were obtained from the areas under the peaks given by the separated compounds. The separations on which the quantitative data were based were as follows.

Methyl *O*-methyl-D-glucoside	V_R (relative to methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucoside)	
	β isomer	α isomer
2,3,4,6-Tetra-	0.74	1.00
2,4,6-Tri-	1.66	2.33
2,3,4-Tri-	1.39	1.84
2,4-Di-[3]	3.26	4.51
2,3-Di-[3]	3.26	4.51
2-Mono[4]	—	—

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[3]Not resolved by gas–liquid chromatography. The relative proportions were determined by the amounts of the two compounds recovered from preparative paper electrophoresis.

[4]Not analyzed by gas–liquid chromatography. Quantitative data based on the amount recovered from preparative chromatography.

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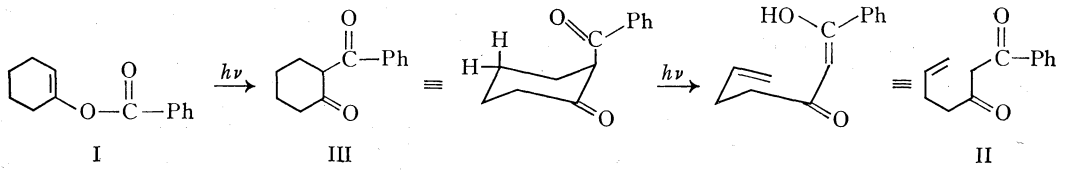
Concerning the irradiation of enol benzoates

C. L. McIntosh

Recently, the rearrangement of enol acetates and benzoates by thermal and photolytic means has been studied extensively. Mazur has shown that irradiation of enol acetates in cyclohexane with a low-pressure mercury arc lamp results in acetyl group migration to the vinyl carbon atom (1). Similarly, in the thermal rearrangement of enol acetates (2*a*, 2*b*), an analogous acyl migration is observed, as well as other



I III II

fragmentation processes. In addition to cleavage reactions, enol benzoates undergo a similar Fries rearrangement at high temperatures (400–500°) (2) to yield the corresponding β-diketones.

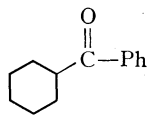
An anomalous rearrangement of cyclohexen-1-yl benzoates (I) has recently been reported (3) to give 1-benzoylhex-5-en-2-one (II), rather than 2-benzoylcyclohexanone (III), the product expected by analogy to the thermal reaction of I. Although several possible mechanisms were put forth to explain this anomaly (3), no specific one was shown to be correct.

In connection with our investigation (4) of a reaction which could be considered the reverse of the Fries reaction, i.e. the photolytic rearrangement of a β-keto sulfone to a vinyl sulfonate ester, the irradiation of cyclohexen-1-yl benzoate (I) was reinvestigated in an effort to determine the mechanism for the unprecedented ring opening of I to give II. It was found that, as reported, irradiation of I in cyclohexane with a low-pressure mercury arc gave 1-benzoylhex-5-en-2-one (10%); however, separation of the reaction mixture by thin-layer chromatography also gave 2-benzoylcyclohexanone (6), a previously unobserved product. It would appear that 2-benzoylcyclohexanone might therefore be an intermediate in the formation of II.

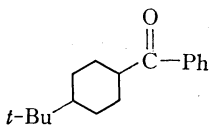
In fact, it was found that, upon irradiation of 2-benzoylcyclohexanone under similar conditions, 1-benzoylhex-5-en-2-one was formed in a high yield (72%). It would seem reasonable, therefore, to say that the expected Fries rearrangement does occur, but that it is rapidly followed by a Norrish type II cleavage of the resulting β-diketone II.[1]

Since 2-benzoylcyclohexanone is enolized only to a small extent (approximately 20% in CCl_4, as determined by nuclear magnetic resonance),[2] the occurrence of a Norrish type II cleavage under these conditions is not unexpected. On the other hand, this second reaction was observed only in the 2-benzoylcyclohexanone systems examined, and not in isopropenyl benzoate, cholest-2-en-3-ol benzoate, and 5α-androst-16-en-3β,17-diol-3-acetate-17-benzoate, a fact which can be explained readily, since no γ hydrogens are available in the latter molecules for abstraction. Also, the failure to find an analogous reaction when enol acetates containing γ hydrogens were irradiated is probably attributable to competition between the Norrish type II cleavage and a more rapid enolization of the β-diketone to give the stable enol form (approximately 100% in cyclohexane (1*b*).

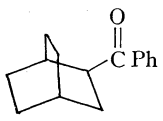
In an effort to substantiate this mechanism, cyclohexyl phenyl ketone (IV) and *cis*-4-*t*-butylcyclohexyl phenyl ketone (V) were irradiated. However, the products of both compounds IV and V showed no formation of a terminal vinyl group on examination by infrared and nuclear mag-



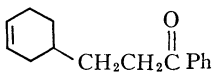
IV



V



VI



VII

[1]Although Kan (12) correctly rationalizes the formation of the 1-benzoylhex-5-en-2-one as going through the intermediate 2-benzoylcyclohexanone, his mechanism subsequently involves an unusual cleavage of this β-diketone. The Norrish type II cleavage suggested here is unexceptional.

[2]The area of the peak at δ 4.35 was 80% of the theoretical as compared with the area of the aromatic peaks; also, it has been shown by ultraviolet spectroscopy that the amount of enolization in ethanol is only 20% (5).

netic resonance spectroscopy. Rather, this examination indicated reduction of the benzoyl group.

The more stable conformers of the cyclohexane rings in IV and V are the equatorial chair form of the cyclohexyl phenyl ketone and the diequatorial twist boat form of the *cis*-4-*t*-butylcyclohexyl phenyl ketone. Neither of these allows the carbonyl oxygen and the γ hydrogen to come within the required distance for abstraction. Instead, hydrogen abstraction from the more readily available solvent cage occurs, with the formation of the reduced products observed.

Only when the geometry was fixed, as in bicyclo[2.2.2]octyl phenyl ketone (VI), was the desired Norrish type II cleavage obtained on irradiation, with the production of 2-(2-cyclohexenyl)ethyl phenyl ketone (VII). Compound VII was identified by comparison with a sample prepared from 2-(2-cyclohexenyl)propionyl chloride (6) and diphenylcadmium.

EXPERIMENTAL

The infrared spectra were recorded on a Beckman IR 5A or 7 spectrophotometer, the ultraviolet spectra on a Cary model 14 spectrophotometer, and the nuclear magnetic resonance spectrum on a Varian A-60 spectrometer, with tetramethylsilane as an internal standard. The melting points are uncorrected.

Irradiations

The irradiations were carried out in two ways.

(*a*) The solution was irradiated in a water-cooled immersion apparatus of approximately 200 ml volume with an 85 W Hanovia medium-pressure mercury lamp through a Vycor filter after it had been degassed with oxygen-free nitrogen.

(*b*) The solution was irradiated in a quartz tube (2.7 × 10.0 cm) of approximately 40 ml volume in a Rayonet Srinivasan photochemical reactor after it had been degassed.

Irradiation of 1-Cyclohexenyl Benzoate (I)

1-Cyclohexenyl benzoate, prepared as described by Mazur (3), b.p. 106–108 °C at 0.5 mm (lit. b.p. 136–138° at 1 mm), was irradiated in cyclohexane as described in method *b*. When separated by thin-layer chromatography (10% ethyl acetate – petrol on Keiselgel), the product mixture gave 1-benzoylhex-5-en-2-one, R_f 0.4 (10%) (3), and 2-benzoylcyclohexanone, R_f 0.3 (6%), m.p. 91–91.5° (lit. m.p. 86.5–88.5° (7)).

Irradiation of 2-Benzoylcyclohexanone

A solution of 2-benzoylcyclohexanone (7) in cyclohexane (1%) was irradiated at 50° (required for solubility) (4 h) as described in method *b*. Separation by thin-layer chromatography as above gave only starting material, R_f 0.2, and 1-benzoylhex-5-en-2-one, R_f 0.3 (72%). The addition of excess saturated cupric acetate to the latter gave the Cu^{2+} complex, m.p. 133–135° (lit. m.p. 133–135° (3)).

Irradiation of Cyclohexyl Phenyl Ketone (IV)

(*a*) Cyclohexyl phenyl ketone (8), m.p. 55–56°, in cyclohexane (0.3%), when irradiated as described in method *a* (3 h), gave a 160% yield of material whose infrared and nuclear magnetic resonance spectra showed no terminal vinyl group, but did indicate reduction of the benzoyl group.

(*b*) Irradiation in cyclohexane (2%) as described in method *b* at 50° (20 h) gave again an increase in weight (110%). The carbon tetrachloride portion of the mixture was shown to be starting material by its infrared and nuclear magnetic resonance spectra, and the rest insoluble polymer.

Preparation of cis-4-t-Butylcyclohexyl Phenyl Ketone (V)

cis-4-*t*-Butylcyclohexylcarbonyl chloride (9) (1 g) was added dropwise in 10 ml of dry benzene to a mixture of aluminium chloride (1 g) in benzene (50 ml), with stirring. After the mixture was stirred for an additional 3 h, it was hydrolyzed with water (30 ml) and extracted twice with ether; then the ether layer was washed with water, dried, and evaporated to dryness. Crystallization of the residue from methylene chloride – petrol gave *cis*-4-*t*-butylcyclohexyl phenyl ketone (55%), m.p. 108–109°; $\nu_{max}^{CCl_4}$ 1 688 cm^{-1} (C=O); λ_{max}^{EtOH} 240 (log ϵ 4.08), 319 (log ϵ 1.96), and 275 (shoulder) (log ϵ 2.41) mμ.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.62; H, 9.55.

Addition of 2,4-dinitrophenylhydrazine sulfate reagent gave a 2,4-dinitrophenylhydrazone, m.p. 157–159°; λ_{max}^{EtOH} 363 (log ϵ 4.29), 218 (shoulder) (log ϵ 4.26), and 251 (shoulder) (log ϵ 4.03) mμ.

Irradiation of cis-4-t-Butylcyclohexyl Phenyl Ketone (V)

(*a*) A solution of *cis*-4-*t*-butylcyclohexyl phenyl ketone (0.1%) in cyclohexane was irradiated as described in method *a* (1.5 h); evaporation of the solvent gave a 175% yield of material whose infrared and nuclear magnetic resonance spectra showed no terminal vinyl group, but did indicate reduction of the benzoyl group.

(*b*) Irradiation of this compound in cyclohexane (7%) as described in method *b* (24 h) at 50° gave, on evaporation of the solvent, a mixture of products (120%) which, when separated by thin-layer chromatography (10% ethyl acetate – petrol), contained no compound showing a terminal vinyl group in its infrared or nuclear magnetic resonance spectra.

Preparation of Bicyclo[2.2.2]octyl Phenyl Ketone (VI)

This ketone was prepared from bicyclo[2.2.2]octylcarbonyl chloride (10) as described for compound V above. Recrystallization from methanol gave bicyclo[2.2.2]octyl phenyl ketone (43%), m.p. 89–

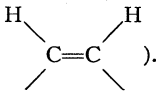
90°; $\nu_{max}^{CCl_4}$ 1 687 cm^{-1} (C=O); λ_{max}^{EtOH} 242 (log ϵ 4.07), 277 (log ϵ 2.95), and 318 (log ϵ 2.03) mμ.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.09; H, 8.47. Found: C, 83.65; H, 7.98.

Addition of 2,4-dinitrophenylhydrazine sulfate gave a 2,4-dinitrophenylhydrazone, m.p. 194–195°; λ_{max}^{EtOH} 365 (log ϵ 4.34) mμ.

Irradiation of Bicyclo[2.2.2]octyl Phenyl Ketone (VI)

(*a*) After irradiation of this ketone (1 h) in cyclohexane (0.15%) as described in method *a*, separation by thin-layer chromatography (10% diethyl ether – petrol) gave starting material, R_f 0.6 (60%), and 2-(2-cyclohexenyl)ethyl phenyl ketone, R_f 0.4 (15%), $\nu_{max}^{CCl_4}$ 1 690 cm^{-1} (C=O); λ_{max}^{EtOH} 242 (log ϵ 4.08) and 278 (log ϵ 2.96) mμ; δ 5.59 p.p.m. (multiplet, 2H,



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Addition of 2,4-dinitrophenylhydrazine sulfate gave a 2,4-dinitrophenylhydrazone, m.p. 172–173°; λ_{max}^{EtOH} 219 (log ϵ 4.14) and 376 (log ϵ 4.24) mμ.

Anal. Calcd. for $C_{21}H_{22}N_4O_4$: C, 63.94; H, 5.62. Found: C, 63.21; H, 5.94.

(*b*) Irradiation in cyclohexane (8%) at 50° as described in method *b* (3 h) gave a mixture of products. Separation by thin-layer chromatography (10% ethyl acetate – petrol) gave starting material (R_f 0.8 (50%)), 2-(2-cyclohexenyl)ethyl phenyl ketone (R_f 0.5 (15%)), and acetophenone (R_f 0.6 (15%)),[3] the latter being identified by its infrared spectrum and its 2,4-dinitrophenylhydrazone derivative.

Preparation of 2-(2-Cyclohexenyl)ethyl Phenyl Ketone

The acid chloride of 3-(2-cyclohexenyl)propionic acid (6) was prepared by refluxing the acid (5 g) in thionyl chloride (20 ml, 2 h), followed by removal of the excess solvent at room temperature under vacuum. The resulting material was then added in benzene (25 ml) to diphenylcadmium (13.6 g) in dry benzene (100 ml) very quickly. The mixture was stirred (2 h) at reflux and cooled to room temperature; then 6 *N* sulfuric acid (100 ml) was added, and the mixture was shaken, separated, and washed twice with ether (100 ml). The combined ether layers were washed with water, dried, and evaporated to dryness. The residue was separated on a column (3.0 × 42 cm) of silica gel. Elution with 10% ethyl acetate – petrol (b.p. 35–60°) gave the desired fraction, which was further purified by separation on a Varian Aerograph vapor-phase chromatograph (5% FFAP, 5 ft × $\frac{1}{4}$ in. column at 240° with 60 cc of helium/min) to yield 2-(2-cyclohexenyl)ethyl phenyl ketone, b.p. 87° at 0.1 mm, identical with that obtained from the above irradiations.

[3]Acetaldehyde was formed as the result of a second Norrish type II cleavage of the initially formed VII, which was a substituted butyrophenone (11).

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