).

[13] L. Birkofer and R. Ritter, *Angew. Chem., Int. Ed. Engl.*, **4**, 417 (1965); J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, **88**, 3390 (1966).

Jones oxidation[14] of this alcohol gave **5**, identical with the photolysis product from **1** by comparison of their vpc retention times and rather complex ir and 220-MHz nmr spectra.

Experimental Section

Materials and Equipment.—Solvent for the photochemical experiments was Matheson Coleman and Bell *tert*-butyl alcohol (chromatoquality). All vpc was done using a Varian Aerograph Model 700 Autoprep or Model A-90-P3 with one of the following columns: A, 30% QF-1, 10 ft × $^3/_8$ in.; B, 30% Carbowax, 10 ft × $^3/_8$ in.; E, 30% QF-1, 50 ft × $^1/_4$ in.; F, 30% SE-30, 10 ft × $^3/_8$ in. The column oven was operated at 90–190°, and helium carrier gas flow rate was 100–120 ml/min. Unless otherwise noted both ir and nmr spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer Model 237B spectrophotometer and the latter on a Varian Model HR-220 (220 MHz) spectrometer. Melting points are corrected. Photochemical experiments were carried out with a Hanovia Model L mercury lamp (No. 679A-36) in a quartz immersion well and using a uranium glass (Corning No. 3320) filter.

Photolysis of 6-Propyl-2-cyclohexenone (1).—A solution of 400 mg of **1** in 400 ml of *tert*-butyl alcohol was flushed with nitrogen for 15 min and then irradiated for 14 days under nitrogen with magnetic stirring. At the end of this period the mixture was poured into water and extracted with pentane. The pentane was washed with water, dried, and removed to give 308 mg of yellow oil. Analytical vpc on columns B and F indicated the presence of at least 18 products, four of which accounted for 32%[6] of the volatile material. These were isolated and identified. The data are given below in the order of elution from column B; the ratios of the four products were 1:1.11:10:1.74.

The first product was shown to be 2-propylcyclohexanone (**4**) by comparison of its ir spectrum and vpc retention time with those of a sample prepared by hydrogenation of **1** in methanol over palladium on carbon. A semicarbazone of the latter sample was prepared, mp 118–119°, (lit.[15] mp 116–118°, 118–121°, 119–120°), as well as a 2,4-dinitrophenylhydrazone, mp 150–151.5° (lit.[16] mp 153–154°).

The second product was shown to be 2-allylcyclohexanone (**8**). The ir spectra and melting points of the 2,4-dinitrophenylhydrazones derived from the photolysis product and from an authentic[16] sample of **8** were identical [mp 149–151°, mmp 149–151° (lit.[16] mp 149–150°)].

Spectroscopic data established that the third product was 8-methylbicyclo[4.2.0]oct-2-en-1-ol (**3**): ir 3610 (m), 3410 (m), 3010 (m), 1375 (m), 1270 (m), 1220 (m), 1112 (s), 1080 (s), 1025 (m), 995 (m), 940 cm^{-1} (m); nmr δ 0.73–1.27 (m), 1.12 (d, J = 7 Hz), 4 H, 1.32–2.73 (broad m, 8 H), 5.45–5.97 (m, 2 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.05; H, 10.11.

The fourth product was identified as 5-methylbicyclo[2.2.2]-octan-2-one from its spectra: ir 2950 (s), 2910 (sh), 2860 (s), 1730 (vs), 1470 (m), 1450 (m), 1400 (m), 1370 (m), 1218 (m), 1075 cm^{-1} (m); nmr δ 1.10 (d, J = 7 Hz, 3 H), 1.20 (m, 1 H), 1.51 (m, 1 H), 1.64–2.27 (m, 9 H); mass spectrum *m/e* 138.10409 (M^+) (calcd for $C_9H_{14}O$: *m/e* 138.10446). This assignment, along with the exo stereochemistry (see **5**), was confirmed by establishing the identity of this photoproduct with the synthetic ketone described below. The two samples gave identical complex ir and 220-MHz nmr spectra and had identical vpc retention times.

6-Propyl-2-cyclohexenone (1).—To a solution of 10.0 g of the anisol **10**[17] in 50 ml of ether and 150 ml of dry liquid ammonia was added 2.00 g of lithium ribbon. The mixture was stirred rapidly for 2 hr and then 18.5 ml of absolute ethanol was added. After 1 hr the blue color had disappeared and the ammonia was allowed to evaporate. Water was added with caution, and the mixture was extracted with ether. Removal of the ether left 10.0 g of oil which was treated with 15 ml of 10% HCl and 50 ml of methanol and then heated at reflux for 1 hr. This mixture was then added to water and extracted with ether. The ether solution was washed with saturated $NaHCO_3$ and dried; the solvent was removed through a Vigreux column to leave 8.86 g of liquid which could be purified directly by preparative vpc to give **1**. Alternatively, the crude product was converted to **11** (mp 183–184° from *n*-butyl alcohol) according to the procedure of Stork.[9] Treatment of **11** with pyridine[9] gave **1**. Vpc-purified material was analytically pure: ir 3030 (w), 2955 (s), 2930 (s), 2870 (s), 2725 (w), 1660 (s), 1620 (w), 1380 cm^{-1} (s); nmr δ 0.92 (t, J = 6 Hz, 3 H), 1.32 (m, 3 H), 1.74–2.34 (m, 4 H), 2.04 (m, 2 H), 5.84 (dt, $J_1 = 10$, $J_2 = 2$ Hz, 1 H), 6.77 (dt, $J_1 = 10$, $J_2 = 2$ Hz, 1 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.38; H, 10.37.

***exo*-Bicyclo[2.2.2]oct-2-ene-5-carboxylic Acid (12b).**—A mixture of **12b** and **13b** was prepared as previously described.[10,11] A 34.0-g sample of this mixture was dissolved in 344 ml of methanol, neutralized with 8.95 g of NaOH, and treated with 344 ml of 5% aqueous $NaHCO_3$. To this solution was added at room temperature over 1 hr with stirring a solution of 103.5 g of KI and 56.6 g of iodine in 344 ml of water. After 2 hr sufficient saturated aqueous $NaHSO_3$ was added to reduce all excess iodine, and the iodolactone was extracted into ether. This yielded 38.7 g of iodolactone (mp 72–74.5° from hexane). The aqueous reaction mixture was now acidified and extracted with ether which was washed and dried. This furnished 9.74 g of **12b**, mp 48–50° from pentane or after sublimation (lit.[11] mp 46–47°): ir 3500–2400 (broad), 3040 (s), 2940 (s), 2860 (s), 1705 (vs), 1410 (m), 1225 (s), 690 cm^{-1} (s).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.95; H, 7.92.

A 50-mg sample of **12b** was treated with excess CH_2N_2 in ether. Removal of solvent left an oil which by vpc analysis was shown to contain only one component. Preparative vpc on column B gave a liquid which was shown to be **12a** by comparison of its vpc retention time and ir spectrum with those of authentic **12a**.[10]

5-*exo*-Hydroxymethylbicyclo[2.2.2]oct-2-ene (12c).—To a solution of 2.26 g (59.4 mmol) of $LiAlH_4$ in 100 ml of ether was added dropwise at room temperature over 1 hr 6.26 g (39.7 mmol) of **12b** in 50 ml of ether. The mixture was heated at reflux for 22 hr and then quenched[18] with 2.3 ml of water, 2.3 ml of 15% aqueous NaOH, and 6.9 ml of water. Subsequent work-up gave 5.53 g (97%) of **12c**, which was purified by preparative vpc on column A: ir 3635 (m), 3335 (broad), 3045 (m), 2945 (s), 3460 (s), 1625 (w), 1055 (m), 1030 (m), 670 cm^{-1} (s).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.18; H, 10.31.

5-*exo*-Methylbicyclo[2.2.2]oct-2-ene (12e).—A 5.68-g sample of alcohol **12c** was converted to the tosylate with *p*-toluenesulfonyl chloride in pyridine in the usual fashion (10.77 g, 89%). This crude tosylate was dissolved in 60 ml of ether and added dropwise over 30 min to a solution of 20 g of $LiAlH_4$ in 100 ml of ether. The resulting solution was heated at reflux for 28 hr and then worked up as described for **12c** above.[18] Removal of solvent left 4.42 g (99%) of oil, which by vpc on column B was a single component. Preparative vpc gave pure **12e** as a liquid: ir 3045 (m), 2950 (s), 2860 (s), 1615 (w), 1465 (m), 1445 (m), 1370 (m), 1362 (m), 835 (m), 680 cm^{-1} (s); nmr δ 0.84 (m, 1 H), 0.94–1.63 (m), 1.01 (d, J = 7 Hz), 8 H, 1.31 (m, 1 H), 2.14 (m, 1 H), 2.42 (m, 1 H), 6.12 (dd, $J_1 = J_2 = 8$ Hz, 1 H), 6.32 (dd, $J_1 = J_2 =$ 8 Hz, 1 H).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.40; H, 11.42.

5-*exo*-Methylbicyclo[2.2.2]octan-2-one (5).—To a solution of 419 mg of $LiAlH_4$ in 15 ml of ether was added 2.00 g of olefin **12e**. The solution was cooled to 0° and 1.20 ml of boron trifluoride etherate in 2 ml of ether was added dropwise. The mixture was stirred at 0° for 15 min and then at room temperature for 2 hr. The reaction was quenched with 1.2 ml of water, and the resulting solution was treated dropwise with 3.57 g of $Na_2Cr_2O_7$ in 2.64 ml of concentrated H_2SO_4 and 14.4 ml of water over 1 hr at room temperature. After 2 hr more, water was added and the product was extracted into ether. Removal of ether

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[14] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953); C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

[15] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2014 (1950), and references cited therein.

[16] G. Opitz, H. Mildenberger, and H. Suhr, *Justus Liebigs Ann. Chem.*, **649**, 47 (1961).

[17] This ether was prepared from *o*-propylphenol according to the method of G. N. Vyas and N. M. Shah: "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 836.

[18] V. M. Mićović and M. L. J. Mihailović, *J. Org. Chem.*, **18**, 1140 (1953).

after washing and drying left 2.12 g (94%) of oil, which from ir and nmr evidence appeared to be a mixture of ketones **5** and **14**. A solution of 2.02 g of this mixture of ketones in 20 ml of ether was reduced with $LiAlH_4$ in the usual way to give 1.91 g (93%) of a solid showing hydroxyl but not carbonyl absorption in the ir. To 1.79 g of this solid was added 3.5 ml of bis(trimethylsilyl)-acetamide,[13] and the mixture was allowed to stand for 19 hr. The product was extracted into pentane, washed with water, and dried. There was recovered 2.22 g (82%) of a liquid showing no hydroxyl absorption in the ir. Vpc on column E gave a partial separation of these ethers into three components in the ratios 1:2:1. The third component was collected and shown to be homogeneous on reinjection. Hydrolysis of this ether in 2 *M* aqueous HCl followed by Jones oxidation[14] of the alcohol **15b** gave a single ketone (**5**). This was purified by vpc on column B and was identical with the photoproduct described above.

Registry No.—**1**, 33777-32-1; **3**, 33777-33-2; **5**, 33890-38-9; **12c**, 33780-85-7; **13e**, 14926-88-6.

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Synthesis of a Hydroxyxanthone Dicarboxylic Acid, Cassiaxanthone. Reactions of γ-Resorcylic Acid with Phenols

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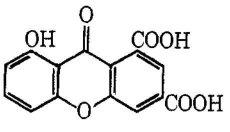
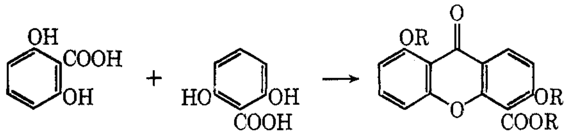
Cassiaxanthone (**1**)[1] and cassiolin (pinselin)[2] (**4h**) are, to our knowledge, the only xanthones from *Cassia* species so far reported. It is interesting that these both have a carboxylic acid function on the xanthone nucleus. None of the other xanthones isolated from higher plants are of this type.[3]



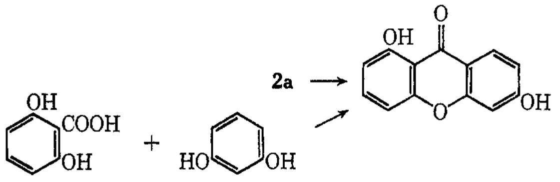
1

In the course of investigating possible routes to the synthesis of cassiaxanthone, γ-resorcylic acid was condensed with a number of phenols, using either polyphosphoric acid (PPA)[4] or $POCl_3$ and $ZnCl_2$.[5] These reactions generally afforded, besides or instead of the expected xanthone, a mixture of other products. We have examined this mixture and found that the main components are (a) 1,6-dihydroxyxanthone-5-carboxylic acid (**2a**) resulting from self-condensation (eq 1); (b) 1,6-dihydroxyxanthone resulting from self-condensation and subsequent decarboxylation or from condensation of γ-resorcylic acid with resorcinol resulting from decarboxylation (eq 2); (c) esters of **2a** (**3a**, **3c**, **3e**) (eq 3); and (d) polymeric products.

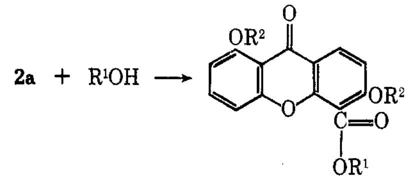


(1)

2a, R = H
b, R = Me



(2)



(3)

3

Compd	R¹	R²
a	Phenyl	H
b	Phenyl	Me
c	3,5-Methylphenyl	H
d	3,5-Methylphenyl	Me
e	Ethyl	H
f	Ethyl	Me

The proportion of the various products obtained is shown in Table I. Most of the crude product (see last column), not accounted for in other columns, was an insoluble material which remained at the origin of a thin layer chromatogram, and is probably polymeric.

It is apparent that the temperature, the reagent, and the nature of the participating phenol all influence the results.

Attempted condensation of γ-resorcylic acid with phenol at lower temperatures yielded only a small amount of the expected product, 1-hydroxyxanthone. The two main products were the result of self-condensation of γ-resorcylic acid. One was 1,6-dihydroxyxanthone-5-carboxylic acid. The second was a compound of mp 196–197°. Preliminary examination suggested that this might be 1,8-dihydroxyxanthone formed by condensation ortho to both hydroxyl groups of resorcinol.[6] This possibility was ruled out by nmr spectrum which showed a peak at δ 8.41 for a proton peri to the xanthone carbonyl.

Clues to the structure of the compound were afforded by its ir spectrum and that of its methylation product, and by its mass spectrum. In the ir spectrum of the methylated product, in contrast to that of the parent compound, there was a peak at 1760 cm^{-1} suggesting the presence of a phenyl ester grouping, the carbonyl

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[1] M. S. R. Nair, T. C. McMorris, and M. Anchel, *Phytochem.*, **9**, 1153 (1970).

[2] C. E. Moppett, *J. Chem. Soc. D*, 423 (1971).

[3] J. Carpenter, H. O. Locksley, and F. Scheinmann, *Phytochem.*, **8**, 2013 (1969).

[4] F. Uhlig and H. R. Snyder, *Advan. Org. Chem.*, **1**, 35 (1960).

[5] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 880.

[6] Analytical values for C, H, and O were in good agreement. The R_f was higher than that of 1,6-dihydroxyxanthone. Comparison of the melting point and uv spectrum with those reported in the literature[7-10] for samples prepared by a different method did not permit an unequivocal conclusion as to identity.

[7] A. Baeyer, *Justus Liebigs Ann. Chem.*, **372**, 80 (1910).

[8] D. L. Dreyer, Ph.D. Thesis, University of Washington, 1960. University Microfilms, Inc., Ann Arbor, Mich.

[9] P. Yates and G. H. Stout, *J. Amer. Chem. Soc.*, **80**, 1691 (1958).

[10] O. R. Gottlieb, M. Taveira Magalhaes, M. Ottoni da Silva Pereira, A. A. Lins Mesquita, D. de Barros Correa, and G. G. De Oliveira, *Tetrahedron*, **24**, 1601 (1968).