The Photolysis of Ethyl Chloroformate in Hydrocarbons

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It has been reported that alkoxycarbonyl radicals are produced by the reactions of alkyl formates with alkyl1,2) or methoxy3) radicals, and by those of methyl chloroformate with methyl radicals.4) In the peroxide-induced reaction of methyl formate with an olefin such as oct-1-ene, the formation of methyl pelargonate can arise from the addition of methoxycarbonyl radicals to the olefin.5) Although the alkoxycarbonyl radicals would also be produced in some of the primary steps in the photolysis of alkyl formates6) or esters of aliphatic carboxylic acids,7) this photolytic decomposition mainly takes place in the formyl- or acyl-alkoxy bond fission. An illustration is provided by the fact that the photolysis of methyl formate in cyclohexane gives cyclohexylcarbinol as the major product.8) The photolysis of esters of formic and other aliphatic carboxylic acids, therefore, is not suitable for the generation of alkoxycarbonyl radicals. Photolyses of ethyl cyanoformate and diethyl oxalate have been reported from this laboratory to give ethoxycarbonyl radicals, though the photolyses are related to the cyanation9) and the α-ketocarboxylation10) of the substrates respectively.

Although the thermodynamic properties of alkoxycarbonyl radicals have been discussed by Gray and Thynne,2) little information concerning the stability and the reactivity of the radicals has been given for lack of convenient methods for the generation of such radicals. In a previous communication,11) we have reported that the photolysis of ethyl chloroformate affords ethoxycarbonyl radicals and supplies a method for the direct carboxylation of hydrocarbons. The present paper will show the full results of the photolysis of ethyl chloroformate (ECF) in hydrocarbons; these results indicate the occurrence of selective carbon-chlorine bond breaking to give ethoxycarbonyl radicals. The reactivity of the radical in such hydrocarbons as cyclohexane, cyclohexene, oct-1-ene, and benzene will also be discussed in some detail.

Results and Discussion

The photolysis of ECF was carried out with an unfiltered high pressure mercury arc without a solvent, or in cyclohexane, cyclohexene, oct-1-ene, and benzene. During the course of the

TABLE I. GASEOUS PRODUCTS FORMED BY THE PHOTOLYSIS OF ECF IN CYCLOHEXANE AND CYCLOHEXENE

ECF	Hydrocarbon	Irradiation time	Product				
			Volume*	Ratio**			
g.	g.	hr.	cc.	CO	CO_2	C_2H_6	C_2H_4
100	—	25	700	$0.1>$	1	0.56	0.056
80	Cyclohexane, 20	4	240	***	1	0.73	0.05
18	Cyclohexane, 40	4	200	***	1	1	***
80	Cyclohexene, 20	4	7	***	1	0.14	0.11
18	Cyclohexene, 40	4	7	***	1	0.13	0.13

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

** The products-ratios were determined by gas chromatography using 1 m. of silica-gel column at 25°C.

*** The amounts were too small to be measured.

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1) J. C. J. Thynne, *Proc. Chem. Soc.*, **1961**, 18; *Trans. Faraday Soc.*, **58**, 1533 (1962).

2) P. Gray and J. C. J. Thynne, *Nature*, **191**, 1357 (1961).

3) J. C. J. Thynne, *Proc. Chem. Soc.*, **1962**, 295.

4) J. C. J. Thynne and P. Gray, ibid., **1962**, 141.

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

6) R. Borkowski and P. Ausloos, *J. Am. Chem. Soc.*, **83**, 1053 (1961).

7) P. Ausloos, ibid., **80**, 1310 (1958); M. H. J. Wijnen, ibid., **82**, 1847 (1960).

8) K. Shima and S. Tsutsumi, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **64**, 1945 (1961).

9) T. Tominaga, Y. Odaira and S. Tsutsumi, This Bulletin, 37, 596 (1964).

10) Y. Odaira, T. Tominaga, T. Sugihara and S. Tsutsumi, *Tetrahedron Letters*, **1964**, 2527.

11) C. Pac and S. Tsutsumi, This Bulletin, **36**, 234 (1963).

TABLE II. GASEOUS* AND LIQUID PRODUCTS FORMED BY THE PHOTOLYSIS OF ECF IN HYDROCARBONS

ECF g.	Hydrocarbon g.	Irradiation time hr.	Product**	mmol.
83	Cyclohexane, 168	6	Carbon dioxide	60
			Ethane	60
			Ethyl cyclohexanecarboxylate	6
			Bicyclohexyl	9
83	Cyclohexene, 164	14	Carbon dioxide	7
			Ethane	1
			Ethylene	1
			Ethyl cyclohexanecarboxylate	18
			Ethyl cyclohexene-3-carboxylate	***
			3, 3′-Bicyclohexenyl	21
60	Oct-1-ene, 178	12	Carbon dioxide	8
			Ethane	2
			Ethylene	2.6
			Ethyl pelargonate	6—7
			Ethyl 3-chloropelargonate	***
80	Benzene, 22	50	Carbon dioxide	5
			Ethane	5
			Ethylene	***
			Ethyl benzoate	50—100 mg.
			Biphenyl	***

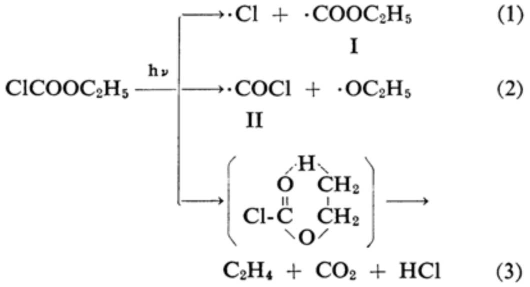
* In all cases, traces of carbon monoxide, ethyl chloride, and acetaldehyde were detected.

** In the case of cyclohexane, traces of ethylene, chlorocyclohexane, ethylcyclohexane, and diethyl carbonate were found. In the case of oct-1-ene, other unidentified products were observed.

*** The amounts were negligible.

irradiation, hydrogen chloride and the other gases were evolved; small amounts of the condensable products were trapped at −60°C at the end of the irradiation. The condensable products, which were analyzed by gas chromatography, mainly consisted of ethyl chloride, along with traces of acetaldehyde, while *n*-butane could not be detected. The gases formed, which were also analyzed by gas chromatography, included carbon monoxide, carbon dioxide, ethane, and ethylene. Both in cyclohexane and in the absence of a solvent, carbon dioxide and ethane were the major products, while carbon monoxide and ethylene were found to be the minor products. In the case of cyclohexene, the yields of gaseous products were very small, and the product-ratios were different from those found in the case of cyclohexane. The results concerning gaseous products obtained from the photolysis of ECF in cyclohexane and cyclohexene are summarized in Table I. The liquid products found in the photolysis of ECF in cyclohexane, cyclohexene, oct-1-ene, and benzene are listed in Table II.

Primary Processes of the Photolysis of ECF.—On the basis of the suggestions regarding the photolysis of esters of formic or aliphatic carboxylic acids,[7] the possible primary processes of the photolysis of ECF might be shown as follows:



The ethoxycarbonyl radical I, produced by the breaking of the carbon-chlorine bond (Eq. 1), is decomposed into carbon dioxide and an ethyl radical (Eq. 4-a) with an activation energy somewhat greater than 1—2 kcal./mol.[2] The chloroformyl radical II produced by the homolysis of the chloroformyl-ethoxy bond (Eq. 2) breaks down into carbon monoxide and a chlorine atom (Eq. 4-b) with the activation energy of 6.3 kcal./mol.[12]

$$\underset{\mathrm{I}}{\cdot COOC_2H_5} \rightarrow CO_2 + \cdot C_2H_5 \qquad (4\text{-a})$$

$$\underset{\mathrm{II}}{\cdot COCl} \rightarrow CO + \cdot Cl \qquad (4\text{-b})$$

According to schemes 1, 3, and 4-a, if ethyl radicals are quantitatively converted to ethane

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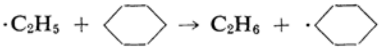
[12] W. G. Burn and F. S. Dainton, *Trans. Faraday Soc.*, **48**, 39 (1952).

and/or ethylene by their hydrogen-abstraction from a substrate or by disproportionation, the stoichiometric relationship between C_2-hydrocarbons and carbon dioxide must be given by Eq. 5:

$$([C_2H_4] + [C_2H_6])/[CO_2] = 1 \tag{5}$$

where $[C_2H_4]$, $[C_2H_6]$, and $[CO_2]$ indicate the moles of the corresponding compounds. It has been suggested that the disproportionation of ethyl radicals is suppressed by the use of organic solvents and that, in some cases, it does not take place at all.[13] The proportion of ethylene in gaseous products, therefore, might be expected to determine how process 3 participates in the photolysis of ECF. As is shown in Table I, with the increase in the amount of cyclohexane added. the values of the C_2-hydrocarbons/CO_2 ratio were changed from 0.62 to unity. When ECF was sufficiently diluted with cyclohexane, equal amounts of ethane and carbon dioxide were obtained, and the formation of ethylene became negligible. The dilution with cyclohexane apparently completes the conversion of ethyl radicals to ethane:



(6)

and Eq. 5 is satisfied. These results, therefore, strongly suggest that process 3 does not play an important role in the primary processes of the photolysis of ECF in cyclohexane.

On the other hand, the amounts of carbon monoxide might indicate the extent of the primary process 2. The findings in Table I show that the amounts of carbon monoxide are very small in all cases; hence process 2 would be negligible. From a comparison of the activation energy for the decomposition of the radical II with that for the decomposition of the radical I, however, it might be expected that a significant amount of the former radical might be likely to react with the other species before the decomposition. Contrary to the above expectation, however, the liquid products obtained from the photolysis of ECF in excess cyclohexane were not contaminated with cyclohexanecarbonyl chloride. Moreover, the amounts of acetaldehyde and diethyl carbonate which are derived from ethoxy radicals produced through process 2 are very small:

$$C_2H_5O\cdot + R\cdot \rightarrow CH_3CHO + RH \tag{7}$$

$$2C_2H_5O\cdot \rightarrow CH_3CHO + C_2H_5OH \tag{7'}$$

$$C_2H_5O\cdot \xrightarrow{\text{hydrogen donor}} C_2H_5OH \tag{8}$$

$$C_2H_5OH + ClCOOC_2H_5 \rightarrow (C_2H_5O)_2CO + HCl \tag{9}$$

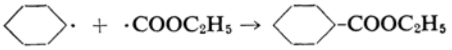
$$C_2H_5O\cdot + \cdot COOC_2H_5 \rightarrow (C_2H_5O)_2CO \tag{10}$$

These results are consistent with the conclusion that the primary process 2 plays a negligible role in the photolysis of ECF.

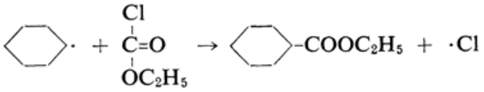
Thus we may decide that, in the photolysis of ECF, the breaking of the carbon-chlorine bond occurs in a selective manner, and that the photolysis of ECF can serve for the generation of ethoxycarbonyl radicals.

The Reactions of Ethoxycarbonyl Radicals.—As Table II shows, the liquid products from the photolysis of ECF in cyclohexane consisted of ethyl cyclohexanecarboxylate, bicyclohexyl, and traces of a mixture of chlorocyclohexane, ethylcyclohexane, and diethyl carbonate, while cyclohexanecarbonyl chloride could not be detected in any liquid fraction.

With respect to the formation of ethyl cyclohexanecarboxylate, two alternative interpretations are possible, as is shown in schemes 11 and 12, the radical-association scheme and the chain-reaction scheme. In the latter scheme, if a cyclohexyl radical is generated, the ester must be produced.



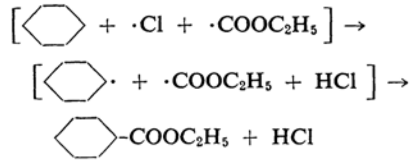
(11)



(12)

When the dibenzoyl peroxide-catalyzed reaction of ECF in cyclohexane was carried out, the ester was not observed, but bicyclohexyl was produced. Therefore, the latter interpretation (chain reaction) is ruled out; the association scheme 11 can be adopted in this case.

Assuming that the radical I diffuses in the solvent and associates with a cyclohexyl radical, the dimerization product, diethyl oxalate, may be expected to be formed, since carbamoyl radicals, $\cdot CONH_2$, can dimerize to give oxamide.[14] The difference in these reactions must be ascribed to the difference in stability between the radical I and the carbamoyl radical, not to a difference in electronic properties. The radical I might not have life time enough to dimerize. Therefore, it is very unlikely that the radical I diffuses in the solvent; it should be considered that ethyl cyclohexanecarboxylate might be produced in a solvent cage, involving the cage wall.



(13)

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[13] J. Smid, A. Rembaum and M. Szwarc, *J. Am. Chem. Soc.*, 75, 3315 (1956); M. Matsuoka, P. S. Dixon, A. P. Stefani and M. Szwarc, *Proc. Chem. Soc.*, 1962, 304; J. N. Bradley, *J. Chem. Phys.*, 35, 748 (1961).

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

Gray and Thynne have shown that the activation energies for the decomposition of alkoxycarbonyl radicals are somewhat greater than those for the decomposition of acyloxy radicals.[2] An acetyloxy radical, even in the liquid phase, does not attack alkanes; the entity of the radical reaction in such a system has been suggested to be a methyl radical,[15] though acetyloxy radicals are scavenged by iodine molecules.[16] In our experiments, the ratio of the association of the radical I with a cyclohexyl radical to the decomposition exhibits values of 0.1 or less, showing, in the liquid phase, fairly good accordance with the above authors' suggestion. The radical I might have life time enough to associate with a cyclohexyl radical in the solvent cage.

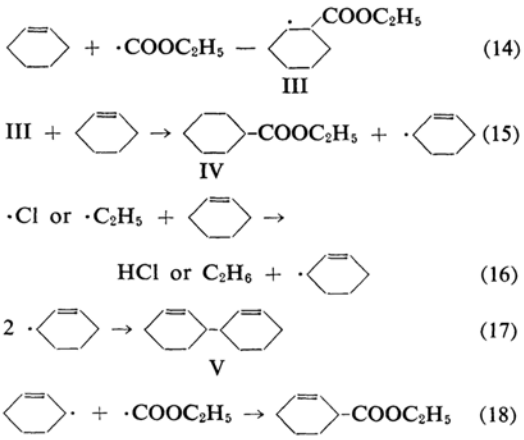
In order to observe the reactivity of the radical I to double bonds, cyclohexene and oct-1-ene were employed as solvents. The dilution with cyclohexene suppressed the formation of gases to a great extent, but the amounts of gases formed did not vary, though the concentration of ECF in cyclohexene was greatly changed. These results might indicate that a facile addition of the radical I to cyclohexene takes place, and that the decomposition is greatly suppressed. This interpretation is well supported by the results in Table II and by the well-known fact that olefins are good scavengers of various radicals.

The ratio of ethyl cyclohexanecarboxylate to carbon dioxide might give a measure of the reactivity of the radical I to cyclohexene. The value of the ratio, 2.5, indicates that the addition of the radical I to cyclohexene predominates over the decomposition at least 2.5 times. It is, however, difficult to explain why the amount of C_2-hydrocarbons were much less than that of carbon dioxide, and why ethylcyclohexane was not detected. It is most likely that ethyl radicals add to cyclohexene, and that the resulting species react further with cyclohexene to give unreclaimed, heavier compounds.

In the photolysis of esters of formic and aliphatic carboxylic acids[6] it has been suggested that the migration of a hydrogen atom (process 3) takes place in the excited singlet state. Therefore, the formation of ethylene via process 3 might not be quenched by cyclohexene. On the other hand, the formation of carbon dioxide might be much suppressed by the facile addition of the radical I to cyclohexene, and some of the ethyl radicals from the decomposition of the radical I might be trapped by cyclohexene. Thus, the proportion of ethylene in gaseous products is increased, and that of ethane is decreased compared with the results in the case of cyclohexane or in the absence of a solvent.

It was expected that the radical I would associate with a cyclohexen-3-yl radical in a manner similar to that in the case of cyclohexyl radicals to give an amount of ethyl cyclohexene-3-carboxylate comparable with that of ethyl cyclohexanecarboxylate obtained from the photolysis of ECF in cyclohexane. However, the amount of ethyl cyclohexene-3-carboxylate was negligible. These unexpected results can be explained by assuming that the addition of the radical I to cyclohexene is very rapid. Since the radical I is almost scavenged by cyclohexene, the concentration of the radical I might be so lowered that the association with the cyclohexen-3-yl radical, even in a solvent cage, can not take place to any appreciable extent.

The reaction scheme is shown as follows:



According to the above scheme, a stoichiometry is given by Eq. 19:

$$([\mathrm{HCl}] + [\mathrm{C_2H_6}] + [\mathrm{IV}])/2[\mathrm{V}] = 1 \qquad (19)$$

where [HCl], [C_2H_6], [IV], and [V] indicate the moles of the corresponding products. Since the number of chlorine atoms is equivalent to the amount of the radical I, [HCl] can be approximately replaced by [CO_2]+[IV]:

$$([\mathrm{CO_2}] + [\mathrm{C_2H_6}] + 2[\mathrm{IV}])/2[\mathrm{V}] \sim 1 \qquad (20)$$

The observed values of the ratio in Eq. 20 are 1.05, showing good accordance with those expected from the scheme.

Another possible product, ethyl 2-chlorocyclohexanecarboxylate, could not be detected in any appreciable amounts. Although a methyl radical has been reported to abstract the chlorine atom in methyl chloroformate in the vapor phase,[4] the species III might not abstract the chlorine atom in ECF. The above finding can be interpreted in three ways: 1) The chlorine

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[15] L. Herk and M. Szwarc, *J. Am. Chem. Soc.*, **82**, 3558 (1960).

[16] H. J. Shine and D. H. Hoffman, ibid., **83**, 2782 (1961).

atom-abstraction may be sterically hindered by the configuration of the cyclohexane ring. 2) Since cyclohexene has highly labile allylic hydrogen atoms, the species III may predominantly abstract the hydrogen atoms. 3) The chlorine atom in ECF may be insensitive to abstraction with radical species other than a methyl radical in the liquid phase.

A chain terminal olefin, such as oct-1-ene, eliminates such steric hindrance and does not have so reactive hydrogen atoms. When the photolysis of ECF in oct-1-ene was carried out, a variety of products was formed, including a moderate amount of ethyl pelargonate and traces of ethyl 3-chloropelargonate. Moreover, the amount of ethyl chloride found was very small in all cases. Therefore, it is likely that the third possibility is correct, that is, that the chlorine atom in ECF is insensitive to abstraction with the species III and VI and with ethyl radicals in the liquid phase.

$$C_6H_{13}\text{-}\dot{C}HCH_2COOC_2H_5$$

VI

The formation of a variety of products is ascribed to the competing reactions of various radicals formed primarily and secondarily. All of the liquid fractions obtained, however, showed essentially identical infrared absorption spectra, exhibiting strong bands corresponding to esters of aliphatic carboxylic acid without any other carbonyl bands. Moreover, the amounts of gases formed and the product ratios were comparable to those in the case of cyclohexene. These results show that the radical I adds not only to cyclohexene, but also to oct-1-ene, and with less decomposition.

In the case of benzene, the effective light for the photolysis of ECF appears to be quenched by benzene, since the absorption maximum of ECF lies below 2500 Å. Therefore, a precise investigation could not be undertaken, though small amounts of ethyl benzoate and traces of biphenyl were detected.

Experimental

Materials.—ECF, cyclohexane, and benzene were obtained commercially and purified in usual ways. Cyclohexene was prepared by the dehydration of cyclohexanol,[17] and oct-1-ene, by the pyrolysis of *n*-octyl acetate.[18] All of the materials were distilled before use.

The Analysis of Gaseous and Condensable Products.—In the study of gaseous products for Table I, the photolysis of ECF was carried out in a quartz cell (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 cell. The gases formed were passed through an aqueous alkaline solution after a trap at −60°C and were collected in a gas buret, with which the volumes of the neutral gaseous products were measured. The product ratios were determined by gas chromatographic measurements (silica-gel column: 1 m. at 25°C). At the end of the irradiation, a slow stream of nitrogen was bubbled into the irradiated mixture, and the condensable products collected in the trap were subjected to gas chromatography (tricresyl phosphate column: 3 m. at 25°C). Acetaldehyde was identifed by the paper chromatography of its 2, 4-dinitrophenylhydrazone.

The Photolysis of ECF in Cyclohexane.—A mixture of ECF (83 g.) and an excess of cyclohexane (168 g.) was irradiated with an internally-mounted high-pressure mercury arc (600 W.) at room temperature for 6 hr. in an atmosphere of nitrogen. During the course of the irradiation, 1400 cc. of neutral gaseous products was evolved. After the unchanged materials had been removed from the irradiated mixture, the remaining oil was distilled under reduced pressure to yield traces of a mixture of chlorocyclohexane, ethylcyclohexane, and diethyl carbonate (b. p. 30—60°C/35 mmHg), 1 g. of ethyl cyclohexanecarboxylate (b. p. 93—96°C/35 mmHg, n_D^{26} 1.4510) and 1.5 g. of bicyclohexyl (b. p. 65—70°C/3 mmHg, n_D^{26} 1.4743). The mixture of chlorocyclohexane, ethylcyclohexane, and diethyl carbonate was analyzed by gas chromatography (silicone-oil column: 3 m. at 80°C). The fraction of ethyl cyclohexanecarboxylate showed only one peak in its gas chromatogram (silicone-oil column: 3 m. at 170°C) and an infrared absorption spectrum identical with that of an authentic sample. An anilide derived from this fraction showed no melting point depression upon admixture with an authentic anilide; melting point and mixed melting point 143—143.5°.

(Found: C, 76.69; H, 8.06. Calcd. for $C_{13}H_{17}ON$: C, 76.81; H, 8.43%)

The fraction of bicyclohexyl was analyzed by gas chromatography (silicone-oil column: 3 m. at 170°C); it was contaminated with only a small amount of ethyl cyclohexanecarboxylate (3.8 wt.%).

The Photolysis of ECF in Cyclohexene.—The photolysis of ECF (83 g.) in cyclohexene (164 g.) for 14 hr. gave 50 cc. of neutral gaseous products and two fractions, one of them with a b. p. of 88—99°C/28 mmHg (n_D^{26} 1.4570, 3.1 g.) and the other with a b. p. of 110—132°C/28 mmHg (n_D^{26} 1.4953, 2.9 g.); both of these showed two peaks in their gas chromatograms (silicone-oil column: 3 m. at 170°C). One of the peaks had the same retention time as that of ethyl cyclohexanecarboxylate, while the other was considered to be the peak of 3, 3′-bicyclohexenyl on the basis of findings to be described later. The area-ratios of the former peak to the latter in two fractions showed the values of 5.7 and 0.15 respectively; thus the yields of ethyl cyclohexanecarboxylate and 3, 3′-bicyclohexenyl were each calculated to be 3 g. The lower boiling fraction was further analyzed by gas chromatography under

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

[18] W. J. Bailey and W. H. Hale, *J. Am. Chem. Soc.*, **81**, 647 (1959).

different conditions (dioctyl sebatate column: 4 m. at 120°C); this analysis showed the presence of a trace of ethyl cyclohexene-3-carboxylate.[19] This fraction showed an infrared absorption spectrum essentially identical with that of ethyl cyclohexanecarboxylate, and an anilide derived from the fraction showed no melting point depression upon admixture with anilide of cyclohexanecarboxylic acid (m. p. 143.5°C and mixed m. p. 143—143.5°C). The higher boiling fraction showed the absorption bands characteristic of double bonds at 3040 and 1640 cm^{-1} and, on treatment with bromine, afforded two white crystals, the one (m. p. 153—156°C) more soluble and the other (m. p. 187—189°C) less soluble in chloroform; these were considered to be tetrabromides of 3, 3'-bicyclohexenyl (lit.[20] the more soluble isomer, m. p. 159—162°C, and the less soluble one, m. p. 188—190°C).

The Photolysis of ECF in Oct-1-ene.—The photolysis of ECF (60 g.) in oct-1-ene (178 g.) for 12 hr. gave 100 cc. of neutral gaseous products and the following fractions; b. p. 109—115°C/27 mmHg, 1.7 g. and b. p. 125—149°C/1 mmHg, 1.9 g. These two fractions exhibited infrared absorption spectra essentially identical with the strong bands of the aliphatic carboxylic acids at 1740 (C=O) and 1160 (C-O) cm^{-1} respectively. The lower boiling fraction showed five peaks in its gas chromatogram (silicone oil column: 1.5 m. at 165°C), in which the largest peak had the same retention time as that of ethyl pelargonate, while the retention time of the smallest one was identical with that of ethyl 3-chloropelargonate. An anilide derived from the lower boiling fraction showed no melting point depression upon admixture with anilide of pelargonic acid; m. p. 56.5—57.5°C and mixed m. p. 56.5—58°C.

(Found: C, 77.33; H, 9.91. Calcd. for $C_{15}H_{23}\cdot ON$: C, 77.25; H, 9.87%)

The higher boiling fraction was analyzed by gas chromatography (silicone oil column: 1.5 m. at 165°C) and found to consist of seven or more components; these were not, however, identified.

The Photolysis of ECF in Benzene.—When a mixture of ECF (80 g.) and benzene (22 g.) was photolyzed for 50 hr., 100 cc. of neutral gaseous products and 100 mg. of a fraction (b. p. 65—75°C/10 mmHg) were obtained. The liquid fraction, when analyzed by gas chromatography (silicon oil column: 3 m. at 160°C), was found to consist of ethyl benzoate, along with traces of biphenyl and only a small amount of another, unidentified component. Further investigations were not carried out.

The Dibenzoyl Peroxide-Catalyzed Reaction of ECF in Cyclohexane.—A mixture of ECF (18 g.) and cyclohexane (40 g.) containing 2 g. of dibenzoyl peroxide was refluxed at 83—85°C for 24 hr. under a nitrogen atmosphere. During the course of the reaction, carbon dioxide was evolved, but no other gaseous products were observed. After the unchanged materials had been removed, the remaining oil was distilled under reduced pressure to yield 0.2 g. of a fraction (b. p. 100—130°C/25 mmHg). During the distillation, benzoic acid was sublimed. In the gas chromatogram of the fraction, a peak showed the same retention time as that of bicyclohexyl, but there was no peak with a retention time the same as or near the same as that observed in ethyl cyclohexanecarboxylate (silicone oil column: 3 m. at 170°C).

Summary

The photolysis of ECF in cyclohexane, cyclohexene, oct-1-ene, and benzene has been carried out. It has been concluded that carbon-chlorine bond breaking has occurred to give ethoxycarbonyl radicals in a selective manner. The reactions of the radical in hydrocarbons have been qualitatively discussed, and it has been suggested that the radical had a life long enough to associate with a cyclohexyl radical in a solvent cage, but not a life long enough to dimerize and be added to carbon-carbon double bonds with less decomposition. Thus, cyclohexane, cyclohexene, oct-1-ene, and benzene were carboxylated. No chain reactions were observed in light- and dibenzoyl peroxide-induced reactions of ECF in hydrocarbons; i. e., ECF was unreactive to alkyl radicals and radicals bearing an ethoxycarbonyl group on their α-carbon. The photolysis of ECF supplies a convenient method for the generation of ethoxycarbonyl radicals.

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[19] An authentic sample was prepared according to directions of Boorman and Linstead; *J. Chem. Soc.*, **1935**, 258.

[20] E. H. Farmer and C. G. Moor, ibid., **1951**, 131.