formaldehyde[14] and the formaldehyde vapors were carried by a stream of N_2 over the surface of a stirred THF solution (50 ml) of α-lithiated lithium nonanoate (3.28 g, 0.02 mol) containing 1 molar equiv of HMPA. The reaction was terminated after complete depolymerization of paraformaldehyde. The reaction solution was cooled in an ice bath and neutralized with dilute (10%) hydrochloric acid until acidic. The aqueous layer was separated and extracted with ethyl ether. To ensure complete removal of HMPA, the ether layer was extracted with four portions of dilute hydrochloric acid. The ether layer was dried and α-heptylhydracrylic acid was recovered by evaporation of solvent, yield 2.85 g (90%). The crude product was purified by crystallization from acetonitrile.

Other similarly prepared α-alkylhydracrylic acids (Table I) were purified by crystallization (solvent in parenthesis): α-dodecyl, α-tetradecyl, and α-hexadecyl (hexane); α-phenyl (ethyl alcohol). α-Butylhydracrylic acid was distilled in vacuum.

Preparation of 2-Heptylacrylic Acid.—2-Heptylhydracrylic acid (2.0 g, 0.01 mol) and phosphoric acid (one drop) were stirred in a R.B. flask (10 ml) equipped with a short-path distillation head and heated to 180° in a Wood's metal bath under vacuum (0.5 mm) for 30 min. The temperature was raised to 270° to decompose the estolides and to distil pure 2-heptylacrylic acid (head temperature, 122°), yield 1.7 g (94%). The long-chain derivatives were also recrystallized, 2-dodecylacrylic acid from hexane and 2-tetradecyl- and 2-hexadecylacrylic acids from acetone. Table II records properties and yields.

Registry No.—Formaldehyde, 50-00-0.

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[14] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 397.

Investigations on Vinylogous Fries and Photo-Fries Rearrangements[1]

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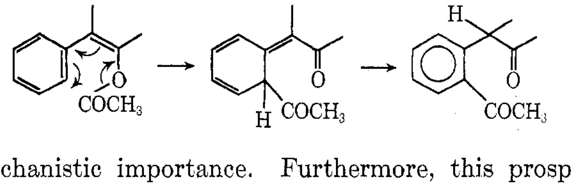
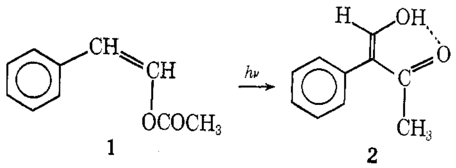
The photo-Fries rearrangement has been widely investigated and extended to simple vinyl esters,[2] as well as to the 1,3-dienyl acetate system, which is reported to undergo both 1,3- and 1,5-acyl migration.[3] The latter finding raises questions concerning the photoreactivity of β-phenyl vinyl acetate derivatives which may *a priori* undergo 1,3-acyl migration as a simple vinyl system or 1,5 migration to the ortho ring position, which would constitute a vinylogous Fries rearrangement (eq 1), a new reaction of potential synthetic and mechanistic importance. Furthermore, this prospect prompted studies on the thermal reactivity of this system which were carried out both in the presence and absence of Lewis acids.



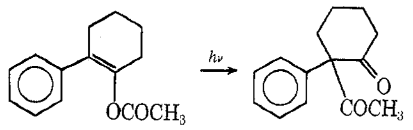
(1)

Irradiation (254 nm) of phenylacetaldehyde enol acetate (1), as a mixture of the cis and trans isomers,[4] in benzene or acetonitrile solution, yielded the known α-acetyl phenylacetaldehyde (2)[5] as the only apparent primary photoproduct, which was determined by monitoring (glc) the reaction at less than 5% conversion with the use of an internal standard. Throughout the reaction course, no additional products were in evidence in significant amounts, although 2 was found to be photolabile and attained a maximum concentration of about 25%. The product 2, mp 69–70°, was isolated by silica gel chromatography and characterized by elemental and spectral analysis (see Experimental Section). This result parallels the known photorearrangement of β-phenyl enamides, which also undergo 1,3-acyl migration.[6]



1 2

With the hope of enhancing the prospect of 1,5-acyl migration, the photochemistry of 1-acetoxy-2-phenylcyclohexene (3)[7] was also investigated, in which case (1) the phenyl and acetoxy groups are fixed in the requisite cis configuration for concerted migration, and (2) 1,3 migration is sterically more hindered. However, only the product of 1,3 migration, the previously unknown 2-acetyl-2-phenylcyclohexanone (4), was produced together with small amounts of 2-phenylcyclohexanone. The assignment of structure 4 was readily deduced from elemental and spectral analysis (see Experimental Section).



3 4

In the absence of Lewis acids, this system was found to be remarkably heat stable. Both 1 and 3 were quantitatively recovered after being heated in benzene or acetonitrile solution at 550° for 30 min in sealed tubes, as evidenced by glc and infrared analysis. Compound 3 remained essentially unchanged on passage through a Vycor tube packed with glass helices (1 × 25 cm) at 750°. On the other hand, when the helices were packed to a height of 50 cm, only trace amounts of starting material and volatile products were detected.

On heating 3 at 210° in benzene together with an equimolar amount of boron trifluoride etherate and an internal standard, slow decomposition occurred (about 50% in 1.5 hr); however, only trace amounts of products could be detected by glc analysis, suggestive of a polymerization process. The bulk of the material was apparently polymerized, as well, on treatment of 3 under standard Fries conditions with aluminum chlo-

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[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. (b) Taken in part from the Ph.D. thesis of J. E. A., North Dakota State University.

[2] (a) V. I. Stenberg in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, pp 127–153; (b) D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967).

[3] Y. Mazur and M. Gorodetsky, *J. Amer. Chem. Soc.*, **86**, 5213 (1964).

[4] D. T. Witiak and B. B. Chaudhari, *J. Org. Chem.*, **30**, 1467 (1965).

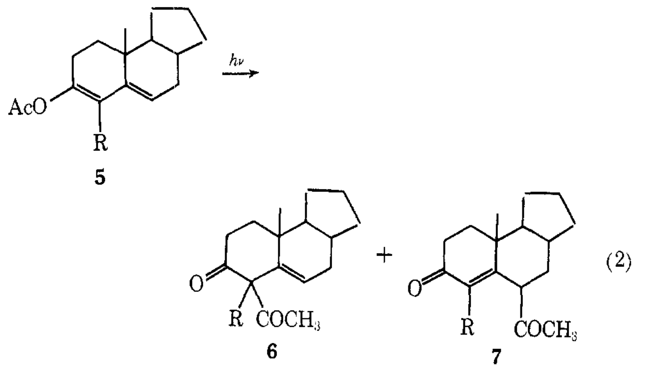
[5] H. Yasuda, *Yakugaku Zasshi*, **79**, 623 (1959); *Chem. Abstr.*, **53**, 21885e (1959).

[6] R. W. Hoffmann and K. R. Eicken, *Tetrahedron Lett.*, 1759 (1968).

[7] A. N. Kost and I. P. Sugrobova, *Vestn. Mosk. Univ., Ser. II*, **18**, 75 (1963); *Chem. Abstr.*, **59**, 7460d (1963).

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.



(2)

R = H or CH_3

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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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).