TABLE II

BORON FLUORIDE ALKYLATION OF BENZENE WITH DEUTERATED ALCOHOLS

Alcohol	Wt. in 100 g. of benzene, g.	Reaction conditions	Infrared spectrum of product alkylate,[a] μ
2-Butanol-*d*	10	0°, 1 hr.	No deuterium
2-Pentanol-*d*	8.5	61°, 2.5 hr.	4.6(m)[b]
1-Propanol-*d*	7	61°, 24 hr.	4.43(w)[c]
1-Butanol-*d*	7	61°, 68 hr.	4.4(w),[c] 4.6(m)[b]
1-Pentanol-*d*	8	61°, 68 hr.	4.4(w),[c] 4.6(m)[b]
1-Pentanol-*d*	10	61°, 20 hr.[d]	4.6(s),[c] 4.6(s)[c]

[a] w, weak; m, medium; s, strong intensity. [b] Side chain C–D. [c] Ring C–D. [d] Mixture was wet with several drops of D_2O. Some unreacted alcohol was recovered from this run which had an infrared spectrum identical with 1-pentanol.

Alkylations with Deuterated Alcohols.—The hydroxy hydrogen of several alcohols was largely replaced either by two exchanges with deuterium oxide or by treatment of the sodium alkoxide with deuterium oxide. The infrared spectra showed that the alcohols used were 75–90% deuterated. In all but one case the solution of the alcohol in benzene was saturated with boron fluoride at 0°, maintained at the appropriate temperature for a given length of time and worked up in the usual way. The alkylate products were examined for deuterium in the infrared. For the case of 2-pentanol-*d* at 61°, the solution of alcohol in heptane was saturated with boron fluoride and added dropwise and with stirring to benzene maintained at 61°. The results are summarized in Table II.

Alcohol-Boron Fluoride Complexes in Inert Media.—A solution of approximately 10% of the alcohol in the hydrocarbon was saturated with boron fluoride; with the secondary and tertiary alcohols the mixture was stirred in an ice-bath for an hour and worked up with aqueous sodium hydroxide in the usual way. In the primary cases, the dense complex was allowed to settle as a lower layer and the mixture was maintained in a constant temperature flask using hexane as the heating bath. The results are summarized in Table III.

TABLE III

STABILITY OF ALCOHOL–BORON FLUORIDE COMPLEXES

Alcohol	Medium	Reaction conditions	Result
2-Pentanol	Pentane	0°, 1 hr.	No reaction[a]
t-Amyl alcohol	Heptane	0°, 1 hr.	Complete reaction[b]
3-Methyl-2-butanol	Heptane	0°, 1 hr.	Complete reaction[b,c]
1-Pentanol	Hexane	65°, 3 days	Almost complete reacn.[d]
1-Pentanol[e]	Hexane	65°, 3 days	Almost complete reacn.[d]

[a] No rearrangement to 3-pentanol evident in the infrared spectrum. [b] No recovered alcohol apparent in the infrared. [c] Solution after normal work-up gave positive tests for olefin. [d] Infrared showed traces of unreacted alcohol. Product was mostly a non-volatile oil. [e] One milliliter of water was added.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MICHIGAN]

γ-Ray Initiated Reactions. III. Aldehyde Reactions Affected by Carbon Tetrachloride

BY EL-AHMADI I. HEIBA[1] AND LEIGH C. ANDERSON

RECEIVED AUGUST 13, 1958

Under the influence of γ-rays, *n*-aliphatic aldehydes undergo hydrogen-chlorine exchange with excess of carbon tetrachloride yielding the corresponding acyl chlorides. When carbon tetrachloride concentration was decreased, self condensation of the aldehydes took place and the best yield of the corresponding dehydrated aldol was obtained when carbon tetrachloride concentration was kept at one-fifth mole per mole of aldehyde. The aldol type of condensation with reactive methylenic compounds was found to be general when aliphatic or aromatic aldehydes were used. The yield of the reaction was found to be affected by the dose rate and by the substituents in the aromatic aldehydes. A proposed mechanism is discussed.

Winstein and Seubold[2] have reported that carbon tetrachloride inhibited the decarbonylation of isovaleraldehyde and β-phenylisovaleraldehyde when methyl radicals derived from the thermal decomposition of di(*t*-butyl) peroxide were used as initiators. The formation of the corresponding acid chloride was suggested to be due to a chain reaction propagated by steps 2 and 3.

$$\dot{C}H_3 + R\overset{H}{C}{=}O \longrightarrow R\dot{C}O + CH_4 \qquad (1)$$

$$R\dot{C}O + ClCCl_3 \longrightarrow RCOCl + \cdot CCl_3 \qquad (2)$$

$$RCHO + \dot{C}Cl_3 \longrightarrow R\dot{C}O + HCCl_3 \qquad (3)$$

In the present investigation it has been found that these reactions are general when γ-rays are used as the chain initiator. When *n*-aliphatic aldehydes (1 mole) in solution in carbon tetrachloride (6 moles) under a dry nitrogen atmosphere were irradiated, a significant amount of ionizable chlorine resulted and the acid chloride in the form of its acid was separated in a yield of 10 to 20%. The isolation of hexachlorethane from the reaction product indicates the formation of trichloromethyl radicals during the radiation; hexachloroethane was not found in the absence of aldehydes.

At low concentration of carbon tetrachloride the formation of acid chlorides diminished and self condensation of the aliphatic aldehydes took place. The maximum yield of the corresponding aldol type of condensation was obtained when carbon tetrachloride was present at 0.2 or 0.1 molar ratio of the aldehyde used. Under these latter conditions the crotonization of aliphatic aldehydes and the alkylations of reactive methylenic compounds ($R'CH_2$.-COR'') with aromatic aldehydes took place readily. None of these condensations was effected by γ-radiation in the absence of carbon tetrachloride.

Irradiation of aliphatic aldehydes alone or even in the presence of water[3] did not produce any condensation products. The aldol type of condensation under the influence of γ-rays and in the presence of carbon tetrachloride was not due to the presence of hydrochloric acid that might be

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(1) Post-Doctoral Fellow under Michigan Memorial Phoenix Project No. 98 given by the Chrysler Corporation.

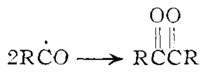
(2) S. Winstein and F. H. Seubold, THIS JOURNAL, **69**, 2916 (1947).

(3) Compare Y. Hirshberg and L. Farkas, *ibid.*, **59**, 2453 (1937).

formed during irradiation. Irradiation of a reaction mixture containing two moles of triethylamine for each mole of ionizable chlorine formed in reactions carried out in the absence of triethylamine, gave the same condensation products with the same yields. On the other hand, the latter reaction mixture did not yield any condensation without irradiation even when triethylamine was added in the form of its hydrochloric acid salt.

Exclusion of an acid- or base-catalyzed mechanism for the aldol type condensation suggests that the condensation cannot be explained by the mechanism proposed by Lapworth,[4] by Arndt and Eistert or by Hauser and co-workers.[5] The aldol type of condensation reactions was found to be retarded by the presence of quinones (*e.g.*, 9,10-phenanthraquinone) and to be dependent on the radiation dose and the concentration of the aldehyde used —factors that determine the rate of production and the concentration of free radicals.[6]

The presence of hexachloroethane in the irradiated mixtures of aldehydes and excess of carbon tetrachloride as shown by its isolation indicates that the trichloromethyl radical is probably responsible for the propagation of the chain which leads to production of the $R\dot{C}O$ radicals (step 3). At low concentration of carbon tetrachloride and at low temperatures the $R\dot{C}O$ radicals may be removed by combination[7] (step 4) rather than decarbonylation[8] (step 5) or they could abstract a hydrogen

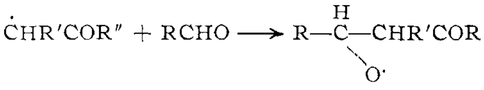
 (4)

$$2R\dot{C}O \longrightarrow R\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}R \qquad (4)$$

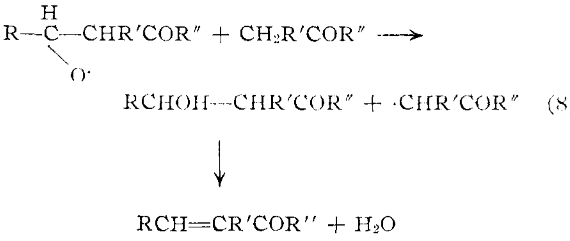
$$R\dot{C}O \longrightarrow \dot{R} + CO \qquad (5)$$

atom from the reactive methylene compound. The carbonyl group α-carbon hydrogen bond in the reactive methylene compound could be a preferential point of attack for the $R\dot{C}O$ radical (step 6) due to its electron acceptance in the transition state.[9] Thus if the resulting $\cdot CHR'COR''$ radical could propagate a chain, then a chain reaction mechanism for the aldol type of condensation occurring under the conditions used in this work might be formulated as

$$R\dot{C}O + CH_2R'COR'' \longrightarrow RCHO + \cdot CHR'COR'' \qquad (6)$$

 (7)

$$\dot{C}HR'COR'' + RCHO \longrightarrow R-\overset{H}{\underset{O\cdot}{C}}-CHR'COR'' \qquad (7)$$

 (8)

$$R-\overset{H}{\underset{O\cdot}{C}}-CHR'COR'' + CH_2R'COR'' \longrightarrow RCHOH-CHR'COR'' + \cdot CHR'COR'' \qquad (8)$$

$$\downarrow$$

$$RCH{=}CR'COR'' + H_2O$$

Such a sequence of reactions could be argued for the following reasons. 1. The $\cdot CHR'COR''$ radical should have resonance stability[10] and thus could be removed by radical combination rather than propagating a chain as in steps 6, 7 and 8. 2. Soliman[11] reported that a radical of this structure was obtained by sunlight irradiation of desoxybenzoin and was removed as its dimer, didesyl. In our presenti nvestigation we were unable to isolate didesyl by irradiating desoxybenzoin with benzaldehyde and the only isolated product was that from the corresponding aldol type of condensation. Such a result indicates that the presence of the R'–$\dot{C}HCOR''$ radical ($R' = R'' = C_6H_5$) in our reaction mixture is doubtful.

On the other hand, 4,4,4-triphenylbutan-2-one with benzaldehyde gave a good yield of the corresponding aldol type of condensation without the formation of other products which might have been produced by the migration of a phenyl group as was reported in similar radicals.[12]

In the presence of excess of aldehyde molecules which have an oxidizing character,[13] the $R\dot{C}O$ radicals due to their electron-donating properties could be complexed with the aldehyde molecules through an electron transfer. The possibility of free radical–molecule complexes has been considered,[14] and if one allows comparison with the behavior of hydrocarbonyl complex,[15] then the electron of the $R\dot{C}O$ radical in the $R\dot{C}O$–aldehyde molecule complex would tend to rest on the carbonyl oxygen of the aldehyde molecule. The resulting complex could abstract a proton from the reactive methylenic compound ($R'CH_2COR''$) if the hydrogen of the methylene group is brought into the vicinity of the negatively charged oxygen atom of the aldehyde molecule in the complex.

The behavior of the $R\dot{C}O$-aldehyde molecule complex in producing an anion may be considered as analogous to the behavior of the complex between a basic reagent and an aldehyde molecule that was proposed[16] to catalyze the aldol type of condensation. If the aldol type of condensation proceeded in this way the steps could be written as

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(4) A. Lapworth, *J. Chem. Soc.*, **79**, 1269 (1901); A. C. O. Hann and A. Lapworth, *ibid.*, **85**, 46 (1904).

(5) F. Arndt and B. Eistert, *Ber.*, **69**, 2381 (1936); C. R. Hauser and W. B. Renfrow, This Journal, **59**, 1823 (1937); **60**, 463 (1938); C. R. Hauser and D. S. Breslow, *ibid.*, **62**, 2389 (1940); see also H. R. Snyder, H. A. Kornberg and J. R. Romig, *ibid.*, **61**, 3556 (1939).

(6) W. A. Waters, *Trans. Faraday Soc.*, **37**, 775 (1941).

(7) M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

(8) E. F. P. Harris and W. A. Waters, *Nature*, **170**, 212 (1952).

(9) M. S. Kharasch, E. V. Jensen and W. H. Urry, This Journal, **69**, 1100 (1947); H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **28**, 333 (1936); A. B. Ash and H. C. Brown, *Record. Chem. Progress (Kresge–Hooker Sci. Lib.)*, **9**, 81 (1948).

(10) D. H. Volman and R. K. Brinton, *J. Chem. Phys.*, **22**, 929 (1954).

(11) J. Kenyon, A. Abdel Rassaul and G. Soliman, *J. Chem. Soc.*, 1774 (1956).

(12) D. Y. Curtin and M. J. Hurwitz, This Journal, **74**, 5381 (1952).

(13) J. Weiss, *Trans. Faraday Soc.*, **37**, 782 (1941).

(14) G. A. Russell and H. C. Brown, This Journal, **77**, 4031 (1955); G. A. Russell, *ibid.*, **79**, 2977 (1957); F. R. Mayo, *ibid.*, **76**, 5392 (1954); G. S. Hammond, C. E. Boozer, G. E. Hamilton and J. N. Sen, *ibid.*, **77**, 3238 (1955); M. T. Jaquiss and M. Szwarc, *Nature*, **170**, 312 (1952).

(15) J. Weiss, *J. Chem. Soc.*, 245 (1942).

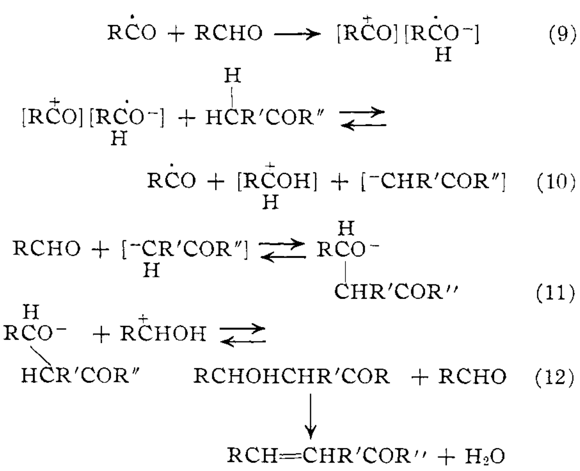
(16) H. B. Watson, *Trans. Faraday Soc.*, **37**, 711 (1941).

TABLE I

CONDENSATION OF ALDEHYDES WITH CERTAIN ACTIVE HYDROGEN COMPOUNDS

Aldehyde	Reactive methylenic component	Products isolated	B.p. °C.	B.p. Mm.	M.p., °C.	Conversion,[a] %
Benzaldehyde	Methyl ethyl ketone	2-Methyl-1-phenylbut-1-ene-3-one[b]	130	12	38.9	20.6
Benzaldehyde	Desoxybenzoin	(*cis* and *trans*)-1,2-Diphenyl-1-benzoylethylene[c]	110–115	0.05	90–91 100–101	28
Benzaldehyde	Phenylpropanone-2	3,4-Diphenylbut-3-ene-2-one[d]	145–147	15	57.8	36
Benzaldehyde	Phenyl ethyl ketone	3-Benzylidenepropiophenone-2[e]	122–127	0.1		11.7
Anisaldehyde	Methyl ethyl ketone	α-Methyl anisylideneacetone			29	32
Benzaldehyde	Cyclohexanone	Dibenzylidenecyclohexanone			124	47
Benzaldehyde	Butanal	(i) 2-Ethyl-2-hexenal[f]	61–62	12		
		(ii) 2-Ethylcinnamaldehyde[g]	72–74	0.2	18	34
Butanal	Butanal	2-Ethylhexenal	61–62	12		86
Acetaldehyde	Butanal	(i) 2-Ethyl-2-butenal[h]	38–41	18		28
		(ii) 2-Ethylhexenal	61–62	12		
Acetaldehyde	Methyl ethyl ketone	(i) 3-Methylpent-2-ene-4-one[i]	138–140			32
		(ii) Polymer of acetaldehyde[j]				
Isovaleraldehyde	Isovaleraldehyde	(i) 2-Isopropyl-5-methyl-2-hexenal[k]	78	10		27
		(ii) Polymer of isovaleraldehyde[l]	115–135	0.5		
Benzaldehyde	Diethyl malonate	Diethyl benzylidenemalonate[m]	168–170	5		12

[a] Based upon aldehyde used. [b] Oxime, m.p. found 109–110°; C. Harries and G. H. Müller, *Ber.*, **35**, 970 (1902), reported m.p. 103–104°. The semicarbazone m.p. found 215° dec.; C. U. Gheorghiu and B. Arwentiew, *Ann. Sci. Univ. Jassy*, **16** 536 (1931), reported m.p. 204°. *Anal.* Calcd. for $C_{12}H_{15}N_3O$: C, 66.36; H, 6.91; N, 19.35. Found: C, 66.48; H, 6.97; N, 19.48. [c] Sublimation of the residual oil followed by fractional crystallization from petroleum ether–ethanol the two isomers were separated and both gave oxime m.p. 208–209° (Von I. Thiele and P. Ruggle, *Ann.*, **393,** 71 (1912)). [d] The yield of the condensation product was 64% when 0.75 mole of benzaldehyde was used. [e] The compound gave a semicarbazone, prisms from ethanol, m.p. 202–204°. *Anal.* Calcd. for $C_{17}H_{17}N_3O$: N, 15.05. Found: N, 14.95; *cf.* R. C. Abell, *J. Chem. Soc.*, **79,** 929 (1901). [f] Semicarbazone, m.p. 154°; compare L. K. Evans and A. E. Gilman, *ibid.*, 565 (1943). [g] The yield should not be considered as a comparable figure due to self condensation of butanal. The 2-ethylcinnamaldehyde gave a 2,4-dinitrophenylhydrazone as dark red prisms from glacial acetic acid, m.p. 199–200°. [h] *Cf.* E. E. Royals and K. C. Brannock, THIS JOURNAL, **76,** 1180 (1954). [i] The semicarbazone prisms from ethanol, m.p. found 199–200°; G. E. Hennion, R. B. Davies and D. E. Maloney, THIS JOURNAL, **71,** 2813 (1949), reported m.p. 190–191°. [j] Acidic solution of 2,4-dinitrophenylhydrazine sulfate gave the hydrazone derivative of acetaldehyde. [k] *Cf.* P. Schorigin, W. Issaguljanz and A. Bussewa, *Ber.*, **66B,** 1431 (1933). [l] The polymer gave with an acidic solution of 2,4-dinitrophenylhydrazine sulfate the hydrazone derivative of isovaleraldehyde. [m] The diethyl ester was refluxed for 24 hours in 48% hydrobromic acid and when the solution was cooled it gave an acid m.p. and mixed m.p. with cinnamic acid 132–134°.



$$R\dot{C}O + RCHO \longrightarrow [R\overset{+}{C}O][R\underset{H}{\dot{C}}O^-] \qquad (9)$$

$$[R\overset{+}{C}O][R\underset{H}{\dot{C}}O^-] + H\overset{\substack{H\\|}}{C}R'COR'' \rightleftarrows R\dot{C}O + [R\underset{H}{\overset{+}{C}}OH] + [^-CHR'COR''] \qquad (10)$$

$$RCHO + [^-\underset{H}{C}R'COR''] \rightleftarrows R\underset{\substack{|\\CHR'COR''}}{\overset{H}{C}}O^- \qquad (11)$$

$$R\underset{\substack{\diagdown\\HCR'COR''}}{\overset{H}{C}}O^- + R\overset{+}{C}HOH \rightleftarrows RCHOHCHR'COR + RCHO \qquad (12)$$

$$\downarrow$$

$$RCH{=}CHR'COR'' + H_2O$$

Experimental[17]

In a typical experimental run, 0.25 mole of the aldehyde, 0.25 mole of the reactive methylene component and 0.05 mole of carbon tetrachloride were mixed in a tube. A dry stream of nitrogen was allowed to bubble through the solution for 0.5 hour to free it from oxygen and the tube was then sealed. After being irradiated for 65 hours at a rate of 100,000 REP. per hour at room temperature the tube was opened and the unreacted materials were removed by distillation or by fractional crystallization if they were solids. The residual products were separated, purified and characterized by comparison with authentic samples.

The Preparation of 4,4,4-Triphenylbutan-2-one.—A cold solution of cadmium dimethyl prepared from magnesium (9 g.), excess of methyl iodide and anhydrous cadmium dichloride (35 g.) was mixed into a 100-ml. dry benzene solution of α,α,α-triphenylpropionyl chloride (47 g.) prepared by the method of Hellerman.[18] The reaction mixture was refluxed for one hour, and was then cooled, decomposed with dilute hydrochloric acid and extracted with ether. The ethereal extract was washed several times with 5% aqueous sodium hydroxide to free it from acid, dried, evaporated to a small volume and cooled. Colorless prisms (7.2 g.), m.p. 139–140°, crystallized. After recrystallization from ether, 4,4,4-triphenylbutan-2-one melted at 141°. This ketone had been prepared previously by two different methods.[19] Evaporation of ether from the mother liquor left 11.2 g. of an unidentified viscous oily material.

Condensation of Benzaldehyde with 4,4,4-Triphenylbutan-2-one.—4,4,4-Triphenylbutan-2-one (4 g.), benzaldehyde (6 g.) and carbon tetrachloride (0.8 g.) were irradiated for 88 hours. The excess of benzaldehyde was removed by distillation and the residual solid crystallized from ethanol to give colorless needles (3 g.), m.p. 155–156°. The substance did not depress the melting point when mixed with the compound prepared from the condensation of 4,4,4-triphenylbutan-2-one and benzaldehyde in 50% sulfuric acid in acetic acid solution. The condensation product, which is probably 4-phenyl-3-triphenylmethyl-3-buten-2-one, has an ultraviolet absorption spectrum maximum at λ295 mμ, $\Sigma_{\max}$ 22,200. *Anal.* Calcd. for $C_{29}H_{24}O$: C, 89.69; H, 6.2. Found: C, 89.49; H, 6.45.

Reaction of Butanal with Excess of Carbon Tetrachloride.—Butanal (24 g.), dried over anhydrous sodium sulfate and freshly distilled through a 3-foot packed column, was mixed in a tube with reagent grade carbon tetrachloride (336 g.). The air was displaced by dry nitrogen and the tube irradi-

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[17] All melting points and boiling points are uncorrected. All microanalyses were done by Spang Microanalytical Laboratory, Ann Arbor, Mich.

[18] L. Hellerman, THIS JOURNAL, **49,** 1735 (1927).

[19] R. L. Garner and L. Hellerman, *ibid.*, **68,** 824 (1946); J. B. Conant and H. W. Scherp, *ibid.*, **53,** 1943 (1931).

ated at 100,000 REP. per hour for 65 hours. Due to the difficulty of isolating butyryl chloride and to avoid heating, the reaction mixture was shaken with ether and extracted with dilute aqueous sodium bicarbonate solution. The alkaline extract was acidified with dilute hydrochloric acid, ether extracted and dried. Evaporation of the ether and distillation of the residue gave a colorless oil (5.6 g.), b.p. 159–161°, $n^{20}\mathrm{D}$ 1.3390. The acid gave an anilide, m.p. 96°, that did not depress the melting point of butyranilide. The neutral fraction was dried over anhydrous sodium sulfate and distilled to give butanal and carbon tetrachloride. The residual oil (2.3 g.) on standing liberated hexachloroethane (300 mg.), m.p. 198°, and the oil was shown to be a polymer of butanal.

Analysis of the irradiation product of one of the runs using benzaldehyde (0.4 mole), butanone-2 (0.4 mole) and carbon tetrachloride (0.04 mole) indicated the presence of 8×10^{-4} mole of chloride ion. Assuming that this chloride ion might be present as hydrogen chloride and thus be responsible for an acid-catalyzed system, a run was made using the above concentrations of reagents plus 1.6×10^{-3} mole of trimethylamine. The same condensation products were obtained with the same yields.

ANN ARBOR, MICH.

[CONTRIBUTION NO. 493 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Syntheses by Free-radical Reactions. IX. Use of Free Radicals from Flames

BY C. S. CLEAVER, L. G. BLOSSER AND D. D. COFFMAN

RECEIVED SEPTEMBER 9, 1958

The free radicals which propagate flames have been used by a novel technique to bring about organic syntheses. The technique involved rapidly passing a stream of aqueous organic reactant through the inner cone of a flame. In this manner, various flames converted aqueous acetic acid to glycolic acid nitrate, succinic, glycolic, hydroperoxyacetic, and chloroacetic acids. These products provided evidence for the abstraction from the flames of nitric oxide and the hydroxyl, hydroperoxy and chlorine-free radicals to effect syntheses. Similar transformations occurred when solutions of pivalic acid, propionic acid, *t*-butylamine and *t*-butyl alcohol were passed through flames.

A novel technique has been devised by means of which the propagating free radicals of flames have been used stoichiometrically to bring about organic syntheses. Flames with temperatures in excess of 800° were employed. The technique involved rapidly passing normal to the flame path, but through or near to the inner cone of the flame (see Fig. 1) an aqueous stream containing in solution an organic reactant. The aqueous stream apparently behaved as a cold wall of solvent which continuously extracted from the flame the free radicals which then reacted with the organic solute.

Synthesis in Flames.—The products isolated after an aqueous solution of an organic reactant had been passed through the inner cone of a methane-oxygen or hydrogen–oxygen flame are listed in Table I. *t*-Butyl alcohol and *t*-butylamine gave $\alpha,\alpha,\alpha'\alpha'$-tetramethyltetramethylene glycol and $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylenediamine, respectively, the products from dehydrogenative coupling reactions. Pivalic acid and propionic acid gave $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid and C_6-dibasic acids, respectively, also by the coupling reaction. Other products from pivalic and propionic acids included the hydroxy and hydroperoxy derivatives. Acetic acid gave exactly analogous products; namely, succinic acid, glycolic acid and hydroperoxyacetic acid. Acetaldehyde and other carbonyl products were formed in minor quantities. Hydrogen peroxide was identified as a product after passage of either water or aqueous acetic acid through a flame.

The formation of the coupled products can be accounted for in terms of the chemistry of hydroxyl radicals which are known to propagate flames[1] and which evidently attacked the organic reactant during passage through the flame. Thus, $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylenediamine from *t*-butylamine, $\alpha,\alpha,\alpha',\alpha'$-tetramethyltetramethylene glycol from *t*-butyl alcohol, $\alpha,\alpha,\alpha',\alpha'$-tetramethyladipic acid from pivalic acid, C_6-dibasic acids from propionic acid, and succinic acid from acetic acid are products typical of the oxidative coupling effected

TABLE I

PRODUCTS FROM VARIOUS REACTANTS PASSED THROUGH A FLAME

Aqueous organic reactant	Products
t-Butyl alcohol (4%)[a]	$\alpha,\alpha,\alpha',\alpha'$-Tetramethyltetramethylene glycol[i] and resin
t-Butylamine sulfate (13%)[b]	$\alpha,\alpha,\alpha',\alpha'$-Tetramethyltetramethylenediamine[j] 2,2,5,5-Tetramethyldihydropyrazine[k] Unidentified materials containing oxygen and nitrogen
Sodium pivalate (25%)[b]	$\alpha,\alpha,\alpha',\alpha'$-Tetramethyladipic acid[c] Hydroperoxypivalic acid[d] Hydroxypivalic acid[e]
Propionic acid (2%)[a]	C_6-Dibasic acids[f] α- and β-Hydroperoxypropionic acids[g] Lactic and hydracrylic acids[h]
Acetic acid (2%)[a]	Succinic acid[l] Glycolic acid[l] Hydroperoxyacetic acid[l] Hydrogen peroxide[m]

[a] H_2/O_2 flame (1:1). [b] CH_4/O_2 flame (1:2). [c] Identified by m.p., mixed m.p., compositional analyses, neut equiv. [d] Identified by reduction to hydroxypivalic acid, peroxide test. [e] Identified by m.p., mixed m.p., C + H analyses, neut. equiv. [f] Probable mixture of adipic, α,α'-dimethylsuccinic and α-methylglutaric acids; identified by comparison of peak elution volumes. [g] Identified by peroxide test. [h] Identified by comparison of peak elution volumes. [i] Identified by X-ray diffraction pattern comparison with authentic material. [j] Identified by C + H analysis, b.p., neut. equiv. [k] Identified by C + H analyses, m.p. [l] See Experimental section for method of identification. [m] Identified by titration with permanganate, ceric, and by iodometric techniques.

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(1) B. Lewis and G. von Elbe, "Combustion, Flames, and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951.