

## Perhalo Ketones. VIII. Hydrolysis of Mono- and Bis(2-hydroxyhexahalo-2-propyl)arenes to Carboxylic Acids

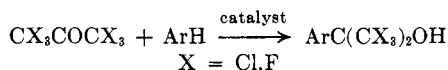
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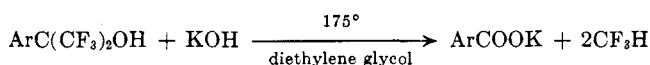
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Thirty-three aromatic compounds, mono- or disubstituted by the C(CX<sub>3</sub>)<sub>2</sub>OH moiety (X = Cl, F), were converted to the corresponding carboxylic acids in generally good to excellent yields at 175° with excess potassium hydroxide in diethylene glycol. The reaction is shown to proceed by slow initial conversation to ArCOCF<sub>3</sub>, followed by rapid cleavage to the acid.

The synthesis in high yields of a series of mono- and bis(2-hydroxyhexahalo-2-propyl)arenes by the interaction of perhalogenated acetones with various types of aromatic compounds in the presence of acid catalysts was reported by the present authors.<sup>2</sup> A simple and



general hydrolytic procedure has now been developed for converting these tertiary alcohols to the corresponding acids. The method, which involves heating at reflux (*ca.* 175°) the halo alcohol with a large excess of potassium hydroxide in diethylene glycol, works best with the hexafluoro compounds. The reaction proceeds



to completion in about 1–3 hr. to yield, upon acidification, the desired mono- or dicarboxylic acid and 2 equiv. of fluoroform almost quantitatively. The method was developed in order to establish the positions of the entering 2-hydroxyhexahalo-2-propyl moieties with respect to substituents already present on the aromatic nuclei. However, the versatility of this procedure, as shown in Tables I–III, taken with the ease of preparation of the starting carbinols from hexafluoroacetone,<sup>2</sup> suggests this approach as a possibly practical one for preparing certain aromatic acids. Since the presence of substituents resistant to alkaline hydrolysis does not hinder the progress of the desired reaction, it is thus possible to prepare aryl mono- and dicarboxylic acids containing alkyl, halo, hydroxy, amino, or methoxy substituents on the aromatic nuclei.

The hydrolysis apparently proceeds in two stages through the intermediacy of an aryl trifluoromethyl ketone, which then undergoes the fluoroform reaction

TABLE I  
HYDROLYSIS OF ArC(CF<sub>2</sub>Cl)<sub>2</sub>OH

Acid produced	% yield	Obsd. m.p., °C.	Lit. <sup>a</sup> m.p., °C.
Salicylic	58	158–160	159
2-Hydroxy-5-methylbenzoic	36	153–154	153
3,5-Dimethyl-4-hydroxybenzoic	3	220–221	222–224 <sup>b</sup>

<sup>a</sup> Except when otherwise noted, literature values in Tables I and II are taken from I. M. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1936. <sup>b</sup> M. S. Neuman and H. L. Gildenhorn, *J. Am. Chem. Soc.*, **70**, 317 (1948).

TABLE II  
HYDROLYSIS OF ArC(CF<sub>3</sub>)<sub>2</sub>OH

Acid produced	% yield	Obsd. m.p., °C.	Lit. <sup>a</sup> m.p., °C.
Benzoic	85	122	122
<i>p</i> -Toluic	85	178	181
3,4-Xylic	30	166–167	166
2,4-Xylic	87	125–126	126–127
2,5-Xylic	89	131–132	132
4-Chlorobenzoic	82	240–242	242
3-Chloro-4-methylbenzoic	41	206	199
2-Chloro-4-methylbenzoic	40	155	155–156
2-Methyl-5-chlorobenzoic	82	168	169
$\alpha$ -Naphthoic	82	160	161
<i>p</i> -Anisic	91	184	184
Salicylic	87	158–160	159
<i>p</i> -Hydroxybenzoic	6	212–214	213–214
<i>p</i> -Aminobenzoic	80	184–186	186–187
4-Amino-3-methylbenzoic	63	169–170	169
4-Amino-2-methylbenzoic	73	176–177	165
2-Amino-5-methylbenzoic	70	172–174	175
4-Amino-3,5-dimethylbenzoic	53	252–254	242
<i>p</i> -Dimethylaminobenzoic	61	235–237	233
4-Amino-3-hydroxybenzoic	59	213–215	216–217 <sup>b</sup>
4-Amino-3-methoxybenzoic	60	186–187	185–186 <sup>c</sup>
1-Amino-2-naphthoic	64	202–203	205

<sup>a</sup> See footnote a, Table I. <sup>b</sup> E. Boyland and P. Sims, *J. Chem. Soc.*, 980 (1954). <sup>c</sup> V. Froelicher and J. B. Cohen, *ibid.*, 119, 1425 (1920).

TABLE III  
HYDROLYSIS OF Ar[C(CF<sub>3</sub>)<sub>2</sub>OH]<sub>2</sub>

Acid produced	% yield	Obsd. m.p., °C.	Lit. m.p., °C.
Isophthalic	91	345–346	345–347 <sup>a</sup>
Terephthalic	88	...	Subl. <sup>b</sup>
4-Methylisophthalic	80	325	330–332 <sup>c</sup>
4,6-Dimethylisophthalic	80	352	355 <sup>d</sup>
2,5-Dimethylterephthalic	73	335 (subl.)	340–350 <sup>e</sup> (subl.)
4,5-Dimethylisophthalic	87	330	320 <sup>f</sup> (subl.)
4,4'-Dicarboxydiphenyl ether	89	312	>285 <sup>g</sup>
4,4'-Dicarboxydiphenyl sulfide	86	325	<i>ca.</i> 315 <sup>h</sup>

<sup>a</sup> Ref. 2. <sup>b</sup> The product was further identified by comparison of its infrared spectrum with that of an authentic sample. <sup>c</sup> T. Wagner-Jauregg and E. Helmert, *Ber.*, **71B**, 2535 (1938). <sup>d</sup> R. Coffey, *Rec. trav. chim.*, **42**, 421 (1922). <sup>e</sup> M. Freund and K. Fleischer, *Ann.*, **414**, 42 (1916). <sup>f</sup> E. Schnapauff, *Ber.*, **19**, 2508 (1886). <sup>g</sup> O. V. Schick, *ibid.*, **69**, 242 (1936). <sup>h</sup> K. W. Rosenmund and H. Harms, *ibid.*, **53**, 2238 (1920).

very rapidly<sup>3</sup> compared with the initial alcohol. In actual experiments, I was recovered unchanged after refluxing 24 hr. with 10% aqueous KOH solution, while II underwent the haloform reaction immediately and

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(2) Perhalo Ketones. V: B. S. Farah, E. E. Gilbert, and J. P. Sibilias, *J. Org. Chem.*, **30**, 998 (1965); VI: E. E. Gilbert, E. S. Jones, and J. P. Sibilias, *ibid.*, **30**, 1001 (1965); VII: B. S. Farah, E. E. Gilbert, M. Litt, J. A. Otto, and J. P. Sibilias, *ibid.*, **30**, 1003 (1965).

(3) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," The Macmillan Co., New York, N. Y., 1962, p. 208.

