BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1926—1931 (1966)

Photochemical Reactions of Ethyl Chloroglyoxylate with Cyclohexane, Cyclohexene, and Toluene

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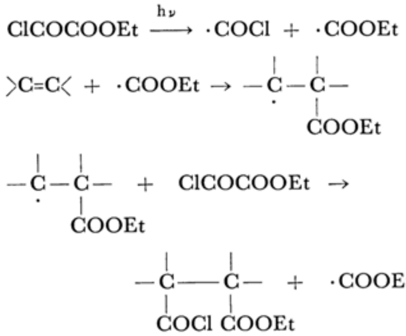
(Received September 30, 1965)

The photochemical reactions of ethyl chloroglyoxylate with cyclohexane, *cyclohexene,* and toluene have been carried out, and the reactivity of an alkyl radical towards ethyl chloroglyoxylate has been qualitatively discussed. A cyclohexyl radical attacks the carbonyl group of the acid chloride function in ethyl chloroglyoxylate to cause a chain reaction; cyclohexanecarbonyl chloride (51%) and ethyl cyclohexylglyoxylate (2—3%) are thus obtained, along with other minor products. On the other hand, a cyclohexen-3-yl or a benzyl radical might be unable to attack ethyl chloroglyoxylate under the conditions investigated.

In a previous paper,[1] it has been reported that the photolysis of ethyl chloroformate affords an ethoxycarbonyl radical in a selective manner, accompanied by the direct introduction of the radical into various hydrocarbons; carboxylated products are thus obtained. In such a photolysis, however, the carboxylated products do not form via any chain reactions.

The direct introduction of various carboxyl groups into hydrocarbons by means of radical reactions has received much attention recently.[2-7] Therefore, the photo- and peroxide-induced reactions of oxalyl chloride with a saturated hydrocarbons, such as cyclohexane, are of interest, since a characteristic chain reaction is operative in the formation of cyclohexanecarbonyl chloride.[8,9] To the related chain reactions, however, little attention has been paid.

In our preliminary report concerning the photochemical reactions of ethyl chloroglyoxylate (ECG) with olefins,[10] it has been suggested that the 1 : 1-adduct of ECG and an olefin might be formed via a chain reaction as follows;



$$\mathrm{ClCOCOOEt} \xrightarrow{h\nu} \cdot\mathrm{COCl} + \cdot\mathrm{COOEt}$$

$$\rangle\mathrm{C{=}C}\langle + \cdot\mathrm{COOEt} \rightarrow -\overset{|}{\underset{\cdot}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{COOEt}}{\mathrm{C}}}-$$

$$-\overset{|}{\underset{\cdot}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{COOEt}}{\mathrm{C}}}- + \mathrm{ClCOCOOEt} \rightarrow -\overset{|}{\underset{\mathrm{COCl}}{\mathrm{C}}}-\overset{|}{\underset{\mathrm{COOEt}}{\mathrm{C}}}- + \cdot\mathrm{COOEt}$$

The present paper will discuss whether or not an in situ-generated alkyl radical can attack ECG, and which site of ECG, if it is attacked, is reactive to the alkyl radical.

Results and Discussion

A mixture of ECG and a hydrocarbon placed in a quartz tube was irradiated with a high pressure-mercury arc without a filter. During the course of the irradiation, hydrogen chloride, carbon dioxide, carbon monoxide, ethane, and ethylene were evolved. Traces of ethyl chloride and acetaldehyde were trapped at −60°C at the end of the irradiation. In an attempt to obtain some information on the present photochemical reactions, the benzoyl peroxide-induced reaction of ECG with cyclohexane was carried out; it gave carbon dioxide and ethane, along with a trace of carbon monoxide as the gaseous products. The results concerning the gaseous products are summarized in Table I.

From the photochemical reaction of ECG with cyclohexane, a 51% yield of cyclohexanecarbonyl chloride was obtained; small amounts of the other products (ethyl cyclohexylglyoxylate, ethyl cyclohexanecarboxylate, and diethyl oxalate) were also detected (Table II).

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[1] C. Pac and S. Tsutsumi, This Bulletin, **38**, 1916 (1965).

[2] L. Friedman and H. Shechter, *Tetrahedron Letters,* **1961**, 238; A. Rieche, E. Schmidtz and E. Gründeman, *Angew. Chem.*, **73**, 621 (1961).

[3] D. Elad, *Proc. Chem. Soc.,* **1962**, 225.

[4] D. Elad, *Tetrahedron Letters,* **1963**, 77.

[5] D. Elad and J. Rochach, *J. Org. Chem.,* **29**, 1855 (1964).

[6] C. Walling and E. S. Huyser, "Organic Reactions," Vol. 13, John Wiley & Sons, Inc., New York (1963), p. 111.

[7] M. T. Ahmed and A. J. Swallow, *J. Chem. Soc.,* **1963**, 3918; D. R. Napier, *J. Org. Chem.,* **30**, 1305 (1965).

[8] M. S. Kharasch, S. S. Kane and H. C. Brown, *J. Am. Chem. Soc.,* **62**, 454 (1940); **64**, 329 (1942).

[9] F. Runge, *Z. Elektrochemie,* **56**, 779 (1952); **60**, 956 (1956).

[10] C. Pac and S. Tsutsumi, *Tetrahedron Letters,* **1965**, 2341.

TABLE I. RATIOS OF GASEOUS PRODUCTS FROM PHOTO- AND PEROXIDE-INDUCED REACTIONS OF ECG WITH CYCLOHEXANE, CYCLOHEXENE, AND TOLUENE

ECG g.	Hydrocarbon g.	Reaction time hr.	Gaseous product				
			Volume[a)] cc.	Ratio[b)]			
				CO	: CO_2	: C_2H_6	: C_2H_4
18	Cyclohexane, 40	5	2500	0.2	: 1	: 1	: —
25	Cyclohexane, 50[c)]	19[c)]	2000	trace	: 1	: 0.8	: —
40	Cyclohexene, 60	25	80	d)	: 1	: 0.3	: 0.2
27	Toluene, 62	41	50	1.1	: 1	: ca. 1	: —

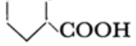
a) Volumes of neutral gaseous products ($CO+C_2H_6+C_2H_4$)

b) The ratios were measured by gas chromatography.

c) Benzoyl peroxide-induced reaction

d) The ratio CO/C_2H_6 was not determined.

TABLE II. LIQUID PRODUCTS FORMED BY PHOTO- AND PEROXIDE-INDUCED REACTIONS OF ECG WITH CYCLOHEXANE, CYCLOHEXENE, AND TOLUENE

ECG g.	Hydrocarbon g.	Reaction time hr.	Conversion of ECG %	Product	Yield[a)] %
18	Cyclohexane 40	5	83	Cyclo-$C_6H_{11}COCl$	51
				Cyclo-$C_6H_{11}COCOOEt$	2—3
				Cyclo-$C_6H_{11}COOEt$	<1
				Diethyl oxalate	<1
				Bicyclohexyl	b)
25	Cyclohexane[c)] 50	19	80	Cyclo-$C_6H_{11}COCl$	49
				Cyclo-$C_6H_{11}COCOOEt$	5—6
				Bicyclohexyl	b)
40	Cyclohexene 60	25	25	Cyclo-$C_6H_{11}COOEt$	20
				Cyclo-C_6H_9-3-COOEt	1
				Diethyl oxalate	7
				3, 3′-Bicyclohexenyl	(2.5 g.)
38	Cyclohexene 10	10	21	Cyclo-$C_6H_{11}COOEt$	d)
				Diethyl oxalate	d)
				3, 3′-Bicyclohexenyl	d)
				 COOH[e)] COOH	ca. 10
27	Toluene 62	41	20	$C_6H_5CH_2COOEt$	ca. 10
				Diethyl oxalate	ca. 10

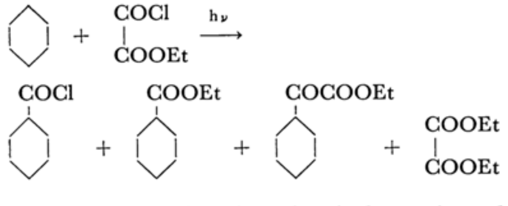
a) Yields were based on ECG not recovered.

b) The amounts were too small to be measured.

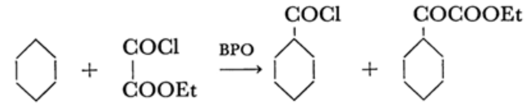
c) Dibenzoyl peroxide-induced reaction.

d) The amounts were not measured.

e) The final product after hydrolysis of the reaction-product.



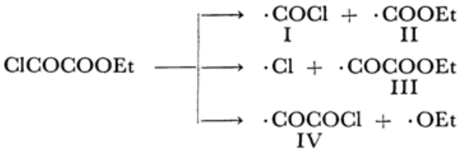
In contrast to the photochemical reaction, the benzoyl peroxide-induced reaction of ECG with cyclohexane gave no detectable amounts of ethyl cyclohexanecarboxylate and diethyl oxalate. The liquid products were cyclohexanecarbonyl chloride (49%), ethyl cyclohexylglyoxylate (–6%), and a trace of benzoyl chloride.



In both cases, the amount of bicyclohexyl formed was negligible. The liquid products are listed in Table II.

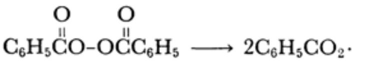
On the basis of the above results, the following scheme can be proposed:

a) Primary processes:



$$ClCOCOOEt \longrightarrow \begin{cases} \underset{I}{\cdot COCl} + \underset{II}{\cdot COOEt} & (1) \\ \cdot Cl + \underset{III}{\cdot COCOOEt} & (2) \\ \underset{IV}{\cdot COCOCl} + \cdot OEt & (3) \end{cases}$$

or



$$C_6H_5\overset{O}{\overset{\|}{C}}O\text{-}O\overset{O}{\overset{\|}{C}}C_6H_5 \longrightarrow 2C_6H_5CO_2\cdot \qquad (4)$$

b) The decomposition of radicals:

$$I \longrightarrow CO + \cdot Cl \qquad (5)$$

$$II \longrightarrow CO_2 + \cdot C_2H_5 \qquad (6)$$

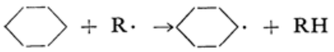
$$III \longrightarrow CO + CO_2 + \cdot C_2H_5 \qquad (7)$$

$$IV \longrightarrow 2CO + \cdot Cl \qquad (8)$$

$$2\ EtO\cdot \longrightarrow EtOH + CH_3CHO \qquad (9)$$

$$C_6H_5CO_2\cdot \longrightarrow \cdot C_6H_5 + CO_2 \qquad (10)$$

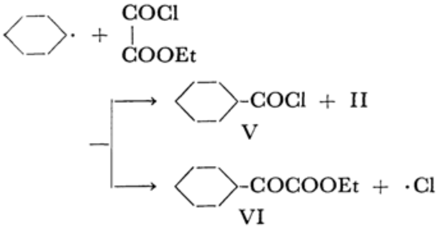
c) Chain initiation processes:



(11)

($R=Cl$, C_2H_5, EtO, $C_6H_5CO_2$, and C_6H_5)

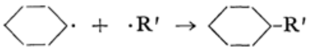
d) Chain propagation processes:



(12)

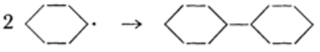
(13)

e) Chain termination processes:



(14)

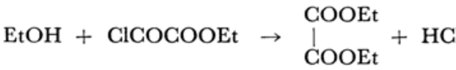
($R'=Cl$, C_2H_5, $COOEt$, $COCl$, and $COCOOEt$)



(15)

$$\cdot C_2H_5 + \cdot Cl \rightarrow C_2H_5Cl \qquad (16)$$

f) Other reaction:



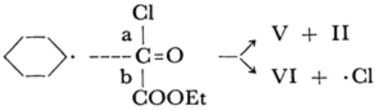
$$EtOH + ClCOCOOEt \rightarrow \begin{matrix} COOEt \\ | \\ COOEt \end{matrix} + HCl \qquad (17)$$

It has been suggested that oxalyl chloride is photolyzed by the light in the 2537 Å region to cause a homolysis of the carbon-carbon bond, while the light in the 3650 Å region breaks down the chlorine-carbon bond.[11] In the present work, a high pressure-mercury arc was used without any filters; hence the primary processes 4 and 5 probably occur in a manner analogous to the photolysis of oxalyl chloride, though no efforts were made to clarify the primary processes of the photodecomposition of ECG. The formation of acetaldehyde suggests that an ethoxy radical might be generated; namely, the process 3 might take place.

The thermochemical data on the radicals I[12] and II[13] are known; the radicals will decompose as is shown in the processes 5 and 6 respectively. The radicals III and IV are likely to decompose as in the processes 7 and 8 respectively, though little is known of thier stability and their reactivity.

The irradiation in cyclohexane proceeds by a radical chain reaction. The gaseous products continuosly evolved for some time after the light source was shut off. In addition, the molar ratio of the cyclohexanecarbonyl chloride formed to the benzoyl peroxide used showed values of about six in the peroxide-induced reaction.

In the chain transfer process, however, three possible sites of ECG may be attacked; namely, the chlorine atom; the carbonyl group of the acid chloride function, and that of the ester function. The chlorine atom might be resistive to an attack by an alkyl radical, since no significant amounts of ethyl chloride and cyclohexyl chloride were produced. The liquid products from the photo- and the peroxide-induced reactions clearly show that the carbonyl group of the acid chloride function is attacked by a cyclohexyl radical, and that the ratio of the formation of the acid chloride V to the keto-ester VI may be controlled by the relative bond strength of the carbon-carbon, b, and the carbon-chlorine, a, bonds. Unfortunately, the dissociation energies of the respective bonds in ECG have not appeared in any of the literature. Carson and Skinner have estimated the bond energy of the carbon-chlorine bond in acetyl chloride to be 76.7 kcal./mol.[14] Concerning the bond energy of the carbonyl-carbonyl bond in biacetyl, two values have been presented, 60 kcal./mol.[15] and 72 kcal./mol.[16] If the values for the dissociation energies of the C–Cl bond in acetyl chloride and of the C–C bond in biacetyl are used instead of those for the dissociation energies of the bonds a and b in ECG, the carbon-carbon fission 12 might be expected to be preferred over the carbon-chlorine fission 13 in the chain transfer process. This interpretation might be qualitatively consistent with the product-distribution.



(12)

(13)

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[11] K. B. Krauskopf and G. K. Rollefson, *J. Am. Chem. Soc.*, **58**, 443 (1936).

[12] W. G. Burn and F. S. Dainton, *Trans. Farady Soc.*, **48**, 39 (1952).

[13] P. Gray and J. C. J. Thynne, *Nature*, **191**, 1357 (1961).

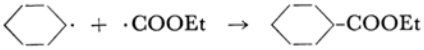
[14] A. S. Carson and H. A. Skinner, *J. Chem. Soc.*, **1949**, 936.

[15] M. Szwarc, *Chem. Revs.*, **47**, 114 (1950).

[16] J. G. Calvert and L. T. Gruver, *J. Am. Chem. Soc.*, **80**, 1313 (1958).

There is, however, a difference in the VI/V ratio between the photo- and the peroxide-induced reactions. In the photochemical reaction, the ratio was about one-third of that obtained from the peroxide-induced reaction. It has been reported that esters of α-keto acids, such as pyruvic and phenylglyoxylic acids, are rapidly photolyzed by light promising n–π^* excitation.[17] Since a high pressure-mercury arc was used as the light source, the α-keto ester VI is probable to decompose with ease. Thus, the decrease in the ratio might be ascribed to the photo-decomposition of VI during the irradiation. In fact, a prolonged irradiation causes a great decrease in VI.

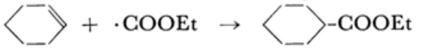
The question, however arises as to whether the formation of ethyl cyclohexanecarboxylate from the photochemical reaction is caused by the attack of a cyclohexyl radical on the ester function in ECG, or by the radical coupling of a cyclohexyl radical with an ethoxycarbonyl radical. If the ester function is attacked, diethyl oxalate, an analogue of ECG, can react with a cyclohexyl radical; if so, ethyl cyclohexanecarboxylate and/or ethyl cyclohexylglyoxylate must be formed. Therefore, the benzoyl peroxide-induced reaction of diethyl oxalate with cyclohexane was carried out. Ethyl cyclohexanecarboxylate and the keto ester VI, however, were not detected in the products, whereas bicyclohexyl was obtained. Thus, it was established that the carbonyl group of the ester function in ECG was not attacked by a cyclohexyl radical. As has been suggested in a previous report,[1] the ethoxycarbonyl radical from the photolysis of ethyl chloroformate has a life long enough to associate with a cyclohexyl radical in a solvent cage at room temperature; hence, the formation of ethyl cyclohexanecarboxylate in the present photochemical reaction might be explained in terms of a radical coupling:



(18)

Diethyl oxalate was produced in the photochemical reaction, but not in the peroxide-induced reaction. Dimerization of ethoxycarbonyl radicals can not account for the formation of diethyl oxalate, since we have shown that the radical has not a life long enough to dimerize.[1] It is most reasonable that diethyl oxalate is produced by the reaction of ECG with ethanol as is shown in the process 17. The ethanol might be generated by the disproportionation between ethoxy radicals and/or the hydrogen abstraction of an ethoxy radical from a hydrogen donor. Therefore, it is comprehensible that diethyl oxalate is not produced by the peroxide-induced reaction, which might not involve the generation of ethoxy radicals.

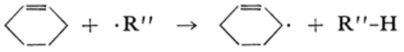
The irradiation of ECG in an excess of *cyclohexene* gave no detectable amounts of an acid chloride. The liquid products obtained showed strong infrared absorption bands assignable to an ester, while no bands corresponding to an acid chloride were observed. As has been shown in Table II, the products mainly consisted of ethyl cyclohexanecarboxylate and 3, 3′-bicyclohexenyl; the amount of cyclohexene-3-carboxylate was small. From these results, it may be concluded that a cyclohexen-3-yl radical has no ability to attack ECG under the present conditions. The results may be interpreted as follows:



(19)

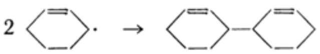
VII

(20)



(21)

R″=Cl and C_2H_5



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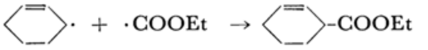
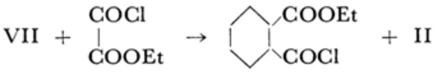


(23)

When an excess of *cyclohexene* was used, VII might predominantly abstract an allylic hydrogen atom of cyclohexene and might have less chance to attack ECG. When a smaller amount of cyclohexene was used than that of ECG, some of the derivative of cyclohexane-1, 2-dicarboxylic acid, VIII, were obtained. It might, therefore, be considered that VII attacks ECG to yield the product VIII.



(24)

In the case of *toluene*, no significant amount of phenylacetyl chloride was formed. The liquid products from the photochemical reaction of ECG with toluene revealed strong bands of an ester in the infrared absorption spectra, whereas the absorption band at 1800 cm^{-1} was observed as the shoulder of the ester bands. Therefore, the amount of the acid chloride, if produced at all, was negligible. The above results suggest that a benzyl radical does not attack ECG, and the ethyl phenylacetate is formed via a radical-association reaction between a benzyl radical and an ethoxycarbonyl radical.

Experimental

Materials.—Cyclohexane, toluene, and diethyl oxalate were obtained commercially and purified in usual ways. Cyclohexene was prepared by the dehydration of cyclohexanol.[18] ECG was prepared by

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[17] P. A. Leermakers, P. C. Warren and G. F. Vesley, ibid., **86**, 1768 (1964).

[18] G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. 1, 183 (1956).

the action of thionyl chloride on ethyl potassium oxalate according to the directions of Southwick.[19] The hydrocarbons were stored over sodium wire. All of the materials were distilled before use.

The Analysis of Gaseous Products and the Apparatus Used.—All of the photochemical reactions were carried out in a quartz tube (50 cm. long, 2 cm. in diameter) immersed in a water bath maintained at room temperature, and with a high pressure mercury arc (600 W.) mounted 1 cm. from the tube. The general procedures used for the analysis of gaseous and condensable products were identical with those described previously.[1] The ratios of the gaseous products were determined by gas chromatographic measurements under two sets of conditions (molecular-sieve 5A column: 2.5 m. at 63°C, and silica-gel column: 2.5 m. at 65°C). Under the former set of conditions, the ratio of carbon monoxide to ethane was determined, while that of carbon dioxide to C_2-hydrocarbons was measured under the latter set.

The gas-liquid chromatographic (g. l. c.) measurements of liquid products were carried out using a 5 mm. × 1 m. column packed with 5% of silicone DC 550 on Chromosorb (A) and a 5 mm. × 2 m. column packed with 5% of dioctyl sebatate on Chromosorb (B).

The Irradiation of ECG in Cyclohexane.—A mixture of ECG (18 g., 0.18 mol.) and cyclohexane (40 g., 0.5 mol.) was irradiated for 5 hr. in an atmosphere of nitrogen. During the course of the irradiation, 2500 cc. of neutral gases was evolved. After the irradiation, the evolution of gases had slowed sufficiently. After the unreacted cyclohexane (ca. 30 g.) had been removed from the irradiated mixture, the remaining oil was distilled under reduced pressure to yield the following fractions:

Fraction 1 (3 g.), b. p. 38—50°C/15 mmHg, which consisted largely of ECG, along with traces of ethylcyclohexane and cyclohexyl chloride, as determined by g. l. c. assay (A).

Fraction 2 (8 g.), b. p. 69—72°C/13 mmHg, which showed infrared absorption bands at 1790 (-COCl), 1770, 1750, and 1180 $(-\underset{\overset{\|}{O}}{C}-O-)$ cm^{-1}, and which was treated with aniline to give hexahydrobenzanilide, m. p. 143.5°C (Found: C, 76.52; H, 8.45. Calcd. for $C_{13}H_{17}ON$: C, 76.81; H, 8.43%).

After treatment with absolute methanol, the ratios of methyl cyclohexanecarboxylate to diethyl oxalate and to ethyl cyclohexanecarboxylate were determined by g. l. c. assay (A). Diethyl oxalate and ethyl cyclohexanecarboxylate were each contaminated less than 2%. It was confirmed that diethyl oxalate and ethyl cyclohexanecarboxylate in methanol were not cahnged significantly under the g. l. c. conditions.

Fraction 3 (1 g.), b. p. 103—113°C/13 mmHg, which showed infrared absorption bands assignable to an acid chloride (1790 cm^{-1}) and an ester (1730 and 1180 cm^{-1}). G. l. c. measurements (A) showed that this fraction consisted of ethyl cyclohexylglyoxylate, (ca. 0.7 g.), cyclohexanecarbonyl chloride (ca. 0.3 g.), and a trace of bicyclohexyl. The α-keto ester was identified by mixed melting point tests of its 2, 4-dinitrophenylhydrazone (2, 4-DNP), m. p. 159—159.5°C, which was recrystallized from ethanol (Found: C, 52.92; H, 5.53. Calcd. for $C_{16}H_{20}N_4O_6$: C, 52.74; H, 5.53%).

When the period of the irradiation described above was prolonged for 19 hr., a lower yield of the acid chloride (45%) was obtained, and the α-keto ester could not be isolated as its 2, 4-DNP, although its presence was confirmed by g. l. c. assay (A).

An authentic 2, 4-DNP of ethyl cyclohexylglyoxylate was prepared in the following way. The hydrogenation of mandelic acid on Adam's catalyst gave hexahydromandelic acid;[20] esterification with ethanol followed. A solution of ethyl hexahydromandelate (500 mg.) in acetic acid (50 ml.) was stirred with ice cooling, into which a solution of chromic acid (350 mg.) in acetic acid (50 ml.) was added drop by drop. After 5 hr. of stirring at room temperature, the evaporation of acetic acid in vacuo left a residue. To the residue there was added 100 ml. of water, and the aqueous solution was extracted three times with 100 ml. of ether. The etheral layer was washed with water, and dried over magnesium sulfate, and the solvent was evaporated in vacuo. The remainig, slightly yellow oil was treated with an aqueous solution of 2, 4-dinitrophenylhydrazine in 2 N hydrochloric acid, and then the resultant 2, 4-DNP was recrystallized from ethanol, m. p. 159.5°C (Found: C, 52.90; H, 5.55. Calcd. for $C_{16}H_{20}N_4O_6$: C, 52.74; H, 5.53%).

The Peroxide-induced Reaction of ECG with Cyclohexane.—A mixture of ECG (25 g., ca. 0.18 mol.) and cyclohexane (50 g., 0.6 mol.) containing benzoyl peroxide (2 g., 0.0083 mol.) was refluxed for 19 hr. at 84—85°C under an atmosphere of nitrogen. During the course of the reaction, 2000 cc. of neutral gases was evolved. After the unreacted cyclohexane (47 g.) and ECG (5 g.) had been removed, the remaining oil was distilled under reduced pressure to yield 8 g. of cyclohexanecarbonyl chloride, b. p. 68—72°C/15 mmHg, and 1.5 g. of ethyl cyclohexylglyoxylate, b. p. 112—115°C/15 mmHg. The former fraction showed no infrared absorption bands of esters. The fraction was converted to hexahydrobenzanilide, which was identified by a mixed melting point determination. The latter fraction showed strong bands of an ester and a moderate band of an acid chloride, and was found, by using a g. l. c. assay (A), to consist of ethyl cyclohexylglyoxylate (ca. 1.4 g.), cyclohexanecarbonyl chloride (ca. 0.1 g.) and a trace of bicyclohexyl.

The Peroxide-induced Reaction of Diethyl Oxalate with Cyclohexane.—A mixture of diethyl oxalate (17 g., ca. 0.12 mol.), cyclohexane (42 g., 0.5 mol.), and 2 g. of benzoyl peroxide was refluxed at 84—86°C for 26 hr. under an atmosphere of nitrogen. During the reaction, carbon dioxide was evolved. After the unreacted cyclohexane (38 g.) had removed, the remaining oil was distilled under reduced pressure to yield 15 g. of diethyl oxalate, b. p. 88—90°C/25 mmHg, and 2 g. of a fraction, b. p. 90—100°C/25 mmHg. The latter fraction was found, by g. l. c. assay (A), to consist largely of diethyl oxalate, plus a small amount of bicyclohexyl. No ethyl cyclohexanecarboxylate and ethyl cyclohexylglyoxylate could not be detected by g. l. c. assay (A).

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[19] P. L. Southwick and L. L. Seivard, *J. Am. Chem. Soc.*, **71**, 2535 (1949).

[20] H. A. Smith, D. M. Alderman, Jr., C. D. Schacklett and C. M. Welch, ibid., **71**, 3772 (1949).

The Irradiation of ECG in Cyclohexene.—The irradiation of a mixture of ECG (40 g., 0.3 mol.) and cyclohexene (60 g., 0.8 mol.) for 25 hr. gave 80 cc. of neutral gases, unreacted cyclohexene (55 g.) and ECG (30 g.), plus the liquid fractions described below:

Fraction 1 (2.5 g.), b. p. 85—88°C/15 mmHg, which showed infrared absorption bands at 1770 (shoulder), 1740, and 1180 cm^{-1}, but no bands at 1790—1800 (COCl), 3100 (=C–H), and 1670 (C=C) cm^{-1}. The g. l. c. analysis (B) indicated that this fraction consisted of ethyl cyclohexanecarboxylate (1.6 g.), diethyl oxalate (0.7 g.), and ethyl cyclohexene-3-carboxylate[21] (0.2 g.).

Fraction 2 (3 g.), b. p. 100—108°C/15 mmHg, which showed infrared absorption bands assignable to a double bond at 3100 and 1670 cm^{-1}, in addition to the bands of an ester. The g. l. c. analysis (A) showed that this fraction consisted of ethyl cyclohexanecarboxylate (0.5 g.) and 3, 3′-bicyclohexeneyl (2.5 g.).

The remaining brownish oil was refluxed with absolute ethanol, and then distilled to give two fractions. One fraction (0.3 g.), b. p. 120—140°C/15 mmHg, showed six peaks in the gas chromatogram (B). The other (0.7 g.), b. p. 140—155°C/15 mmHg, showed five peaks in the gas chromatogram (B); one of these peaks had the same retention time as that of diethyl hexahydrophthalate, but it was very small. Further investigations were not carried out.

A mixture of ECG (38 g., 0.31 mol.) and cyclohexene (4 g., 0.05 mol.) was irradiated for 2.5 hr., and then another 2 g. of cyclohexene was added into the irradiated mixture. The irradiation was continued for an additional 3.5 hr., and then 4 g. of cyclohexene was added. The mixture was further irradiated for 7 hr. After the unreacted ECG (30 g.) and cyclohexene had removed, the remaining oil was distilled under reduced pressure to yield the following fractions:

Fraction 1 (0.2 g.), b. p. 50—60°C/0.9 mmHg, was found to be a mixture of ethyl cyclohexanecarboxylate, diethyl oxalate, and 3, 3′-bicyclohexenyl.

Fraction 2, (2.5 g.), b. p. 80—110°C/0.9 mmHg, was hydrolyzed with ethanolic potassium hydroxyde, and then acidified to give ca. 1 g. of a solid, which, when recrystallized from water, was found to have a m. p. of 223—224°C. This solid showed no melting point depression upon admixture with authentic *trans*-hexahydrophthalic acid prepared according to the method of Price and Szwarc.[22] (Found: C, 55.44; H, 7.36. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03%).

The Irradiation of ECG in Toluene.—The irradiation of a mixture of ECG (27 g., 0.2 mol.) and toluene (62 g., 0.67 mol.) for 41 hr. gave 50 cc. of neutral gases. After the unreacted ECG (22 g.) and toluene (55 g.) had been removed, the distillation of the remaining oil afforded 1.5 g. of a fraction, b. p. 110—130°C/17 mmHg, which showed infrared absorption bands at 1770, 1750, and 1180 cm^{-1}, while the band at 1800 cm^{-1} (COCl) was observed on the shoulder of the 1750—1770 cm^{-1} region. Aromatic absorption bands at 3030, 1610, 1010, and 710 cm^{-1} were also observed. When this fraction was analyzed by g. l. c. (A), it was shown to consist of diethyl oxalate (0.5 g.) and ethyl phenylacetate (1 g.). This fraction was hydrolyzed with aqueous sodium hydroxide, and the resultant acid was identified as phenylacetic acid by a mixed melting point determination, m. p. and mixed m. p. 76—77.5°C (Found: C, 70.76; H, 5.88. Calcd. for $C_8H_8O_2$: C, 70.57; H, 5.92%).

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21) An authentic sample was prepared according to the directions of Boorman and Linstead; *J. Chem. Soc.*, **1935**, 258.

22) C. C. Price and M. Szwarc, *J. Am. Chem. Soc.*, **62**, 2894 (1940).