75.8 g. Comparison of the infrared spectrum of this fraction with that of mixtures of known composition shows it to contain 43 ± 2% of the low-melting benzoyl derivative of II, 25 ± 5% of the high-melting derivative and 31 ± 2% of benzoylcyclopentadienylmanganese tricarbonyl.

Competitive Benzoylation of II and Anisole.—To a stirred solution containing 65.4 g. (0.3 mole) of II, 64.8 g. (0.6 mole) of anisole, 42.3 g. (0.3 mole) of benzoyl chloride in 400 ml. of carbon disulfide was added 52.2 g. (0.39 mole) of aluminum chloride. The addition required 90 min. and occasional cooling was required to maintain the temperature at 25°. After standing overnight, the mixture was subjected to the customary work-up. Fractional distillation through a Nester spinning band column yielded 22.9 g. of anisole; 60.1 g., 92%, of II; and 57.8 g., 90.8%, of *p*-methoxybenzophenone, m.p. 62.5–63.5° (lit.[22] 61–62°).

The *p*-methoxybenzophenone was further identified by hydrolysis to the *p*-hydroxy derivative, m.p. 133–134° (lit.[22] 135°).

Butylation of I.—Isobutylene (32 g., 0.57 mole) was bubbled slowly into a stirred mixture containing 102 g. (0.5 mole) of I, 13.3 g. (0.1 mole) of aluminum chloride and 350 ml. of carbon disulfide. In the course of the 6 hours required for the addition, the temperature rose to a maximum of 39°. The mixture was stirred overnight at room temperature then worked up in the usual manner.

Removal of the solvents and then fractional distillation through a small Nester spinning band column gave 60 g. of I and 49.6 g. of alkylated derivatives boiling above 143° at 29 mm. Three fractions were obtained (among others) which analyzed correctly for the mono-, di- and tributylated derivatives of I.

Mono-*t*-butyl, b.p. 150° at 28–29 mm., n^{20}_D 1.5600. *Anal.* Calcd. for $C_{12}H_{13}MnO_3$: C, 55.4; H, 5.0; Mn, 21.2. Found: C, 55.6; H, 5.13; Mn, 20.9.

Di-*t*-butyl, b.p. 164–168° at 10 mm., m.p. 70–71°. *Anal.* Calcd. for $C_{16}H_{21}MnO_3$: C, 60.8; H, 6.64; Mn, 17.4. Found: C, 60.9; H, 6.76; Mn, 17.2.

Tri-*t*-butyl, b.p. 160–163° at 3.5 mm., n^{20}_D 1.5326. *Anal.* Calcd. for $C_{20}H_{29}MnO_3$: C, 64.5; H, 7.80; Mn, 14.8. Found: C, 64.0; H, 7.54; Mn, 14.8.

Alkylation of I with Cyclohexyl Chloride.—Cyclohexyl chloride (23.6 g., 0.2 mole) was added dropwise over a one-hour period to a stirred mixture of 40.8 g. (0.2 mole) of I, 3.32 g. of aluminum trichloride and 150 ml. of carbon disulfide. The evolution of hydrogen chloride started almost immediately and the temperature rose slowly to 35°. When addition was complete the mixture was stirred for an additional hour, then chilled, hydrolyzed with cold dilute hydrochloric acid, extracted with ether, dried with sodium carbonate and the solvents removed by distillation. The residues were distilled at *ca.* 2 mm. through a small spinning band fractionating column to yield the fractions

Take-off temp., °C.	Wt., g.	Remarks
70	10	I
70–109	2.3	
109–110	7.5	
110–114	9.05	n^{20}_D 1.5686
114–149	2.4	
149–152	4.6	n^{20}_D 1.5804
152–160	2	n^{20}_D 1.5700

The fraction boiling at 110–114° analyzed well for the **monocyclohexyl** derivative.

Anal. Calcd. for $C_{14}H_{15}MnO_3$: C, 58.7; H, 5.24; Mn, 19.2. Found: C, 58.8; H, 5.17; Mn, 19.1.

The fraction boiling 149–152° analyzed for the **dicyclohexyl** compound.

Anal. Calcd. for $C_{20}H_{25}MnO_3$: C, 65.3; H, 6.8; Mn, 15.0. Found: C, 65.8; H, 6.87; Mn, 15.0.

Acknowledgment.—The authors wish to thank Mr. R. T. Lundquist of these laboratories for the determination of the ratio of isomers in the benzoylated products.

DETROIT MICH.

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[22] "Dictionary of Organic Compounds," Vol. II, Oxford University Press, New York, N. Y., p. 732.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Diaryliodonium Salts. XI. Salts Derived from Phenoxyacetic and β-Phenoxyethanesulfonic Acids[1,2]

BY F. MARSHALL BERINGER AND ROBERT A. FALK

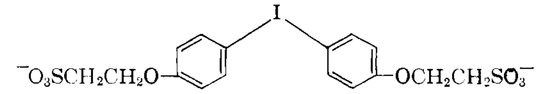
RECEIVED DECEMBER 9, 1958

β-Phenoxyethanesulfonyl chloride was condensed with phenyliodoso diacetate, and the product was hydrolyzed to the betaine $4\text{-}C_6H_5\overset{+}{I}C_6H_4OCH_2CH_2SO_3^-$. The same sulfonyl chloride with iodine(III) trifluoroacetate gave a product which was hydrolyzed and isolated as a barium salt, $Ba^{++}/_2 4,4'\text{-}\overset{+}{I}(C_6H_4OCH_2CH_2SO_3^-)_2$. As these materials do not contain the iodonium groups in a cation, their aqueous solutions do not give precipitates with halide ions. Symmetrical and unsymmetrical salts were similarly obtained from phenoxyacetic acid. The proofs of structures of all the iodonium salts rest on reactions with iodide ions to give 4-iodophenyl ethers, which were prepared independently.

In studies of the reactions of iodonium salts with nucleophiles in aqueous or largely aqueous solutions, it has been noticed that the appearance of

$$C_6H_5\overset{+}{I}C_6H_5 + \overset{-}{X} \longrightarrow C_6H_5X + C_6H_5I$$

a second phase of insoluble products caused an increase of rate.[3] One method of avoiding this heterogeneity, the use of organic solvents or cosolvents, has the limitation that the empirical kinetic order of the reaction may decrease from second toward first with decreasing solvent polarity.[3,4] A second method would be to have substituents on the iodonium cation such that the products would be water-soluble. One of the compounds here reported has an iodonium-containing anion which meets these requirements.



An additional useful property of such an anion is that it is not precipitated from solution by halide

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[1] Preceding paper, F. M. Beringer, E. M. Gindler, M. Rapoport and R. J. Taylor, THIS JOURNAL, **81**, 351 (1959).

[2] This paper is taken from the dissertation of Robert A. Falk, submitted in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[3] F. M. Beringer and E. M. Gindler, THIS JOURNAL, **77**, 3203 (1955); F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956).

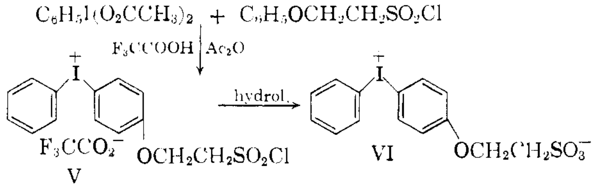
[4] F. M. Beringer and E. M. Gindler, THIS JOURNAL, **77**, 3200 (1955).

ions or other anions which usually give insoluble diphenyliodonium salts. It will thus be possible to study, for example, the kinetics of the reaction in water of iodide ion with an iodonium group.

β-Phenoxyethanesulfonic Acid Derivatives.—Because of the mild conditions under which anisole was converted to 4-methoxy- and 4,4′-dimethoxydiphenyliodonium salts,[5] it was decided that an alkyl phenyl ether bearing a sulfonic acid derivative in the alkyl group would be an appropriate starting material. In the following reaction sequence compounds II, III and IV have not been previously reported.

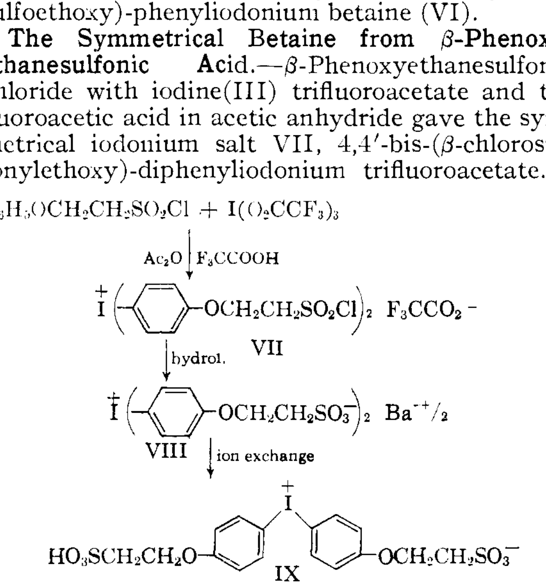
$$\begin{tikzcd} \underset{\text{I}}{C_6H_5OCH_2CH_2Cl} \arrow[r, "Na_2SO_3", "(43\%)"'] & \underset{\text{II}}{C_6H_5OCH_2CH_2SO_3Na} \arrow[d, "PCl_5"', "(60\%)"] \\ \underset{\text{IV}}{C_6H_5OCH_2CH_2SO_2NH_2} & \underset{\text{III}}{C_6H_5OCH_2CH_2SO_2Cl} \arrow[l, "NH_3"', "(\sim 100\%)"] \end{tikzcd}$$

The Unsymmetrical Betaine from β-Phenoxyethanesulfonic Acid.—It was found convenient to condense phenyliodoso diacetate with β-phenoxyethanesulfonyl chloride (III) in a mixture of trifluoroacetic acid and acetic anhydride, conditions under which anisole had proved reactive.[5]



Removal of solvent left a residue of iodonium salt V, which in turn was hydrolyzed to phenyl-4-(β-sulfoethoxy)-phenyliodonium betaine (VI).

The Symmetrical Betaine from β-Phenoxyethanesulfonic Acid.—β-Phenoxyethanesulfonyl chloride with iodine(III) trifluoroacetate and trifluoroacetic acid in acetic anhydride gave the symmetrical iodonium salt VII, 4,4′-bis-(β-chlorosulfonylethoxy)-diphenyliodonium trifluoroacetate.[6]



Hydrolysis gave the disulfonate VIII, isolated as the barium salt, which on treatment with an appropriate ion-exchange resin gave the metal-free betaine IX.[6]

Structures of Iodonium Salts from β-Phenoxyethanesulfonic Acid.—The unsymmetrical salt VI and the symmetrical salt IX both gave on treatment with iodide ion in hot aqueous solution the β-(4-iodophenoxy)-ethanesulfonate ion, independently prepared from 4-iodophenol and the β-bromoethanesulfonate ion and characterized as the S-benzylthiuronium salt, X.

$$\begin{tikzcd} \text{VI} \arrow[r, "I^-", "-C_6H_5I"'] & \underset{\text{(as S-benzylthiuronium salt, X)}}{4\text{-}IC_6H_5OCH_2CH_2SO_3^-} & \text{IX} \arrow[l, "I^-"'] \\ & 4\text{-}IC_6H_4OH + BrCH_2CH_2SO_3 \arrow[u, "HO^-"'] & \end{tikzcd}$$

Iodonium Salts from Phenoxyacetic Acids.—By reactions similar to those described above for β-phenoxyethanesulfonyl chloride (III), phenoxyacetic acid was converted to symmetrical and unsymmetrical salts[6] and, by their degradation, to 4-iodophenoxyacetic acid.[7]

$$\begin{tikzcd} C_6H_5OCH_2COOH \arrow[rd, "C_6H_5I(O_2CCH_3)_2", "{H_2SO_4 + Ac_2O, \text{ then } I^-}"'] \arrow[dd, "{I(O_2CCH_3)_3, \; HOOCCF_3 \text{ in } Ac_2O, \text{ then } HI}"] & \\ & \underset{\text{XI}}{4\text{-}C_6H_5\overset{+}{I}C_6H_4OCH_2COOH\ I^-} \arrow[d, "heat"', "-C_6H_5I"] \\ \underset{\text{XII}}{(4\text{-}HOOCCH_2OC_6H_4)_2\overset{+}{I}\ \overset{-}{I}} \arrow[r, "heat"] & \underset{\text{XIII}}{4\text{-}IC_6H_4OCH_2COOH} \end{tikzcd}$$

The iodonium salts were isolated as various charge types. Thus the unsymmetrical salt was obtained as both the carboxylic acid ($4\text{-}C_6H_5\overset{+}{I}C_6H_4OCH_2COOH\ \overset{-}{I}$, XI) and as the betaine ($4\text{-}C_6H_5\overset{+}{I}C_6H_4OCH_2CO_2^-$, XIa) formed by loss of hydrogen iodide, while the symmetrical salt was obtained as the dicarboxylic acid ($4,4'\text{-}\overset{+}{I}(C_6H_4OCH_2COOH)_2\ \overset{-}{I}$, XII), the monoionized betaine ($4,4'\text{-}\overset{+}{I}(C_6H_4OCH_2CO_2^-)_2\ H^+$, XIIa) and as the barium salt of the anion ($4,4'\text{-}\overset{+}{I}(C_6H_4OCH_2CO_2^-)_2\ Ba^{++}/_2$, XIIb).

Phenoxyacetic acid, 4-iodophenoxyacetic acid and salts XI and XIIa when titrated potentiometrically with sodium hydroxide at 25° gave pK_a's in the range 3.0–3.3, indicating that the iodine is too far from the carboxylic acid to affect its ionization significantly.

Acknowledgment.—F. M. B. wishes to acknowledge the hospitality of Yale University, where this article was written during a year's appointment, 1958–1959, and the support of the Alfred P. Sloan Foundation, Inc. The research was carried out in

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(5) F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, M. Mausner, G. Masullo and E. Sommer, THIS JOURNAL, **81**, 342 (1959).

(6) Structures were originally assigned by analogy with those from anisole: F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, *ibid.*, **75**, 2705 (1953).

(7) E. Mameli, E. Gambetta, G. Rimini, *Gazz. chim. ital.*, **50I**, 166 (1920); *C. A.*, **14**, 3067 (1920).

the laboratories of the Sperry Gyroscope Co., Inc., Great Neck, L. I., N. Y., and we are glad to acknowledge this privilege.

Experimental[8,9]

Starting Materials.—Phenol, phenoxyacetic acid and β-chloroethyl phenyl ether were purchased from Distillation Products Industries, Inc., while sodium β-bromoethanesulfonate was obtained from K and K Laboratories, Long Island City, N. Y Phenol with iodine and potassium hydroxide gave 4-iodophenol, m.p. 92–93° after vacuum distillation and crystallization from hexane; reported m.p. 92°,[10] 93–94°.[11] The iodination of phenoxyacetic acid was repeated[7] to give in low yield **4-iodophenoxyacetic** acid, m.p. 156–160°; reported m.p.'s 155–156°,[7] 159.5–160°.[12] Phenyliodoso diacetate[13] and iodine(III) trifluoroacetate[14] were prepared as previously reported.

Sodium β-Phenoxyethanesulfonate (II).—β-Chloroethyl phenyl ether (469.5 g., 3.0 moles) was added to a solution of sodium sulfite (390 g., 3.0 moles) in 1380 ml. of water. The vigorously stirred mixture was boiled under reflux for 21 hours and cooled to 20° to give a crystalline precipitate of sodium β-phenoxyethanesulfonate (II). (If the solution was too cold, unreacted starting ether would also crystallize.) The product was washed with ether, sucked dry and then dried further at 125° to give 289 g. (1.29 moles, 43%) of II.

S-Benzylthiuronium β-(4-Iodophenoxy)-ethanesulfonate (X).—4-Iodophenol (12.1 g., 55 mmoles), sodium β-bromoethanesulfonate (10.5 g., 50 mmoles) and sodium hydroxide (2.0 g., 50 mmoles) in 50 ml. of water were heated under reflux for 12 hours. The cold reaction mixture (two phases) was extracted several times with ether, acidified, extracted further, made alkaline, and allowed to stand at 0°. The precipitate (*ca.* 0.8 g.) of sodium β-(4-iodophenoxy)-ethanesulfonate, was not purified further but was converted directly to an S-benzylthiuronium salt by solution in water and treatment with an aqueous solution of 1 g. of S-benzylthiuronium chloride. The precipitate (0.74 g.) was crystallized from water to give 0.63 g. (1.3 mmoles, 2.6%) of **S-benzylthiuronium β-(4-iodophenoxy)-ethanesulfonate (X)**, m.p. 155–156°, unchanged by another crystallization.

Anal. Calcd. for $C_{16}H_{19}O_4IN_2S_2$: C, 38.87; H, 3.87. Found: C, 38.98; H, 3.96.

β-Phenoxyethanesulfonyl Chloride (III).—Sodium β-phenoxyethanesulfonate (168 g., 0.75 mole) was mixed with phosphorus pentachloride (62.4 g., 0.30 mole). After the initial exothermic reaction the stirred mixture was held at 100° for 2 hours and at 125° for 12 hours. The cooled reaction mixture was added with vigorous stirring to 500 g. of ice and water, giving lumps of crude product, which were washed with cold water. Short-path distillation (126–145° at 0.5–1.0 mm.) gave 99 g. (0.45 mole, 60%) of colorless, crystalline product. Redistillation gave 94.5 g. of **β-phenoxyethanesulfonyl chloride (III)**, b.p. 105–108° (0.5 mm.), m.p. 39–42°.

Anal. Calcd. for $C_8H_9ClO_3S$: Cl, 16.07. Found: Cl, 16.03.

β-Phenoxyethanesulfonamide (IV).—A small amount of the sulfonyl chloride III was treated with anhydrous ammonia in ether to give a crude product, m.p. 95–105°. Crystallization from water followed by drying at 87° gave colorless platelets of **β-phenoxyethanesulfonamide**, m.p. 105–106°.

Anal. Calcd. for $C_8H_{11}NO_3S$: N, 6.96. Found: N (Dumas), 6.94.

β-Phenoxyethanesulfonic Acid and its Barium Salt.—An aqueous solution of 33 g. (147.5 mmoles) of sodium β-phenoxyethanesulfonate was passed through an ion exchange column containing 100 g. (286 meq.) of Dowex-50X, a cation exchange column containing 100 g. (286 meq.) of Dowex-50X, a cation exchange resin in the hydrogen form. Evaporation gave an essentially quantitative recovery of **β-phenoxyethanesulfonic acid**, which was dried over phosphorus pentoxide *in vacuo*, melted below 100° and was not obtained analytically pure.

A sample of this sulfonic acid dissolved in water was treated with an aqueous solution of barium chloride dihydrate. The chilled solution deposited **barium β-phenoxyethanesulfonate**, which could be recrystallized readily from water and melted above 325°.

Iodonium Salts. 4-(β-Sulfoethoxy)-diphenyliodonium Betaine (VI).—To a solution of phenyliodoso diacetate (28.8 g., 89.6 mmoles) in 60 ml. of acetic anhydride and 20.8 ml. (271 mmoles) of trifluoroacetic acid held at or below −15° there was added slowly a solution of 20 g. (90 mmoles) of β-phenoxyethanesulfonyl chloride in 70 ml. of acetic anhydride. After one hour at −15° the reaction mixture was held at 0° for two days. Solvents were removed *in vacuo* at or below 70°. (Trituration of the oily residue with anhydrous ether gave crude 4-(β-chlorosulfonylethoxy)-diphenyliodonium trifluoroacetate. However, this hygroscopic material was hard to handle and usually was not isolated.)

Stirring with water at 60° overnight effected complete hydrolysis. Removal of solvents *in vacuo* below 50° gave a residue, which was crystallized from ethanol–acetone to give 15.6 g. (38.6 mmoles, 43%) of 4-(β-sulfoethoxy)-diphenyliodonium betaine (VI), which after slow crystallization from methanol had a m.p. 212–220°.

Anal. Calcd. for $C_{14}H_{13}IO_4S$: C, 41.60; H, 3.24. Found: C, 41.78; H, 3.39.

4,4′-Bis-(β-sulfoethoxy)-diphenyliodonium Betaine (IX) and its Barium Salt VIII.—To a solution of 20 mmoles of iodine(III) trifluoroacetate[14] in 15 ml. of acetic anhydride held at −20° there was added slowly with stirring a solution of β-phenoxyethanesulfonyl chloride (17.64 g., 80 mmoles) in 30 ml. of acetic anhydride and 5.0 ml. (66 mmoles) of trifluoroacetic acid. After 2 hours at −20°, 12 hours at 0° and 6 hours at 20°, solvent was removed *in vacuo* below 70°. The reddish residue was triturated several times at 0° with anhydrous ether, to remove unreacted β-phenoxyethanesulfonyl chloride, and was then hydrolyzed with 50 ml. of water at room temperature for 12 hours. After removal of the small amount of unreacted oil the strongly acidic aqueous solution was evaporated *in vacuo* below 100°. The oily residue was completely water-soluble, contained no chloride ion by silver nitrate test and presumably consisted largely of **4,4′-bis-(β-sulfoethoxy)-diphenyliodonium betaine (IX)**.

A concentrated aqueous solution of this material was treated with a slight excess of aqueous barium hydroxide, and the excess reagent was removed with carbon dioxide and filtration. The aqueous solution was added to three liters of boiling acetone. The cold solution deposited 5.5 g. (9.3 mmoles, 46%) of crude barium salt VIII. This light brown powder was soluble in water but insoluble in methanol or ethanol. Solution in water, treatment with activated carbon and reprecipitation with acetone gave a light tan material, which was dried *in vacuo* over phosphorus pentoxide.

Anal. Calcd. for $C_{16}H_{16}IO_8S_2Ba_{0.5}$: C, 32.24; H, 2.71; I, 21.29. Found: C, 32.34; H, 3.15; I, 21.08.

4,4′-Bis-(β-sulfoethoxy)-diphenyliodonium Betaine (IX).—Two grams (3.35 mmoles) of the barium salt just described in 100 ml. of water was passed through a column containing 13.8 g. of Dowex 50-X resin. Evaporation of the eluent left an oil which solidified to a reddish powder and was dried *in vacuo*. This acid was titrated with 0.1 *N* sodium hydroxide to a phenolphthalein end-point.

Anal. Calcd. for $C_{16}H_{17}IO_8S_2$: C, 36.37; H, 3.24; I, 24.02; neut. equiv., 528.3. Found: C, 36.53; H, 3.57; I, 23.95; neut. equiv., 524.9.

Structure Proof of Salts VI and IX from β-Phenoxyethanesulfonic Acid.—Separate aqueous solutions of the two salts were treated with a tenfold excess of potassium iodide, the solutions were evaporated to dryness, and the residues were heated at 190° for one hour. Aqueous solutions of these

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(8) Analyses by Schwarzkopf Microanalytical Laboratories, Woodside, Long Island, N. Y.

(9) As most iodonium salts decompose near their melting points, these depend strongly on the duration of heating. In general, after an approximate melting point was taken, a new sample was introduced about 10° below this point, and the temperature was raised 4–5° a minute. In the present work a Kofler hot-stage microscope was used.

(10) A. F. Holleman and I. J. Rinkes, *K. Akad. Wetenschappen*, **19**, 67 (1910); *C. A.*, **5**, 1435 (1911).

(11) E. Noelting and Th. Stricker, *Ber.*, **20**, 3021 (1887).

(12) N. V. Hayes and G. E. K. Branch, THIS JOURNAL, **65**, 1565 (1943).

(13) K. H. Pausacker, *J. Chem. Soc.*, 107 (1953).

(14) F. M. Beringer, H. E. Bachofner, R. A. Falk and M. Leff, THIS JOURNAL, **80**, 4279 (1958).

residues on treatment with aqueous solutions of S-benzylthiouronium chloride gave crude salts, which were crystallized from water and dried. The m.p.'s were: pure authentic S-benzylthiuronium β-(4-iodophenoxy)-ethanesulfonate (X), 155–156°; salt from VI, 153–156°; mixed m.p. of X with salt from VI, 153–156°; salt from IX, 153–155°; mixed m.p. of X with salt from IX, 153–156°.

4-(Carboxymethoxy)-diphenyliodonium Iodide (XI).—To a stirred solution of 7.2 g. (22.4 mmoles) of phenyliodoso diacetate in 20 ml. of acetic anhydride held at or below 0° there were added first 1.2 ml. (22.4 mmoles) of concentrated sulfuric acid and then a suspension of 3.4 g. (22.4 mmoles) of phenoxyacetic acid in 30 ml. of acetic anhydride. The solution was allowed to warm to room temperature and was stirred overnight.

After solvent had been removed *in vacuo* below 70°, the residue was dissolved in 40 ml. of water, extracted three times with ether and treated with aqueous potassium iodide (3.7 g., 22.4 mmoles). The solution stood for several hours at 0° giving a colorless precipitate of **4-(carboxymethoxy)-diphenyliodonium iodide (XI)**, which after drying weighed 9.15 g. (19 mmoles, 85%). Recrystallization from water gave a constant m.p. of 108–111° (introduced onto Kofler hot-stage at 95°).

Anal. Calcd. for $C_{14}H_{12}I_2O_3$: C, 34.88; H, 2.51. Found: C, 34.79; H, 2.27.

4-(Carboxymethoxy)-diphenyliodonium Betaine (XIa).—A sample of the above acid XI (1.8 g., 3.7 mmoles) was dissolved in hot water and titrated with 0.1 *N* sodium hydroxide to a brom phenol blue end-point (*p*H 6.0–7.6). (Potentiometric titration had shown the end-point to be near *p*H 6.5.) Dilution of the solution with acetone precipitated the betaine XIa as a colorless powder. Recrystallization could be accomplished by solution in hot water and addition of acetone to incipient turbidity, followed by keeping near 0° for several hours. After drying for three hours at 100°, such material had a m.p. of 205–207° (introduced onto Kofler hot-stage at 190°).

Anal. Calcd. for $C_{14}H_{11}IO_3$: C, 47.48; H, 3.13. Found: C, 47.20; H, 3.32.

4,4'-Bis-(carboxymethoxy)-diphenyliodonium Betaine (XIIa).—After 1.4 ml. (25 mmoles) of concentrated sulfuric acid had been added to a solution of 40 mmoles of iodine(III) trifluoroacetate in 50 ml. of acetic anhydride at −20°, the solution was cooled to −40°, and 24.3 g. (160 mmoles) of phenoxyacetic acid was added in small portions and with good agitation. The solution was allowed to warm to room temperature over four hours, solvent was removed *in vacuo* below 70°, and 75 ml. of water was added. The aqueous suspension was extracted thoroughly with ether and was then filtered. The clear filtrate was made slightly alkaline with barium hydroxide, treated with carbon dioxide, filtered and passed through a Dowex-50 ion-exchange column in the acid form. The chilled eluate gave 4.0 g. (9.4 mmoles, 23%) of 4,4'-bis-(carboxymethoxy)-diphenyliodonium betaine (XIIa). Recrystallization from water–acetone and vacuum drying at 100° gave material of m.p. 212–215° (inserted onto Kofler hot-stage at 195°), unchanged by further crystallization.

Anal. Calcd. for $C_{16}H_{13}IO_6$: C, 44.88; H, 3.06. Found: C, 45.07; H, 3.27.

4,4'-Bis-(carboxymethoxy)-diphenyliodonium Iodide (XII).—Betaine XIIa (337 mg., 0.79 mmole) dissolved in 20 ml. of hot 20% hydriodic acid gave on cooling colorless needles, which were dried *in vacuo*, washed with anhydrous ether and redried, giving 354 mg. (0.64 mmole, 81%) of **4,4'-bis-(carboxymethoxy)-diphenyliodonium iodide (XII)** as a yellow powder, m.p. 162–164°.

Anal. Calcd. for $C_{16}H_{14}I_2O_6$: C, 34.55; H, 2.54. Found: C, 34.45; H, 2.83.

Attempts to crystallize XII from water gave mixtures of XII and XIIa (formed by loss of hydrogen iodide).

Structure Proofs for Salts XI and XII from Phenoxyacetic Acid.—A sample of 4-(carboxymethoxy)-diphenyliodonium iodide (XI) was heated at 120° for 2 hours. The product was crystallized twice from methylene chloride and twice from ethanol–water to give 4-iodophenoxyacetic acid of m.p. 158–160°, undepressed by admixture with an authentic sample.

Similarly, the decomposition of 4,4'-bis-(carboxymethoxy)-diphenyliodonium iodide (XII) at 165–170° gave 4-iodophenoxyacetic acid of m.p. 156–158° after two crystallizations from methylene chloride and one from ethanol–water; no depression of m.p. on admixture with an authentic sample.

BROOKLYN 1, N. Y.

[CONTRIBUTION NO. 469 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND CO.]

Mechanism of the Photoöxidation of Amides

BY W. H. SHARKEY AND W. E. MOCHEL

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The photoöxidation of N-alkyl amides has been studied using N-pentylhexanamide as a representative of this class. The major products formed were *n*-valeraldehyde and valeric acid from the amine part of the molecule and hexanoic acid and hexanamide from the acid part of the molecule. Formation of these products indicates that photoöxidation involves oxygen attack on the methylene group adjacent to nitrogen. This conclusion has been substantiated by examination of amides substituted with alkyl groups at various positions.

There are a number of reports in the literature on the photochemistry of amides. Examples include studies of the photodegradation of serum albumin[1] and of polyamides.[2] It has been suggested that photodegradation involves reactions of acyl and imino free radicals generated by photolytic scission of the amide group. That photolytic scission occurs under certain conditions was demonstrated by Rideal and Mitchell[3] who irradiated monolayers of stearanilide upon aqueous acid supports with light of wave length 2350–2500 Å. The photolysis products, stearic acid and aniline, appeared to have been formed by reaction of acyl and imino free radicals, respectively, with water. Later, Carpenter[4] reported that N-benzylstearamide and N-β-phenylethylstearamide were degraded in the same manner.

Since comparable studies on simple N-alkyl amides have not been reported, an investigation of the photoöxidation of a representative member of this class was undertaken. *N*-Pentylhexanamide was chosen for study principally because of its low melting point (37–38°). This amide could be examined in the liquid state at temperatures low

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[1] E. K. Rideal and R. Roberts, *Proc. Roy. Soc.* (*London*), **A205**, 391 (1951); R. Roberts, *J. Soc. Dyers and Colourists*, **65**, 699 (1949).

[2] B. G. Achhammer, F. W. Reinhart and G. M. Kline, *J. Research Natl. Bur. Standards*, **46**, 391 (1951).

[3] E. K. Rideal and J. S. Mitchell, *Proc. Roy. Soc.* (*London*), **A159**, 206 (1937).

[4] D. C. Carpenter, THIS JOURNAL, **62**, 289 (1940).