Preparation of $C_2H_5—O—CF_2CH_2F$. Reaction between $CF_2=CHF$ and ethanol was carried out according to the procedure given in Ref. 2(d). B.p. 33° (253 mm.); n_D^{25} 1.3145, d_4^{25} 1.118.

Anal. Calcd. for $C_4H_7F_3O$: C, 37.51; F, 44.50. Found: C, 37.72; F, 44.3.

Hydrolysis of $C_2H_5—O—CF_2CH_2F$ yielded $CFH_2COOC_2H_5$. B.p. 109° (629 mm.); n_D^{25} 1.3745, d_4^{25} 1.085. (Lit.[7] B.p. 117° at 760 mm.).

Preparation of $C_2H_5—O—CF_2CH_2Br$. Reaction between $CF_2=CHBr$ and ethanol was carried out according to the method given in ref. 2(a). B.p. 55–56° (104 mm.); n_D^{25} 1.3980, d_4^{25} 1.512.

Anal. Calcd. for $C_4H_7F_2BrO$: C, 25.40; Br, 42.3. Found: C, 25.26; Br, 42.12.

Hydrolysis of $C_2H_5—O—CF_2CH_2Br$ yielded $CH_2BrCOOC_2H_5$. B.p. 82° (55 mm.); n_D^{25} 1.4484, d_4^{25} 1.501. Lit.[8] d_{20}^{20} 1.5059; n_D^{13} 1.45420.

Preparation of $CH_3—O—CF_2CHFI$. Reaction between $CF_2Cl—CHFI$ and methanol was carried out according to the method given in ref. 2(b). B.p. 59° (107 mm.); n_D^{25} 1.4188, d_4^{25} 2.022.

Anal. Calcd. for $C_3H_4F_3IO$: C, 15.02; F, 23.75. Found: C, 15.12; F, 23.46.

Hydrolysis of $CH_3O—CF_2CHFI$ yielded CHFICOOH but no $CHFICOOCH_3$ m.p. 79.5°. The melting point of this acid has been variously reported as 74°[9] and 78.5–79°.[10]

Anal. Calcd. for $C_2H_2FIO_2$: C, 11.76; F, 9.31; I, 62.25. Found: C, 11.91; F, 9.51; I, 62.32.

Preparation of $C_2H_5—O—CF_2—CHFBr$. Reaction between $CF_2=CFBr$ and ethanol was carried out according to the method given in ref. 2(a). B.p. 62–62.5° (167 mm.); n_D^{25} 1.3710, d_4^{25} 1.571.

Anal. Calcd. for $C_4H_6BrF_3O$: C, 23.19; F, 27.53. Found: C, 23.30; F, 27.26.

Hydrolysis of $C_2H_5—O—CF_2CHFBr$ yielded $CHFBrCOOC_2H_5$. B.p. 98.5° (138 mm.), n_D^{25} 1.4248, d_4^{25} 1.565.

Anal. Calcd. for $C_4H_6BrFO_2$: C, 25.94; F, 10.27. Found: C, 26.24; F, 10.38.

Hydrolysis of $CHFBrCO_2C_2H_5$ with dilute HCl yielded the acid CHFBrCOOH, m.p. 51.5–52.5°, reported[9] 49°.

Anal. Calcd. for $C_2H_2BrFO_2$: C, 15.31; F, 12.11. Found: C, 15.45; F, 11.80.

Reaction between $CF_2Cl—CH_2I$ and MeOH. Twenty-five grams (0.11 mole) of $CF_2Cl—CH_2I$ and 25 ml. of methanol were placed in a 250 cc., three-neck flask equipped with a stirrer, dropping funnel, and reflux condenser. The reaction mixture was cooled to zero degrees, by means of an external bath, and a ten percent solution of potassium hydroxide dissolved in methanol was added dropwise with stirring. After a ten percent excess of the methanolic base had been added (total, 6.72 g. of potassium hydroxide dissolved in 70 ml. of methanol), the temperature of the reaction mixture was raised to reflux for 30 min., cooled to room temperature, poured into cold water, and the heavy ether layer separated. The crude, washed product was dried over anhydrous calcium sulfate and weighed 15.3 g. (62.2%). During the drying process the crude ether eliminated hydrogen fluoride and upon distillation at reduced pressure 5.96 g. (43.2%) of the ester, $CH_2ICO_2CH_3$, b.p. 90° (54 mm.), was isolated. n_D^{25} 1.5202, d_4^{25} 2.011. No $CH_3—OCF_2CH_2I$ was isolated.

Anal. Calcd. for $C_3H_5IO_2$: C, 18.02; H, 2.52; I, 63.50. Found: C, 18.24; H, 2.38; I, 63.71.

Attempted preparation of $CH_3—O—CF_2CH_3$. A 50 percent solution of sodium methoxide in anhydrous methanol was introduced into the Parr hydrogenation bomb, and the bomb was sealed and tested for leaks. When leak-free, the bomb was cooled to −80° C, evacuated with a water aspirator, and 64 g. (1.0 mole) of $CF_2=CH_2$ were forced into the bomb under pressure. The bomb was removed from the cooling bath, placed in the rocker, and allowed to warm slowly to room temperature with constant agitation for about 24 hours. No fluorinated ether was isolated.

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(7) J. C. Bacon, C. W. Bradley, E. I. Hoegberg, Paul Tarrant, and J. T. Cassady, *J. Am. Chem. Soc.*, **70**, 2653 (1948).

(8) W. H. Perkin, *J. Chem. Soc.*, **65**, 427 (1894).

(9) F. Swarts, *Mem. Couronnes Acad. Roy. Belg.*, **61**, 94 (1901); *Chem. Abstr.* II, 12 (1901).

(10) J. D. Park, R. J. Seffl, and J. R. Lacher, *J. Am. Chem. Soc.*, **78**, 59 (1956).

An Unequivocal Synthesis of 3-Chloro-9-Anthrone[1]

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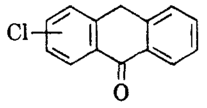
On reduction of 2-chloroanthraquinone with tin and glacial acetic acid, Barnett and Mathews[2] isolated a pure compound, m.p. 156°, which they designated as 2 (or 3) - chloro-9-anthrone (I). Several years later, Barnett and Wiltshire[3] unequivocally prepared 2-chloro-9-anthrone, m.p. 155°. Since a melting point of a mixture of these two showed a depression, it was concluded that I was 3-chloro-9-anthrone. In addition to this, a mixture of the acetate of I, m.p. 146°, and 2-chloro-9-anthryl acetate, m.p. 143°, showed a depression in the melting point.



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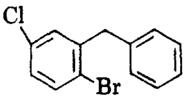

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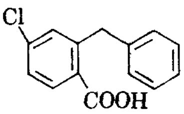
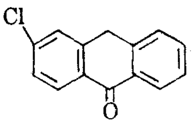


III



IV

Since some of bromide II was available,[4] an unequivocal synthesis of IV was undertaken. The Grignard reagent of II was prepared, carbonated, and the adduct decomposed to give acid III. Cyclization of this acid with concentrated sulfuric acid gave 3-chloro-9-anthrone (IV) m.p. 155–156°.[2] Acetylation of IV with pyridine and acetic anhydride yielded 3-chloro-9-anthryl acetate, m.p. 146–146.5°.[3]

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(1) This note has been abstracted from the Doctorate thesis of P. E. Newallis presented to the Virginia Polytechnic Institute in 1957.

(2) E. De Barry Barnett and M. A. Mathews, *J. Chem. Soc.*, **123**, 2549 (1923).

(3) E. De Barry Barnett and J. L. Wiltshire, *J. Chem. Soc.*, 1822 (1928).

(4) F. A. Vingiello, G. Buese, and P. E. Newallis, *J. Org. Chem.*, **23**, 1139 (1958).

The results obtained are tenable with those of Barnett and his coworkers.

EXPERIMENTAL

5-Chlorodiphenylmethane-2-carboxylic acid (III). A Grignard reagent was prepared under nitrogen from 8.0 g. (0.028 mole) of 2-bromo-5-chlorodiphenylmethane, 0.68 g. (0.028 mole) of magnesium, *ca.* 100 ml. of anhydrous ether and a crystal of iodine. After all of the magnesium had reacted, the reaction mixture was poured into a slurry of crushed Dry Ice and anhydrous ether. The ethereal solution was treated with dilute sodium hydroxide (trace of charcoal), cooled and filtered. The filtrate was acidified and the white precipitate was filtered. After drying in a desiccator overnight the solid had a melting range of 148–149°, 3.2 g. (46%). Recrystallization from ethanol gave an analytically pure sample, colorless rods, m.p. 149–151°.

Anal. Calcd. for $C_{14}H_{11}ClO_2$: C, 68.16; H, 4.50. Neut. Eq. 247. Found: C, 68.00; H, 4.47. Neut. Eq. 250.

3-Chloro-9-anthrone (IV). A mixture of 0.8 g. (0.00032 mole) of 5-chlorodiphenylmethane-2-carboxylic acid and 3 ml. of concentrated sulfuric acid was shaken vigorously and allowed to stand at room temperature for one hour. The mixture was poured into an ice-water mixture and a light yellow precipitate formed. This was filtered, washed with water, and recrystallized from ethanol yielding crystals which melted at 153–154°, 0.62 g. (83%). Further recrystallization from ethanol raised the melting point to 155–156° (Lit.,[2] m.p. 156°).

3-Chloro-9-anthryl acetate. A mixture of 0.4 g. (0.00018 mole) of 3-chloro-9-anthrone, 15 ml. of pyridine and 3 ml. of acetic anhydride was heated on a steam bath for 2 hr. under a nitrogen atmosphere. This was poured into an ice water mixture which gave a yellow powder which was filtered and recrystallized from ethanol. Fine yellow needles, 0.29 g. (42%) were obtained; m.p. 146–146.5° (Lit.,[3] m.p. 146°). The ethanolic solution displayed a strong blue fluorescence.

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An Ozonide of Cholestenone

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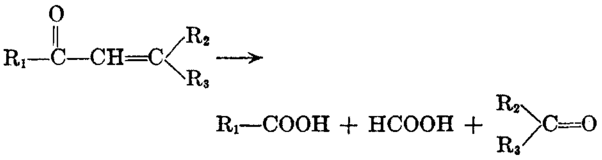
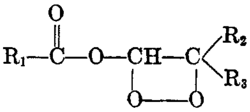
The ozonization of α,β-unsaturated carbonyl compounds occurs with what has been called an "abnormal" course, that is, both the olefinic bond and the adjacent single bond connecting the carbonyl group are cleaved.[1–4] It has been postulated that such a rearrangement occurs (1) through the formation of an abnormal ozonide (I),[1,2] (2) by rearrangement of the intermediate zwitter ion (II),[4] and (3) by abnormal cleavage of a normal ozonide (III) due to the electron release gained by O—H bond heterolysis.[5] In general, in the abnormal reaction, the product of the reaction of the unsaturated carbonyl compound with ozone is not isolated due to its instability.[1]



$$R_1-\overset{O}{\overset{\|}{C}}-CH=C\begin{matrix}R_2\\R_3\end{matrix} \longrightarrow R_1-COOH + HCOOH + \begin{matrix}R_2\\R_3\end{matrix}C=O$$



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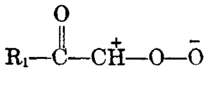

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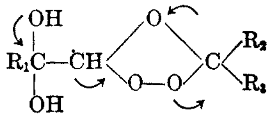
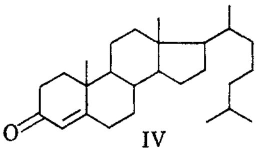
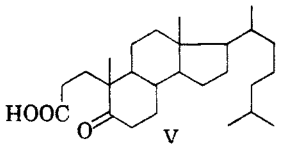


III

In the course of another investigation, the α,β-unsaturated ketone, cholestenone (IV), was ozonized at $-15°$ in a mixture of aqueous acetic acid and ethyl acetate in order to prepare the *seco-nor-keto* acid (V). By concentration of the reaction mixture a 55% yield of crystalline white solid was obtained and this material upon melting decomposed to yield the desired acid V. The composition of the initial product was that expected for the addition of one mole of ozone and one mole of water to the starting enone IV. The compound was peroxidic but not hydroperoxidic as shown by a positive test with potassium iodide and a negative test with lead tetraacetate.[6] The molecular weight was that for a monomer and the infrared spectrum possessed bands for hydroxyl groups but lacked band associated with carbonyl absorption. The material when stored in the dry was stable for many weeks but upon standing in air at room temperature gradually decomposed to give rise to the expected *seco-nor* acid V. Warming the material in benzene transformed it into the acid V and formic acid, demonstrating that it is an intermediate in the "abnormal" ozonization.



IV



V

Based upon the foregoing data, there are at least three structures for a monomeric ozonide derivable from the intermediate hydroxylhydroperoxide VII which would arise by the well-established hydration[4,7] of the zwitterion VI. These structures are

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[1] W. G. Young, A. C. McKinnis, I. D. Webb, and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 293 (1946).

[2] J. E. Leffler, *Chem. Revs.*, **45**, 385 (1949).

[3] J. Knights and E. S. Waight, *J. Chem. Soc.*, 2830 (1955).

[4] R. Criegee, *Record. Chem. Progr.*, **18**, 111 (1957).

[5] D. H. R. Barton and E. Seone, *J. Chem. Soc.*, 4150 (1956).

[6] R. Criegee, *Fortschr. Chem. Forsch.* **1**, 536 (1950).

[7] H. Lettre and A. Jahn, *Ann.*, **608**, 43 (1957).