isojervine triacetate IVb (lack of contribution of 17,17a-double bond); $\lambda_{\max}^{\text{Nujol}}$ 5.79 (s), 5.86 (s), 5.93 (s), 6.11 (s), 8.08 (s) μ. For analysis the material was lyophilized from benzene and dried at 56° (2 mm.) for 3 hr.

Anal. Calcd. for $C_{31}H_{43}O_6N$ (527.7): C, 70.83; H, 8.25. Found: C, 70.44; H, 8.02.

Material exhibiting a completely identical infrared spectrum was obtained from the crystalline 4,5-dihydro derivative[1] of N-acetyl-Δ^4-isojervone (XII) by treatment with perbenzoic acid and subsequent acetylation.

4,5,13,17a-Tetrahydro Derivative XX of Enone–Dienone of XV.—A solution of the enone–dienone (101 mg.) in absolute ethanol (14 ml.) was shaken in a hydrogen atmosphere with 5% palladium on charcoal (105 mg.), and 2 equiv. of hydrogen were consumed in 40 min. After the removal of the solvent and the catalyst, the residue which could not be crystallized was lyophilized from benzene; $\lambda_{\max}^{\text{alc}}$ 238 mμ (ε 9180); $\lambda_{\text{sh}}^{\text{alc}}$ 317 mμ (ε 74); $\lambda_{\max}^{\text{Nujol}}$ 2.95 (m, br), 5.78 (s, sh), 5.85 and 5.93 (s), 6.17 (s, br), 8.08 (s, br), 9.77 (ms), 10.45 (m, br) μ.

Anal. Calcd. for $C_{31}H_{45}O_6N$ (527.68): C, 70.56; H, 8.60. Found: C, 69.85; H, 8.57.

4,5-Dihydrojervisine Base XXI from XVIIIa.—When a solution of the jervisine base 17-monoacetate (51.1 mg.) in absolute ethanol (6 ml.) was hydrogenated in the presence of 5% palladium on charcoal (54 mg.), 1 molar equiv. of hydrogen was consumed in 10 min. The residue, after the filtration and evaporation of the ethanol, could not be crystallized and hence was lyophilized from benzene; $\lambda_{\max}^{\text{alc}}$ 237 mμ (ε 9140); $\lambda_{\text{sh}}^{\text{alc}}$ 325 mμ (ε 64); $\lambda_{\max}^{\text{Nujol}}$ 2.90 (ml), 5.79, 5.85, and 5.91 (s), 8.00 (s) μ.

Acknowledgment.—The authors are indebted to Mr. J. F. Alicino and his associates for the microanalyses and to Dr. N. Coy and her associates for the spectral determinations reported in this paper.

The Photochemical Reactions of Alkyl Phenylglyoxalates in Alcohols[1]

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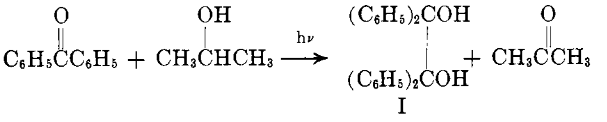
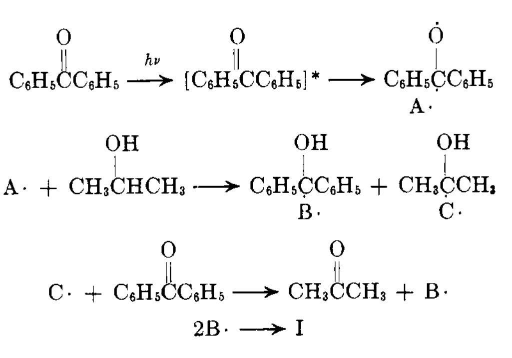
The primary and secondary alkyl esters of phenylglyoxalic acid undergo a photochemical reaction in alcohols in which the phenylglyoxalate is reduced to the mandelate ester of the solvent alcohol and the alcohol moiety of the phenylglyoxalate ester is oxidized. A mechanism involving an intramolecular hydrogen abstraction reaction in the photochemically excited phenylglyoxalate ester is suggested to account for the products of these reactions.

The photochemically induced reactions of aryl ketones in various solvents generally result in reductive dimerization of the aryl ketone to a 1,2-diol and an oxidation of the solvent.[3] A familiar example of such a reaction is the photochemical reduction of benzophenone in 2-propanol, a reaction which yields benzpinacol (I) as the reduction product of the aryl ketone and acetone as the oxidation product of the solvent.



$$C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5 + CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow{h\nu} \underset{\text{I}}{\begin{array}{c}(C_6H_5)_2COH\\ |\\ (C_6H_5)_2COH\end{array}} + CH_3\overset{O}{\overset{\|}{C}}CH_3 \qquad (1)$$

The mechanism of this reaction has been proposed and involves the following sequence of reactions.[3,4]



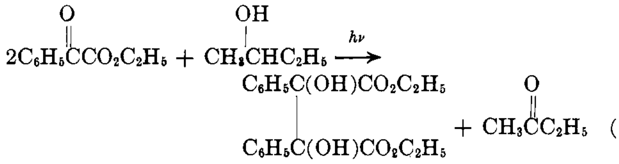
$$C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{h\nu} [C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5]^* \longrightarrow \underset{A\cdot}{C_6H_5\overset{\dot{O}}{\overset{|}{C}}C_6H_5} \qquad (2)$$

$$A\cdot + CH_3\overset{OH}{\overset{|}{C}}HCH_3 \longrightarrow \underset{B\cdot}{C_6H_5\overset{OH}{\overset{|}{C}}C_6H_5} + \underset{C\cdot}{CH_3\overset{OH}{\overset{|}{C}}CH_3} \qquad (3)$$

$$C\cdot + C_6H_5\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + B\cdot \qquad (4)$$

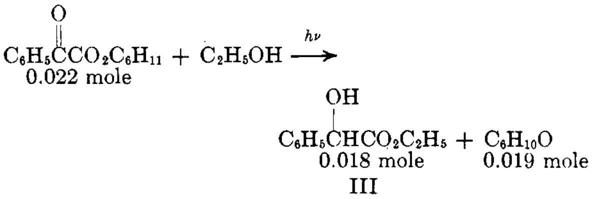
$$2B\cdot \longrightarrow \text{I} \qquad (5)$$

The alkyl esters of phenylglyoxalic acid can be reduced photochemically to the corresponding alkyl esters of α,α′-diphenyltartaric acid presumably by the same mechanistic path shown in eq. 2–5. Thus, at ambient temperatures (about 30°), diethyl α,α′-diphenyltartrate (II) and 2-butanone were found to be the major products obtained from the reaction of ethyl phenylglyoxalate in 2-butanol induced by sunlight.



$$2C_6H_5\overset{O}{\overset{\|}{C}}CO_2C_2H_5 + CH_3\overset{OH}{\overset{|}{C}}HC_2H_5 \xrightarrow{h\nu} \begin{array}{c}C_6H_5C(OH)CO_2C_2H_5\\ |\\ C_6H_5C(OH)CO_2C_2H_5\end{array} + CH_3\overset{O}{\overset{\|}{C}}C_2H_5 \qquad (6)$$

We have found that the photochemical reductions of primary and secondary alkyl phenylglyoxalates in alcohols follow a different and quite unique course at somewhat higher temperatures. The alkyl phenylglyoxalate is reduced to the mandelate ester of the alcohol in which the reaction is performed and the original alcohol moiety of the phenylglyoxalate ester is oxidized. For example, illuminating a solution consisting of cyclohexyl phenylglyoxalate in ethanol at 40° yielded equivalent amounts of ethyl mandelate (III) and cyclohexanone as the major reaction products.



$$\underset{0.022\text{ mole}}{C_6H_5\overset{O}{\overset{\|}{C}}CO_2C_6H_{11}} + C_2H_5OH \xrightarrow{h\nu} \underset{\substack{0.018\text{ mole}\\ \text{III}}}{C_6H_5\overset{OH}{\overset{|}{C}}HCO_2C_2H_5} + \underset{0.019\text{ mole}}{C_6H_{10}O} \qquad (7)$$

No detectable amounts of either ethyl phenylglyoxalate or cyclohexyl mandelate could be found on gas chromatographic analysis of the reaction mixture. At this temperature, only 16% of the cyclohexyl phenylglyoxalate was converted to the dimeric reduction product, dicyclohexyl α,α′-diphenyltartrate.

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[1] This work was supported in part by a research grant (A-5620) from the National Institutes of Health.

[2] National Science Foundation Cooperative Fellow, 1962–1963.

[3] *Cf.* A. Schoenberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947); W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); G. S. Hammond, W. P. Baker, and W. M. Moore, *ibid.*, **83**, 2797 (1961).

[4] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Rectenwald, and R. B. Martin, *ibid.*, **81**, 1068 (1959).

TABLE I

PHOTOCHEMICAL REACTIONS OF ALKYL PHENYLGLYOXALATES IN ALCOHOLIC SOLUTIONS AT 78°

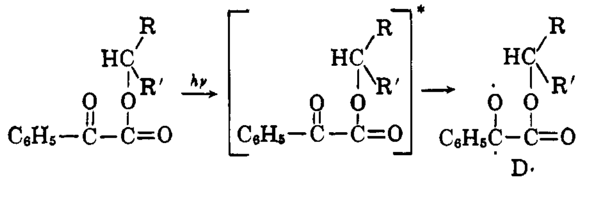
Phenylglyoxalate	Solvent alcohol	Products
(1) Ethyl phenylglyoxalate	2-Butanol	2-Butyl mandelate[a]
(2) Ethyl phenylglyoxalate	Cyclohexanol	Cyclohexyl mandelate[b,a]
(3) Ethyl phenylglyoxalate	*l*-Menthol	*l*-Menthyl mandelate[c,a]
(4) 2-Propyl phenylglyoxalate (0.007 mole)	Ethanol	Ethyl mandelate (0.003 mole) + acetone (0.003 mole)
(5) 2-Hexyl phenylglyoxalate	Ethanol	Ethyl mandelate + 2-hexanone
(6) Cyclohexyl phenylglyoxalate[d] (0.022 mole)	Ethanol	Ethyl mandelate (0.018 mole) + cyclohexanone (0.019 mole)
(7) 2-Octyl phenylglyoxalate	Ethanol	Ethyl mandelate + 2-octanone
(8) 2-Octyl phenylglyoxalate	2-Butanol	2-Butyl mandelate + 2-octanone

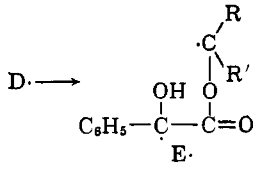
[a] No attempt was made to isolate the acetaldehyde in these reactions. [b] M.p. 56–58°. [c] M.p. 81–82°. [d] Performed at 40°.

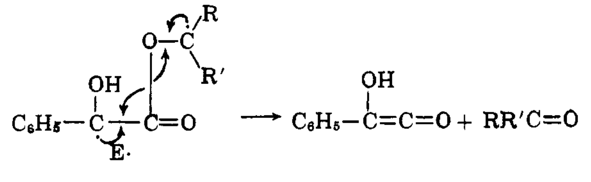
Illuminating ethyl phenylglyoxalate in cyclohexanol yielded cyclohexyl mandelate and no detectable amounts of either ethyl mandelate or cyclohexyl phenylglyoxalate. In another reaction in which a quantitative determination of the products was made, the photochemical reduction of 2-propyl phenylglyoxalate in ethanol at 78° yielded ethyl mandelate and acetone in equivalent amounts. Esters of phenylglyoxalic acid that were reduced to esters of mandelic acid in alcohols with the accompanying exchange of the alcohol moieties are shown in Table I.

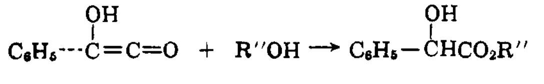
Only in the case of the 2-octyl phenylglyoxalate was any detectable amount of ester exchange occurring prior to the photochemical reduction noted. This was evident from the appearance of 2-octanol in the reaction mixtures of the 2-octyl phenylglyoxalate reactions. In all cases, the mandelate ester found was that of the alcohol in which the photochemical reduction was performed. Although there was some oxidation of the solvent alcohol due to the formation of the dimeric reduction product, the alcohol portion of the phenylglyoxalate used was always oxidized to a greater extent and, in those reactions in which it was quantitatively determined, in an amount equivalent to the mandelate ester formed.

A mechanism for these photochemically induced reduction reactions with the accompanying exchange of the alcohol moieties which is consistent with our observations is shown in the following equations.


(8)


(9)


(10)


$$C_6H_5\text{---}\overset{OH}{\overset{|}{C}}=C=O + R''OH \longrightarrow C_6H_5-\overset{OH}{\overset{|}{C}}HCO_2R'' \quad (11)$$

The photolytic excitation of the alkyl phenylglyoxalate to the triplet diradical D· by way of the n → π* excited state as shown in reaction 8 is similar to that proposed for the photochemical reactions of other aryl ketones. The oxygen part of the diradical D· is suitably positioned to abstract a hydrogen atom from the alcohol portion of the ester as shown in the intramolecular reaction 9 producing the diradical E·. Such intramolecular hydrogen atom abstractions have been reported to occur when the conformational aspects of the diradical are suitable.[5] By the appropriate shifting of electrons in the manner shown in eq. 10, the diradical E· can fragment to the oxidation product of the alcohol portion of the ester and to the enol of phenylglyoxal.[6] This enol is a ketene and might be expected to react faster with the solvent alcohol to form an ester of mandelic acid (eq. 10) than to ketonize to phenylglyoxal. We found no phenylglyoxal in any of our reaction mixtures. The consequence of this sequence of reactions is that the original alcohol portion of the phenylglyoxalate ester is oxidized and the only mandelate ester formed must be that of the alcohol used as the solvent. Further, the amounts of the oxidized alcohol moiety of the starting phenylglyoxalate and the mandelate ester formed should be equivalent.

The formation of acetaldehyde and carbon monoxide in both the direct and benzophenone-sensitized photolyses of ethyl pyruvate reported by Hammond, Leermakers, and Turro[7] could proceed in a manner similar to that proposed here for the alkyl phenylglyoxalates. In this case, the benzophenone-sensitized reaction must involve the triplet state. A mechanism involving an intramolecular hydrogen abstraction reaction was suggested by Leermakers and Vesley[8] to explain the for-

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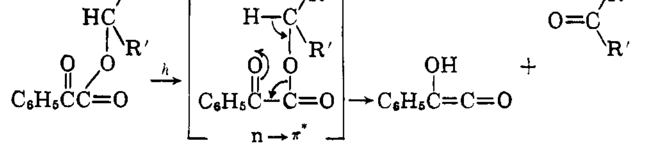
[5] N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, **80**, 2913 (1958); N. C. Yang and C. Rivas, *ibid.*, **83**, 2213 (1961); W. H. Urry and D. J. Trecker, *ibid.*, **84**, 118 (1962).

[6] It has been suggested that the ketene intermediate could arise from a one-step fragmentation of the initial n → π* excited state in the manner shown in the following equation.



This path certainly cannot be excluded. However, in view of the marked effect of temperature on the course of the reaction, the intramolecular hydrogen abstraction reaction by the triplet shown in eq. 9 may accommodate the facts somewhat better.

[7] G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2395 (1961).

[8] P. A. Leermakers and G. F. Vesley, *J. Org. Chem.*, **28**, 1161 (1963).

mation of carbon dioxide and acetoin from the photolysis of pyruvic acid.

The observation that the dimeric reduction products are formed at lower temperatures and the mandelate esters at higher temperatures deserves further comment. The formation of the dimeric reduction product requires an intermolecular hydrogen abstraction from the solvent alcohol by the oxygen moiety of the diradical D·, whereas an intramolecular hydrogen abstraction from the alkyl portion of the phenylglyoxalate ester is required by the proposed mechanism for the formation of the mandelate ester. The reactivity of the α-hydrogen of the solvent alcohol toward abstraction could very likely be greater than that of the α-hydrogen of ester. If such is the case, an increase in temperature would be expected to increase the rate of the slower reaction, namely the intramolecular hydrogen abstraction, more markedly and thereby favor the formation of the mandelate ester.

Experimental

The phenylglyoxalic acid required for the preparation of the esters was prepared by the permanganate oxidation of mandelic acid.[9] The following esters were prepared by the reaction of the phenylglyoxalic acid and the appropriate alcohol in the presence of sulfuric acid.

2-Propyl phenylglyoxalate had b.p. 97° at 2 mm.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.92; H, 6.80.

2-Butyl phenylglyoxalate had b.p. 127–130° at 5 mm.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.90; H, 6.80. Found: C, 70.17; H, 7.03.

2-Hexyl phenylglyoxalate had b.p. 121° at 2 mm.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.76; H, 7.76. Found: C, 72.14; H, 8.02.

2-Octyl phenylglyoxalate had b.p. 142° at 2 mm.

Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.26; H, 8.79. Found: C, 73.19; H, 8.92.

Cyclohexyl phenylglyoxalate had b.p. 167° at 5 mm.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.41; H, 6.95. Found: C, 72.43; H, 7.07.

The alcohols used were commercial materials and redistilled when necessary.

Reaction of Ethyl Phenylglyoxalate and 2-Butanol.—Ethyl phenylglyoxalate (2.5 g., 0.014 mole) was dissolved in 2-butanol (8.0 g., 0.11 mole). The solution was sealed in a Pyrex tube and exposed to the sun for a period of 2 days at ambient temperatures (about 30°). At the end of the illumination, the tube was cooled at 0° for 6 hr. and 1.03 g. (0.0029 mole) of the solid dimeric reduction product, diethyl α,α'-diphenyltartrate, which had m.p. 118–120° from petroleum ether (b.p. 35–60°), crystallized from the solution. Gas chromatographic analysis of the reaction mixture indicated the presence of 2-butanone and only a trace of acetaldehyde.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.04; H, 6.15. Found: C, 67.7; H, 6.21.

Photochemical Reaction of Cyclohexyl Phenylglyoxalate and Ethanol.—A solution consisting of 5.0 g. (0.022 mole) of cyclohexyl phenylglyoxalate in 10 g. of ethanol was illuminated for 16 hr. at 40° with a 275-w. Sylvania sun lamp. Gas chromatographic analysis of the reaction mixture showed that cyclohexanone and ethyl mandelate were formed. No gas chromatographic peaks with retention times the same as those of authentic samples of either cyclohexanol or ethyl phenylglyoxalate were found. Quantitative determination of the amounts of cyclohexanone (1.8 g., 0.019 mole) and ethyl mandelate (3.05 g., 0.018 mole) by gas chromatography was made by using a weighed portion of the reaction mixture with a weighed amount of an internal standard. On standing overnight at about 0°, dicyclohexyl α,α'-diphenyltartrate (0.8 g., 0.0017 mole) crystallized from the solution. After several recrystallizations from petroleum ether, the material melted at 132–133°.

Anal. Calcd. for $C_{28}H_{31}O_6$: C, 72.10; H, 7.30. Found: C, 72.40; H, 7.30.

The infrared spectrum showed the presence of both a hydroxy group (2.92 μ) and a carbonyl (5.79 μ). The n.m.r. spectrum showed three types of protons, those of the cyclohexyl groups (centered at 2.52 p.p.m.), those of the phenyl groups (centered at 7.45 p.p.m.), and those of the hydroxy groups (centered at 5.01 p.p.m.). The integrated peak areas were consistent with these assignments.

Reaction of 2-Propyl Phenylglyoxalate and Ethanol.—A reaction mixture consisting of 1.3 g. (0.007 mole) of 2-propyl phenylglyoxalate in 3.3 g. of ethanol was illuminated with a sun lamp at 78° for 16 hr. At the end of this period, the amounts of acetone (0.17 g., 0.003 mole) and ethyl mandelate (0.40 g., 0.0028 mole) formed were determined by gas chromatography using a weighed portion of the reaction mixture with a weighed amount of *t*-butyl alcohol as an internal standard.

Photochemical Reactions of Alkyl Phenylglyoxalates with Alcohols.—The alkyl phenylglyoxalate was in each case dissolved in a better than 2:1 molar excess of the indicated alcohol. The solution was placed in a Pyrex tube and immersed in an alcohol vapor bath (78°) and illuminated for several hours with a 275-w. Sylvania sun lamp. The products of the reaction were determined qualitatively by gas chromatography. In each case, the reaction mixture gave a chromatographic peak with a retention time identical with that of the mandelate ester of the alcohol in which the reaction was performed. In no case were any detectable amounts of the mandelate ester of the alcohol moiety of the starting phenylglyoxal detected. Cyclohexyl mandelate was isolated from the reaction of ethyl phenylglyoxalate in cyclohexanol, m.p. 56–58°, after recrystallization from petroleum ether.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.08; H, 7.98.

l-Menthyl mandelate was isolated from the reaction of ethyl phenylglyoxalate in *l*-menthol, m.p. 82°, lit.[10] m.p. 84–85°. The infrared spectrum of the material was identical with that of an authentic sample.

The ketones formed in the reactions of the secondary alkyl phenylglyoxalates were qualitatively determined by their gas chromatographic retention times which were identical in each case with those of authentic samples. In the reaction of 2-octyl phenylglyoxalate in 2-butanol, the 2-octanone formed was isolated by distillation under vacuum and the 2,4-dinitrophenylhydrazone prepared, m.p. 56.5–58°, lit.[11] m.p. 58°.

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(9) B. B. Corson, R. A. Dodge, S. E. Harris, and R. K. Hazen, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 241.

(10) A. McKenzie, *J. Chem. Soc.*, **85**, 384 (1904).

(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 316.