Experimental

Preparation of Benzilic Acid Morpholinoethyl-Amide.—A solution of 7.3 g. (0.03 mole) of benzilic acid methyl ester and 6.5 g. (0.05 mole) of morpholinoethylamine in 100 cc. of methanol was refluxed for 24 hours on a steam-bath. After evaporating solvent the residual product was purified by crystallization from ethyl acetate; yield 9.5 g. (95%); m.p. 127–128°. This product was also recrystallized from water, ethyl acetate and from mixtures of ethyl acetate or benzene with Skellysolve B.

The other tertiaryamino amides of Table I were obtained by similar procedures. They were quaternized by refluxing with methyl iodide in methanol solution.

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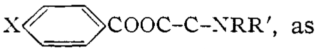
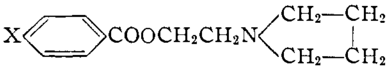
β-Pyrrolidinoethyl *p*-Alkoxybenzoates[1]

BY J. STANTON PIERCE, MICHAEL J. FLETCHER AND SAMUEL L. COOKE, JR.

RECEIVED DECEMBER 15, 1953

In a recent survey of substituted aminoethyl benzoates with the same skeleton formula, , as in Einhorn's β-diethylaminoethyl-*p*-aminobenzoate,[2] out of over 450 compounds tabulated, only six are esters of β-pyrrolidinoethanol (A). The repeated use of diethylaminoethanol in the preparation of local anesthetics, the relationship of this compound to A and the present low cost of pyrrolidine suggest the desirability of the synthesis of a series of compounds of the structure,

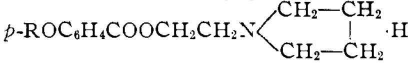


with considerable variation in X. To date, esters have been prepared of A with benzoic acid,[3] *p*-nitrobenzoic and *p*-aminobenzoic acids,[4] *p-n*-butylaminobenzoic acid[5] and cinnamic acid.[5]

The β-pyrrolidinoethyl benzoates in the present study were prepared by condensation of the benzoyl chlorides with A, usually in benzene solution, and were isolated as the hydrochlorides. The pyrrolidinoethanol was prepared by the reaction of a methanol solution of pyrrolidine with ethylene oxide[3,6] at 45–60°.[7] The alkoxybenzoyl chlorides were prepared by the reactions[8]

$$p\text{-HOC}_6\text{H}_4\text{COOC}_2\text{H}_5 \longrightarrow p\text{-ROC}_6\text{H}_4\text{COOC}_2\text{H}_5 \longrightarrow p\text{-ROC}_6\text{H}_4\text{COOH} \longrightarrow p\text{-ROC}_6\text{H}_4\text{COCl}$$

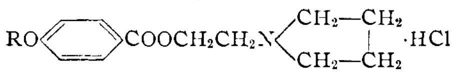
Experimental

β-Pyrrolidinoethyl-*p*-alkoxybenzoate Hydrochloride,  $p\text{-ROC}_6\text{H}_4\text{COOCH}_2\text{CH}_2\text{N}\left\langle\begin{matrix}\text{CH}_2\text{—CH}_2\\ \text{CH}_2\text{—CH}_2\end{matrix}\right|\cdot\text{HCl}$.—In a typical run a solution of *p*-alkoxybenzoyl chloride, dissolved in approximately 2.0 volumes of benzene, was treated slowly with an equimolar quantity of A, in benzene. The mixture was refluxed for 0.5 hour and allowed to stand overnight. The crystalline product was filtered with suction, washed with anhydrous ether, dissolved in water and extracted with isopropyl ether, the ether being discarded. The aqueous solution was made basic with sodium carbonate solution and the oil which separated was dissolved in isopropyl ether. The isopropyl ether solution was filtered and treated with hydrogen chloride. The precipitate which formed was filtered with suction, washed with anhydrous ether, recrystallized from benzene, washed with absolute ether and recrystallized from absolute alcohol.

If crystallization did not occur in the original reaction mixture, the benzene solution was extracted with approximately 4 volumes of 0.5 *N* hydrochloric acid and the aqueous layer was made basic with sodium hydroxide solution. The oil which separated was dissolved in isopropyl ether and converted to the hydrochloride as above. If the hydrochloride did not crystallize readily it was converted into a crystalline solid by trituration with dry ether or absolute alcohol.

TABLE I

β-PYRROLIDINOETHYL *p*-ALKOXYBENZOATE HYDROCHLORIDES[a,b,c]



R	M.p. (uncor.), °C.	Yield, % crude	Chlorine, % Calcd.	Chlorine, % Found
Ethyl	174–174.5	74	11.83	11.36
n-Propyl	147–148	47	11.29	11.43
n-Butyl	157–158	48	10.81	10.74
n-Amyl	136–137	90	10.37	10.32
n-Hexyl	132.5–133	36	9.96	9.65
Cycloamyl	141.5–143	45	10.43	10.52
Cyclohexyl	158.5–160	49	10.02	10.00

[a] β-Pyrrolidinoethyl *p*-chlorobenzoate hydrochloride, m.p. 194–196°, was prepared from *p*-chlorobenzoyl chloride purchased from Distillation Products Industries. *Anal.* Calcd. for $C_{13}H_{17}O_2NCl_2$: Cl (ionized), 12.22. Found: Cl, 12.36. [b] β-Pyrrolidinoethyl *p*-amyloxycinnamate hydrochloride, m.p. 160–160.5°, was prepared from *p*-amyloxycinnamoyl chloride, which was prepared from *p*-hydroxybenzaldehyde by way of *p*-amyloxycinnamic acid.[9] *Anal.* Calcd. for $C_{21}H_{30}O_3NCl$; Cl, 9.65. Found: Cl, 9.64. [c] The activities of these compounds as local anesthetics are being determined by Dr. Harvey B. Haag of the Medical College of Virginia.

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[1] Acknowledgment is made to Dr. E. Emmet Reid, Research Advisor to the Chemistry Department of the University of Richmond, for his advice in this work.

(2) A. Einhorn and E. Uhlfelder, *Ann.*, **371**, 131 (1909).

(3) J. von Braun, O. Braunsdorf and K. Räth, *Ber.*, **55B**, 1666 (1922).

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(6) New Products Bulletin No. 28, E. I. du Pont de Nemours and Co., Inc.

(7) For a similar preparation of diethylaminoethanol, see W. H. Horne and R. L. Shriner, THIS JOURNAL, **54**, 2925 (1932).

(8) J. Stanton Pierce, J. M. Salsbury and J. M. Fredericksen, *ibid.*, **4**, 1691 (1942).

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Elimination Reactions on 1,4-Systems. II. Use of Metals to Prepare 1,3-Butadiene and Derivatives[1]

BY W. M. SCHUBERT AND WAYNE A. LANKA

RECEIVED DECEMBER 9, 1953

In an earlier report on the possible extent of the general reaction 1 in which $n > 0$, it was shown that 1,4-dibromo-2-butyne and 1-bromo-4-phenoxy-2-butyne yielded butatriene when treated with zinc in the solvent diethylene glycol–diethyl ether or acetonitrile.[2] Other examples of the reaction 1 in which $n > 0$ include: the preparation of 1,3-buta-

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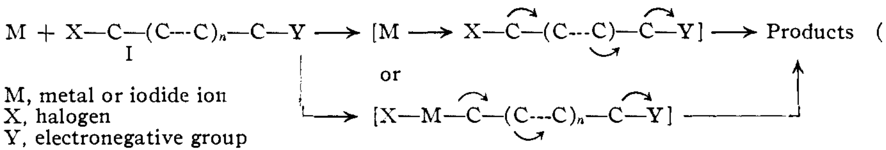
(1) Supported in part by a Cottrell grant of the Research Corporation.

(2) W. M. Schubert, T. H. Liddicoet and W. A. Lanka, THIS JOURNAL, **76**, 1929 (1954).

diene from *trans*-1,4-dibromo-2-butene or 1-bromo-4-phenoxy-2-butene plus zinc or magnesium[3a,b]; the reaction of magnesium and *cis*-3,5-dibromocyclopentene to yield cyclopentadiene[4]; the reaction of sodium iodide in acetone on *trans*-1,4-dibromo-2-butene to yield 1,3-butadiene[3b]; and the reaction of zinc with 1,6-dibromo-2,4-hexadiene to yield 1,3,5-hexatriene.[5]


(1)

M, metal or iodide ion
X, halogen
Y, electronegative group
---, multiple bond

That the group Y in the general reaction 1 in which $n > 0$ can be alkoxy as well as an aryloxy group was shown by the reaction of magnesium with 1-bromo-4-methoxy-2-butene to give 1,3-butadiene in 85% yield. The general reaction was then extended to the action of magnesium in tetrahydrofuran on γ-bromocrotonaldehydediethylacetal. This gave 1-ethoxy-1,3-butadiene in 15% yield of isolated product, identical in boiling point, index of refraction and ultraviolet spectrum with an authentic sample. A considerable portion of the diene was lost by polymerization during its isolation and purification. An ultraviolet spectroscopic analysis of the original solution showed a 78% yield of 1-ethoxy-1,3-butadiene to be present before the isolation procedure was begun.

It also was found that γ-bromocrotonaldehyde diacetate reacted with magnesium in tetrahydrofuran to yield 1-acetoxy-1,3-butadiene. An ultraviolet spectroscopic analysis of the reaction solution showed a 60% yield of the diene to be present. A 37% yield of the pure diene was isolated and found identical with authentic 1-acetoxy-1,3-butadiene.

The elimination reactions forming 1-ethoxy and 1-acetoxy-1,3-butadiene find analogies in some 1,2-elimination reactions brought about by metals (*i.e.*, reaction 1 in which $n = 0$). For example, Wislicenus found that chloroacetaldehyde diethylacetal reacted with sodium to yield vinyl ethyl ether.[6] More recently, Arens and van Dorp observed that the only product resulting from the reaction of magnesium with bromoacetone ethyleneketal followed by hydrolysis was β-hydroxyethylisopropenyl ether.[7]

That the central carbon–carbon bond of compound I need be multiple for the reaction 1 was shown by the failure of either 1,4-dibromobutane or 1-bromo-4-methoxybutane to yield any ethylene on reaction with magnesium.

Experimental

Reaction of Compounds of Type I with Magnesium.—A solution of γ-bromocrotonaldehydediethylacetal[8] (18.3 g., 0.082 mole) in purified tetrahydrofuran (25 ml.) was added dropwise to magnesium turnings (4 g., 0.167 gram atom) in tetrahydrofuran (25 ml.) at such a rate as to maintain gentle reflux. The mixture was heated an additional hour.

The ultraviolet spectrum was taken of an aliquot of the reaction solution diluted with 95% alcohol. The intensity of the single characteristic peak at 237 mμ indicated that a 78% yield of 1-ethoxy-1,3-butadiene was formed. Authentic 1-ethoxy-1,3-butadiene prepared by the method of Flaig[8] showed a single peak in the ultraviolet (in 95% alcohol) at 237 mμ, ε, 19,100. A 1.24-g. (15%) yield of 1-ethoxy-1,3-butadiene, b.p. 35–38° (40 mm.), $n^{25}D$ 1.4582, ϵ_{max} (95% ethanol) 17,900 at 237 mμ, was obtained. The residue of the distillation was a yellow viscous sticky oil (4.67 g.).

The elimination reaction on γ-bromocrotonaldehyde diacetate (12.5 g.) was run similarly except that magnesium amalgam was the metal used and the reaction was initiated with methyl iodide. An ultraviolet spectrum of an aliquot of the reaction solution diluted with ethanol showed a 60% yield of 1-acetoxy-1,3-butadiene to be present. A 37% yield of the diene was isolated by distillation, b.p. 51–52° (31 mm.), $n^{25}D$ 1.4652, ϵ_{max} (broad band) 20,700 at 231 mμ. The properties were in close agreement with those of an authentic sample of 1-acetoxy-1,3-butadiene.[9]

When treated in the same way, γ-methoxycrotyl bromide (15 g.) gave 1,3-butadiene, isolated in 88% yield as the bromination product, *meso*- and *dl*-1,2,3,4-tetrabromobutane.

The reaction of 1-bromo-4-methoxybutane (54 g.) with magnesium in tetrahydrofuran or dibutyl ether gave no ethylene, as evidenced by the failure of the volatile gases entrained in a nitrogen stream to decolorize bromine in carbon tetrachloride. No unsaturated gas was obtained from 1,4-dibromobutane treated in a similar way.

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[3] (a) J. Thiele, *Ann.*, **308**, 333 (1899); (b) A. Lüttringhaus, G. V. Saaf and K. Hauschild, *Ber.*, **71**, 1673 (1938).

[4] E. B. Reid and J. Yost, THIS JOURNAL, **72**, 1807 (1950).

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[6] J. Wislicenus, *Ann.*, **192**, 106 (1878).

[7] J. F. Arens and D. A. van Dorp, *Rec. trav. chim.*, **65**, 729 (1946).

[8] W. Flaig, *Ann.*, **568**, 1 (1950).

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Chemistry of Epoxy Compounds. XV.[1] Oxidation of Linoleic Acid with Peracetic and Performic Acid[2]

BY DANIEL SWERN AND GERALDINE BILLEN DICKEL

RECEIVED SEPTEMBER 30, 1953

The oxidation of monounsaturated fatty materials with organic peracids has been studied extensively and is well understood but similar systematic investigation of polyunsaturated analogs has not been carried out. In the few scattered literature reports (for a review of the literature, see references 3 and 4), purity of starting materials is often unknown and open to serious question, yields of products are low and, of major importance, the nature of the main reaction course is not known with certainty. This note describes the oxidation of a linoleic acid concentrate (90–94% *cis,cis*-9,12-octadecadienoic acid) with peracetic and performic acid. The oxidation reactions were followed quantitatively by measuring consumption of peracid with time and reaction products were isolated and identified.

The oxidation of linoleic acid with peracetic and performic acid proceeds normally, contrary to

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[1] For paper XIV, see THIS JOURNAL, **74**, 6139 (1952).

[2] Presented at the Spring Meeting of the American Chemical Society, Kansas City, Missouri, March 24–April 1, 1954.

[3] D. Swern, *Chem. Rev.*, **45**, 1 (1949).

[4] D. Swern, "Organic Reactions," Vol. VII, Chapter 7, John Wiley and Sons, Inc., New York, N. Y., 1953.