In a second run using twice the above amounts the yield was 71%. The phenolic phenyl ketone formed leaflets from aqueous methanol melting as above, and rods or platelets from methanol alone, m.p. 168.5–170.5°. The lower melting modification when rubbed with a trace of the latter was observed to melt at 167.5–170°.

The acetate of X was prepared from 3.80 g. of the phenol and 6 ml. of acetic anhydride in 10 ml. of pyridine by heating the mixture on the steam-bath for two hours. The product crystallized from methanol in glistening leaves melting at 162.5–163.5°.

Anal. Calcd. for $C_{28}H_{34}O_3$: C, 80.34; H, 8.19. Found: C, 80.11; H, 8.31.

The methyl ether of X was obtained by the portionwise addition of 2 ml. of dimethyl sulfate[12] to the hot (70–80°) stirred suspension of 0.42 g. of the compound in 10 ml. of 25% sodium hydroxide. The neutral product (0.28 g.) after recrystallization from methanol and drying at 80° melted at 134.5–136.5°.

Anal. Calcd. for $C_{27}H_{34}O_2$: C, 83.03; H, 8.78. Found: C, 82.90; H, 8.91.

6-Hydroxy-9-oxodehydroabietophenone (XIV).—A suspension of 1.05 g. of X acetate in 15 ml. of acetic acid was oxidized as described above. Following saponification of the product the free phenol was crystallized from acetone or acetone–methanol forming 0.74 g. (75%) of needles melting at 230–236°. The sample purified for analysis melted at 233.5-236.5°; $[\alpha]^{26}\text{D}$ 53° (α 1.22°, *c* 1.15 in dioxane). The larger needles decrepitated explosively on vacuum drying.

Anal. Calcd. for $C_{26}H_{30}O_3$: C, 80.08; H, 7.74. Found: C, 79.97; H, 7.90.

The acetate of XIV was formed by heating a sample of the above with acetic anhydride in pyridine. The ester crystallized from aqueous methanol in leaves melting at 114–115.5 after drying at 80°.

Anal. Calcd. for $C_{28}H_{32}O_4$: C, 77.75; H, 7.46. Found: C, 77.99; H, 7.73.

In the preparation of the **methyl ether of XIV**, 0.15 g. of the dioxophenol suspended in 8 ml. of 25% sodium hydroxide was shaken at 50–60° with 2 ml. of dimethyl sulfate added in 0.25-ml. portions. The product crystallized from aqueous methanol in leaves melting at 125.5–127.5° after drying at 80°.

Anal. Calcd. for $C_{27}H_{32}O_3$: C, 80.16; H, 7.97. Found: C, 80.36; H, 8.18.

A solution of 0.15 g. of XIV in methanolic hydroxylamine solution was heated in a sealed tube at 100° for three hours. The resulting **oxime** crystallized from aqueous methanol in short rods melting at 234–238° dec. (bath preheated to 210°), the melt effervescing and becoming dark red in color.

Anal. Calcd. for $C_{26}H_{31}O_3N$: N, 3.45. Found: N, 3.54.

ADDED IN PROOF.—Since this paper was submitted M. S. Kharasch and R. M. Acheson, *J. Org. Chem.*, 16, 447 (1951), have described the oxidative degradation of pure II to benzophenone and a mixture of ketonic substances containing little or no III.

SHREWSBURY, MASS. RECEIVED JANUARY 24, 1951

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[12] H. H. Zeiss, U. S. Patent 2,450,706.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Hot Radical Reactions in the Photolysis of Methyl and Ethyl Iodides in the Liquid Phase[1,2]

BY WILLIAM H. HAMILL AND ROBERT H. SCHULER

The photolysis of liquid methyl and ethyl iodides at 2537 Å. with added radioiodine is accompanied by isotopic exchange. The photolysis of methyl iodide in cyclohexane produces cyclohexene and cyclohexyl iodide. The experimental results are consistent with a mechanism in which the primary process involves separation into an iodine atom and a hot alkyl radical. A fraction of the radicals then undergo secondary chemical reactions before they have been reduced to thermal energies. The fraction undergoing each hot radical reaction is independent of light intensity. At this wave length there appears to be no primary recombination of iodine atoms and methyl radicals.

This work was prompted by a need for information regarding the photolysis of alkyl iodides in the liquid phase at high light intensity and at high iodine concentrations in order to facilitate comparison with analogous radiolysis experiments at high fluxes of energetic X-rays and electrons.[3] The crucial postulate common to most mechanisms[4] of these photolyses is that the recombination (1) of the

$$R + I \longrightarrow RI \qquad (1)$$

alkyl radical and the iodine atom occurs by virtue of the Franck–Rabinowitch principle and that recombination with molecular iodine (2) is relatively unimportant because of the observed absence of retardation by iodine, even at appreciable

$$R + I_2 \longrightarrow RI + I \qquad (2)$$

concentrations. The absence of such retardation has been even more clearly demonstrated by the present work. If the back reaction were, indeed, due to such a cage effect then it is not evident how one is to account for a hundred-fold increase in the quantum yield for iodine formation from methyl iodide caused by a small amount of dissolved oxygen.[5]

Experimental

Edwal Laboratories C.P. grade methyl and ethyl iodides were fractionally distilled and, except as noted, were vacuum-distilled from phosphorus pentoxide into the irradiation vessel and sealed. Eastman Kodak best grade cyclohexane was similarly treated for experiments with solutions.

The source of illumination was a Hanovia SC 2537 low pressure mercury discharge lamp in the form of a helical grid, used without filters or collimation, and operated at 350 watts. The lamp was housed in a ventilated box and the light intensity was maintained approximately constant by manual adjustment of the primary current to the high voltage transformer. Samples were exposed to illumination after the lamp had reached a steady temperature.

The 15-mm. diameter quartz tubes in which 5-ml. samples were illuminated were placed reproducibly 3 cm. from the periphery of the lamp. Any changes in geometry that occurred during this work were allowed for by using ethyl iodide itself as an actinometer.

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[1] Presented at the 115th Meeting of the American Chemical Society in San Francisco, March, 1949. From the doctoral dissertation of Robert H. Schuler, University of Notre Dame.

[2] This work was supported, in part, under contract N6 ori 165, T.O. II with the Office of Naval Research.

[3] W. H. Hamill and R. H. Schuler, to be published.

[4] For reviews see E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corporation, New York, N. Y., 1946, p. 237, and G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice Hall, Inc., New York, N. Y., 1939, p. 355.

[5] W. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).

The concentration of iodine was measured between intermittent irradiations of the unopened sample with a Beckman DU spectrophotometer. The quartz tubes in which samples had been illuminated also served as spectrophotometer cells, giving satisfactorily reproducible readings. This method permitted a series of measurements to be taken on a single sample without exposing it to air. Optical densities were measured at 4800, 5000 or 6250 Å., depending upon concentration.

Iodine-128 (25 min.) was prepared by neutron bombardment of one liter of ethyl iodide with the total neutron flux of a 300 milligram radium–beryllium neutron source. The iodine activity was separated by extraction with water containing a little sodium thiosulfate. The aqueous portion was extracted repeatedly with carbon tetrachloride and the aqueous activity was then exchanged with a known weight of iodine, extracted into the alkyl iodide and dried over phosphorus pentoxide. Carrier-free iodine-131 (in aqueous solution) from the Atomic Energy Commission was evaporated to dryness on a watch glass. Exchange was effected by subliming iodine from the same watch glass. Experiments with iodine-131 were subsequent to all others.

Activity was measured with a commercial liquid sample counting tube. The volume of sample required for the determination was 4–5 cc. Correction factors for self absorption and decay were applied. The extent of iodine exchange induced by photolysis was determined from the activity converted to an organic form and from the known amount of added carrier iodide. The former quantity was determined by extracting the sample after irradiation with a measured volume of dilute thiosulfate solution and determining the relative activities of the two fractions after proper corrections had been applied.

The total flux in 5-ml. samples was *ca.* 10^{17} quanta per sec. which was considerably higher than that previously used in similar work. Absorption was complete, even in dilute solution. Because of proximity to the lamp, sample temperatures approximated 40° during illumination. Temperature control was not considered necessary since it has been shown that iodine yield is constant from 0–50°.[6]

Results

Photolysis of Liquid Alkyl Iodides.—The experiments with ethyl iodide, summarized in Fig. 1, show that the rate of production of iodine at constant light flux does not change with time over a rather wide range of concentration and up to iodine concentrations considerably higher than have previously been observed.[5,6] In subsequent experiments ethyl iodide itself was used as an actinometer employing a (defined) quantum yield $\phi_I = 0.4$ atom of iodine per quantum absorbed on the basis of Norton's results.[6]

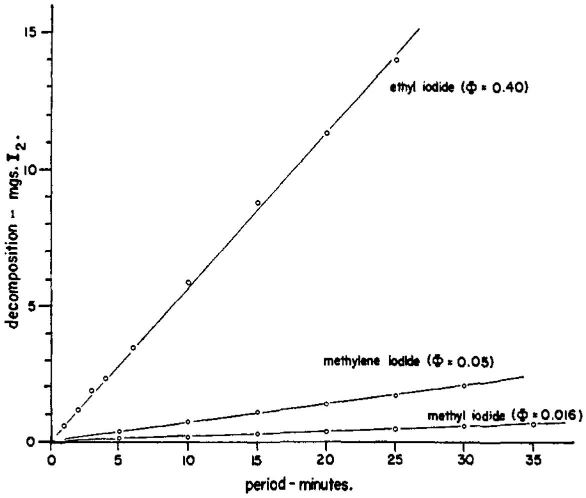

Fig. 1.—Photodecomposition of alkyl iodides.

Methyl iodide was photolyzed in an inverted U-tube. The measurements of series A and B (Fig. 2) were performed independently. Following the measurements of series B the solution was poured into the second arm of the tube and the methyl iodide was distilled iodine-free into the first arm. A final series (C) of observations was then taken. The results of all three series agree within experimental error and correspond to $\phi_I = 0.016$.

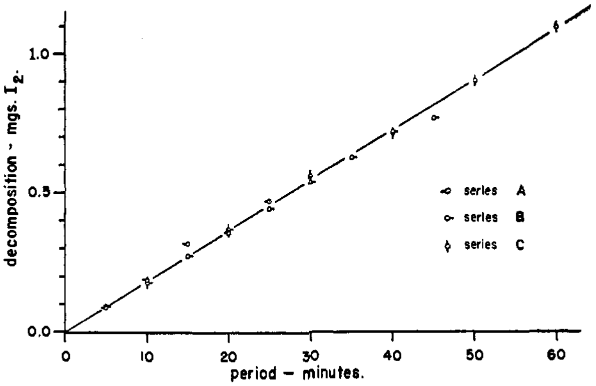

Fig. 2.—Photodecomposition of methyl iodide.

Results for methylene iodide, which are included in Fig. 1 for later comparison with the radiation decomposition,[3] correspond to $\phi_I = 0.048$.

Iodine Exchange and the Back Reaction.—When radioiodine was added to alkyl iodides before photolysis, activity appeared in the organic fraction of the illuminated material. Hydrogen was bubbled through the reaction cell during photolysis to stir the solution and to exclude air. Without stirring the extent of exchange was less, apparently be-

TABLE I

EXCHANGE BETWEEN ALKYL IODIDES AND IODINE INDUCED BY LIGHT AT 2537 Å.

Carrier I_2 g. atom $(10)^6$	Einsteins absorbed $(10)^6$	Alkyl iodide activity, %	Iodine exchanged g. atom $(10)^6$	ϕ exchange
		Methyl Iodide		
570	135	17.5	109	0.81
128	69	32.8	51	0.76
243	96	35.0	104	1.09
74	48	45.4	45	0.94
110[b]	42	28.6	37	.90
110[b]	83	48.8	74	.89
110[a,b]	91	52.0	81	.89
66[a,b]	32	36.1	30	.92
			Av.	0.90
		Ethyl Iodide		
96	101	48.1	76	0.75
201	101	29.4	77	.76
276	101	20.1	86	.85
17	10	22.8	5	.50
71[b]	83	42.6	48	.58
71[b]	42	26.4	25	.59
94[a,b]	166	47.3	80	.48
94[b]	83	36.2	49	.59
			Av.	0.64

[a] Sample volume 10 ml. in these runs, 5 ml. in all others.
[b] Iodine-131 employed in these runs, temperature 25–30°; Iodine-128 employed in other runs, temperature *ca.* 40°.

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[6] B. M. Norton, THIS JOURNAL, **56**, 2294 (1934).

cause of the higher local concentration of inactive iodine formed by decomposition in the photolytic region. The results of the exchange experiments and the quantum yields calculated for the exchange reactions appear in Table I.

In order to check the possibility that exchange of activity might occur between iodine atoms and alkyl iodide molecules, a solution of iodine-128 in ethyl iodide was exposed to the condensed beam of a 1000-watt tungsten lamp for ten minutes at room temperature. The amount of carrier was maintained at a low level in order to exaggerate any possible exchange. The first test, under these somewhat extreme conditions, showed very little exchange. In a second test, with an ethyl iodide filter, no exchange was detected. The positive result had apparently been due to the small ultraviolet component of the tungsten light. It is clear that iodine atoms and ethyl iodide molecules do not exchange measurably under these conditions.[7]

In two experiments with methyl iodide and added iodine-128, carrier methylene iodide was added to the photolyzed material and the sample fractionally distilled after removing free iodine. The high boiling fractions of the two runs contained 4.3 and 5.0% of the organic activity which may be attributed to the formation of methylene iodide since it is a known photolytic product.[8]

Preliminary experiments have indicated that photolysis of liquid normal and isopropyl iodides, with dissolved iodine-128, produces both methyl and ethyl iodides, in small amounts, and the isomeric propyl iodide. These results were not adequately confirmed because of the difficulty of performing efficient fractionation in a limited time.

Photolysis in Hydrocarbon Solutions.—Hexane solutions of methyl iodide and of ethyl iodide which had been photolyzed and then extracted with thiosulfate solution were observed to slowly liberate additional iodine. The rate of liberation was greatly increased by illumination with visible light. This effect was attributed to the decomposition of an olefinic diiodide produced from the solvent as a consequence of photolyzing the solute iodides. Subsequent experiments to study this effect were performed with *ca.* 1% methyl iodide in cyclohexane. Over a range of iodine concentration ϕ_I was 0.10.

When solutions of methyl iodide and iodine-128 in cyclohexane were photolyzed and subsequently fractionated, a large part (*ca.* 20%) of the organic activity did not distil over with methyl iodide. This activity was tentatively ascribed to the formation of cyclohexyl iodide as a reaction product. Several samples which had been irradiated for about 30 minutes were analyzed with a Beckman IR-2 infrared spectrophotometer. No absorption bands different from the irradiated solutions were detected for cell lengths shorter than 1 mm.; at this length a new absorption band was detected at 13.9 μ which was intensified by further liberation of free iodine. A 5% (volume) solution of methyl iodide in cyclohexane was then photolyzed for 185 minutes, the iodine extracted with thiosulfate solution and the sample dried over phosphorus pentoxide. New absorption peaks were observed at 13.9, 12.4, 9.05 and 8.5 μ. The band at 13.9 μ corresponds to cyclohexene and the other three correspond to cyclohexyl iodide. It is estimated that the amounts of olefin and of iodine liberated are equivalent, mole for mole.

Discussion

The results reported in Figs. 1 and 2 extend the independence of quantum yield with respect to iodine concentration to much higher concentrations than have been previously reported and render increasingly improbable the rate-controlling action of either processes (1) or (2). The qualitative facts of considerable photochemical exchange of methyl and ethyl iodides with iodine also clearly imply that primary recombination or deactivation cannot be entirely responsible for the low quantum yield of the decomposition. A possible explanation of these and other difficulties was suggested by direct evidence of energetic radicals (*viz.*, decomposition of propyl radicals) and by a hot-atom mechanism used elsewhere,[9] of which the essential feature is a characteristic "splitting ratio" of the energetic particles along alternate reaction paths.[10] The C–I bond strength for these alkyl iodides approximates 2.3 volts, the excitation energy of the iodine atom is 1 volt, while $h\nu$ at 2537 Å. is 5 volts. The residual energy (*ca.* 1.7 volts if the iodine atom is excited) is largely retained by the light methyl and ethyl radicals. Since ϕ_I is not temperature dependent it is concluded that the yield-controlling steps are hot radical reactions. The mechanism for methyl iodide must also account for: ϕ near unity for iodine exchange; a very small ϕ_I, independent of concentration of iodine; the formation of methylene iodide and methane.

The simplest mechanism consistent with these facts is the following (where $\mathbf{CH_3}$ represents a hot methyl radical)

$$CH_3I + h\nu \longrightarrow \mathbf{CH_3} + I \qquad (3)$$

$$\mathbf{CH_3} + M \longrightarrow CH_3 + M \qquad (4)$$

$$\mathbf{CH_3} + CH_3I \longrightarrow CH_4 + CH_2I \qquad (5)$$

$$\longrightarrow C_2H_6 + I \qquad (6)$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (7)$$

$$CH_2I + I_2 \longrightarrow CH_2I_2 + I \qquad (8)$$

$$I + I + M \longrightarrow I_2 + M \qquad (9)$$

This mechanism deviates from the reported facts for liquid methyl iodide as regards the formation of ethane, since Emschwiller[8a] reported methane as the only gaseous product although ethane has been found in the vapor phase photolysis.[8b,10c] It should also be observed, however, that his "coefficient of utilization" is abnormally large for methyl iodide as compared to ethyl iodide and may imply failure to remove oxygen completely. It is evi-

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[7] Subsequent studies (R. H. S.) show that the exchange $C_2H_5I + I^{131} \rightarrow C_2H_5I^{131} + I$ occurs with $E = 10$ kcal. This exchange would not contribute measurably under present experimental conditions.

[8] (a) G. Emschwiller, *Ann. Chim.*, **17**, 413 (1932); (b) W. West and L. Schlessinger, THIS JOURNAL, **60**, 961 (1938).

[9] R. R. Williams and W. H. Hamill, *J. Chem. Phys.*, **18**, 783 (1950).

[10] Hot radical reactions have been postulated by (a) R. R. Williams and R. A. Ogg, *J. Chem. Phys.*, **15**, 696 (1947), for the photolysis of methyl iodide, (b) M. K. Phibbs and B. de B. Darwent, *Trans. Faraday Soc.*, **45**, 541 (1949), for the photolysis of dimethyl mercury and (c) R. D. Schultz and H. A. Taylor, *J. Chem. Phys.*, **18**, 194 (1950), for the photolysis of methyl iodide, all in the vapor state.

dently impossible to release iodine without forming new carbon–carbon bonds and reaction (6) has been chosen in preference to the formation of ethylene. Since $\phi_{C_2H_6}$ equals $2\phi_I$ it follows that $\phi_{C_2H_6}$ is 0.008. Also ϕ_{CH_4} is 0.05 since it is equal to $\phi_{CH_2I_2}$. The removal of all thermal free radicals by molecular iodine is consistent with the independence of ϕ_I upon iodine concentration. The simplest mechanism for ethyl iodide is

$$C_2H_5I + h\nu \longrightarrow C_2H_5 + I \qquad (3a)$$

$$C_2H_5 + M \longrightarrow C_2H_5 + M \qquad (4a)$$

$$C_6H_5 + C_2H_5I \longrightarrow C_2H_6 + C_2H_4I \qquad (5a)$$

$$C_2H_5 + I_2 \longrightarrow C_2H_5I + I \qquad (7a)$$

$$C_2H_4I \longrightarrow C_2H_4 + I \qquad (10)$$

$$2I + M \longrightarrow I_2 + M \qquad (11)$$

According to the view presented here the fundamental similarity between the two mechanisms is between reactions (5) and (5a). The superficial difference is that the former does not result in the net liberation of iodine whereas the latter produces two net iodine atoms for each hot radical reacting. Since ϕ_I equals 0.40, $\phi_{C_2H_6}$ is 0.20. There is no need to postulate butane formation, by analogy with (6), since carbon–carbon bond formation can more readily occur by (5a) and (10) and agrees with the fact that equal amounts of ethane and ethylene are produced.[8a]

As in the former case the hot radical reaction controls ϕ_I and it is independent of light intensity, of temperature and of iodine concentration. The increase of ϕ_I with $1/\lambda$ is consistent with the greater energy of the hot radical. The larger ϕ_I in the liquid state as compared to the vapor state is contrary to the usual situation where ϕ_{gas} is greater than ϕ_{liquid} and may be correlated with the unusual circumstance that ϕ_I is due exclusively to hot radical reactions. It appears also to be the case in nuclear chemistry that hot atoms will more probably reach thermal energy without reaction in the gaseous state than in the liquid state.[11]

These mechanisms remove the difficulty of accounting for the large increase in ϕ_I caused by small amounts of oxygen. Oxygen, as a trace component, cannot enter into hot radical reactions to any measurable extent, and there is no longer an inconsistency in the postulated reaction between alkyl radicals and oxygen. It is evident, however, that both mechanisms must be regarded as tentative pending further identification of photolytic products.

The large difference in ϕ_I between methyl and ethyl iodides follows from the expected difference in probability factors for reactions (6) and (5a); in general one might expect ϕ_I to be less for methyl iodide than for the higher iodides[12] for the same reason. One also expects an increased yield for isopropyl over normal propyl iodide. By reactions of type (5a) only removal of one of the two hydrogens from the central carbon of normal propyl iodide produces a radical capable of spontaneously yielding an olefin whereas in the isopropyl case loss of any one of the six hydrogens from the terminal methyl groups yields CH_3CHICH_2 which can decompose to propylene and iodine. As the alkyl group becomes still larger one predicts that the increasing possibilities of isomeric free radicals will cause the yield to become smaller because of the decreasing probability of removing hydrogen from a carbon atom adjacent to the iodine and so producing an olefin. The increasing mass of the alkyl group results in a decrease in the fraction of the kinetic energy available to the radical which may also lower the yield.

The present views do not lead to simple predictions regarding solvent effect in general, but they do correctly indicate that the effects observed should depend upon the solvent.[13] They also seem to require chemical change in the solvent as a result of hot-radical processes. Thus in hydrocarbon solution, dehydrogenation would be expected to occur. It has been shown that when methyl iodide is photolyzed in cyclohexane, both cyclohexene and cyclohexyl iodide are produced. The formation of cyclohexyl iodide may plausibly be attributed to the hot radical reaction

$$CH_3 + C_6H_{12} \longrightarrow CH_4 + C_6H_{11}$$

followed by the thermal reaction

$$C_6H_{11} + I_2 \longrightarrow C_6H_{11}I + I$$

The mode of forming cyclohexene, which appears to control the yield of iodine, cannot be accounted for at this time.

To interpret the exchange measurements let the rate of transfer of activity from the inorganic to the organic fraction be

$$-\mathrm{d}S/\mathrm{d}t = R^*X/(X + X')$$

where X and X' are the amounts of active and of inactive inorganic iodine and R^* is a constant at constant light flux. For methyl iodide, since $X + X' = X_0$, the initial amount of iodine, the integrated equation is

$$X_0 \ln (X_0/X) = R^*t$$

For ethyl iodide, since there is a net release of iodine $X + X' = X_0 + Rt$ and $\ln (X_0/X) = (R^*/R) \ln (X_0 + Rt)/X_0$ where R is the net rate of producing iodine by photolysis. The results in the last two columns of Table I are based upon such calculations.

The exchange measurements for ethyl iodide are not precise but it is evident that $1 - \phi_I$ cannot be taken as a measure of deactivation or primary recombination due to cage effects[14] for either of these iodides at 2537 Å. Maximum values of $\phi_{exchange}$ consistent with ϕ_I and the mechanisms above, are 0.99 and 0.80 for methyl and ethyl iodides, respectively. The differences between these and the observed values for $\phi_{exchange}$ may be due, in part, to insufficient stirring but some primary or secondary recombination is not excluded.

It is very improbable that methyl radicals are largely removed by iodine atoms from other mole-

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[11] The n,γ process in ethyl bromide produces *ca.* 15% active organic bromide in the vapor state and *ca.* 50% in the liquid state.[9] For a discussion of such effects see W. F. Libby, THIS JOURNAL, **69**, 2523 (1947).

[12] E. Olaerts and J. C. Jungers, *Faraday Soc. Discussion*, **2**, 222 (1947) report the following quantum yields at 3100 Å. and room temperature in the pure liquid iodides: ethyl, 0.32; *n*-propyl, 0.21, *i*-propyl, 0.77; *n*-butyl, 0.10; *n*-amyl, 0.065.

[13] W. West and J. Fitelson, THIS JOURNAL, **62**, 3021 (1940).

[14] J. Franck and E. Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

cules since the atoms must first have reached equilibrium by (12) and this preliminary exchange itself cannot be much faster than the competitive

$$I + I_2^* \rightleftarrows I^* + I_2 \qquad (12)$$

removal by (13) because of the similarity of concentrations and estimated activation energies.[15] It is

$$R + I_2^* \longrightarrow RI^* + I \qquad (13)$$

very probable, therefore, that methyl radicals recombine with iodine molecules rather than iodine atoms in the liquid state at 2537 Å. It appears from the recent work of Noyes[16] on the photolysis of iodine and recombination of iodine atoms in solution that primary recombination might occur with methyl iodide under more favorable conditions where less energy is given to the radical formed in photolysis.

Acknowledgment.—The authors are grateful to Dr. R. R. Williams, Jr., for helpful discussions of this work. One of us (R. H. S.) is indebted to the Peter C. Reilly Foundation for a fellowship.

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[15] J. Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).

[16] R. M. Noyes, *ibid.*, **18**, 999 (1950).

NOTRE DAME, IND. RECEIVED OCTOBER 9, 1950

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

Chlorinated 3-Trifluoromethylphenols

BY ARAM MOORADIAN, T. J. SLAUSON AND S. J. MARSALA

4-Chloro- and 6-chloro-3-trifluoromethylphenols have been prepared through the corresponding chloro-3-trifluoromethylanilines. By further chlorination of these phenols, 2,4- and 2,6-dichloro-3-trifluoromethylphenols have been isolated and identified. A new series of compounds incidental to the preparation and characterization of these phenols is described.

In the early work of Swarts,[1] *m*-trifluoromethylphenol was prepared by diazotizing *m*-trifluoromethylaniline. It was originally our[2] intention to prepare both alkylated and chlorinated derivatives of this phenol. In our attempts at alkylation, direct alkylation with *t*-butyl alcohol in the presence of aluminum chloride was unsuccessful as were attempts at condensation of lower aldehydes with the phenol in acetic acid solution containing dissolved hydrogen chloride. Rearrangement of ethers and esters in the presence of the usual agents such as sulfuric acid–acetic acid, boron trifluoride, aluminum chloride,[3] heat, heat and diethylaniline were all unsuccessful, the best yield obtained being on the order of 5–10%. The intermediates used in this work are shown in Table I.

TABLE I

$3\text{-}CF_3\cdot C_6H_4OR$

R	Yield, %	B.p. °C.	Mm.	$n^{25}D$	Molecular formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ethyl[a]	50	76	23	1.4442	$C_9H_9F_3O$	56.84	56.46	4.75	4.81		
i-Propyl	51	80–82	21	1.4400	$C_{10}H_{11}F_3O$	58.83	59.23	5.43	5.64		
n-Butyl	57	105–108	23	1.4440	$C_{11}H_{13}F_3O$	60.54	60.12	6.00	6.33		
Allyl	79	90–91	22	1.4547	$C_{10}H_9F_3O$	59.42	59.26	4.48	4.67		
n-Butanoyl	56	110–113	16	1.4415	$C_{11}H_{11}F_3O_2$	56.89	57.03	4.78	4.99		
Carbamyl	25	M.p. 109–111			$C_8H_6F_3NO_2$	46.84	46.83	2.95	2.94	6.82	6.74

[a] E. T. McBee, R. O. Bolt, P. J. Graham and R. F. Tebbe, THIS JOURNAL, 69, 947 (1947).

4-Chloro-3-trifluoromethylphenol and 2-chloro-5-trifluoromethylphenol were prepared by diazotizing the corresponding anilines. These as well as derivatives and intermediates are listed in Table II. In our chlorination studies *m*-trifluoromethylphenol was chlorinated with the intention of introducing three chlorine atoms, but the predominating product was 2,6-dichloro-3-trifluoromethylphenol melting at 54°. Along with this, another dichloride was formed in lesser amounts for, though we were not then able to isolate the pure dichloride, it was possible to prepare a pure *p*-nitrobenzyl ether from the uncrystallized fraction of the chlorination product. In order to establish the structures of these materials, the two monochlorides described above were further chlorinated. When 4-chloro-3-trifluoromethylphenol was chlorinated, a mixture resulted. From this mixture 2,4-dichloro-3-trifluoromethylphenol, m.p. 33–34°, was obtained; the *p*-nitrobenzyl ether of this corresponded to that obtained from the uncrystallizable residue described above.

When 2-chloro-5-trifluoromethylphenol was chlorinated, chlorination proceeded with much greater difficulty. 2,6 - Dichloro - 3 - trifluoromethylphenol was isolated.

The structures of these dichlorides were established by the sulfuric acid hydrolytic procedure of Le Fave.[4] Hydrolysis of the 54° isomer gave 2,4-dichloro-3-hydroxybenzoic acid. This was shown by making the methyl ether which melted at 162–163° as reported in the literature.[5] The 33–34° isomer, on hydrolysis, gave 2,6-dichloro-3-hydroxybenzoic acid. This as well as its methyl ether were compared with authentic samples prepared as de-

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[1] F. Swarts, *Bull. classe sci., Acad. roy. Belg.*, 241 (1913), *Chem. Zentr.*, **84**, II, 760 (1913).

[2] This work was undertaken at the suggestion of Dr. C. M. Suter and Dr. E. J. Lawson.

[3] A. L. Henne and M. S. Newman, THIS JOURNAL, **60**, 1697 (1938).

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