

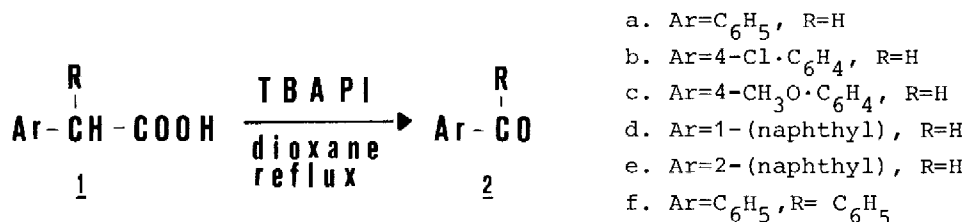
OXIDATIVE DECARBOXYLATION OF ARYLACETIC ACIDS BY MEANS
OF TETRABUTYLAMMONIUM PERIODATE

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Summary: Tetrabutylammonium periodate (TBAPI) in refluxing dioxane is able to convert arylacetic acids into the corresponding nor-aldehydes in good yields.

It is well documented that, apart from the classical cleavage of 1,2-diols and related compounds, periodates can effect also, in some cases, oxidations of activated methylene groups¹. In a following step, the so formed oxidation product can be cleaved rapidly through the intermediacy of a cyclic periodate ester¹. In a recent communication, we have described the use of tetrabutylammonium periodate, $(C_4H_9)_4NIO_4$ (TBAPI), in homogeneous oxidations of sulfides, 2-hydroxy acids and α -bromoketones². We thought that TBAPI might be able to oxidize a relatively activated methylene of an arylacetic acid and chose phenylacetic acid (1a) as a suitable substrate. In refluxing 1,4-dioxane³ with an equimolar amount of TBAPI, the reaction was complete within 12 h and benzaldehyde (2a) was isolated in 50% yields⁺. The reaction was extended to several substrates and yields were in the range of 50-70% of isolated products (Table).



Also diphenylacetic acid (1f) reacted with TBAPI to afford benzophenone (2f) in 85% yield (molar ratio TBAPI/(1f), 2:1). However, when the ratio TBAPI/(1a-e) was raised to 2:1 moles, no improvement in the yields of products was observed⁴.

It has been recently reported⁵ that alkaline solutions of sodium hypochlorite are able to oxidize arylacetic acids to the corresponding nor-aldehydes and acids, the ratio of products depending either on electronic factors or on concentration of hypochlorite. In the case of TBAPI oxidations, it should be pointed out that an aldehyde is the only product isolated and isolated yields are similar to, or higher than those of the described procedure using hypochlorite⁵. TBAPI oxidations of arylacetic acids can be rationalized by

hydroxylation of the relatively activated methylenes and subsequent oxidative cleavage of the so formed 2-hydroxy acids to the next lower carbonyl compound.

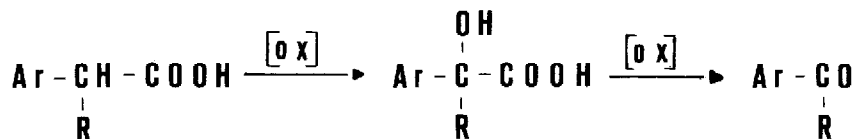


TABLE: Oxidative Decarboxylation of Arylacetic Acids by TBAPI

PRODUCTS ^a	REACTION TIME ^c (h)	YIELDS ^d (%)
2a	12	50
2b	12	65
2c	16	70
2d	8	60
2e	16	50
2f ^b	48	85

a. TBAPI/substrate molar ratio, 1:1. b. TBAPI/substrate molar ratio, 2:1.

c. Time of complete reaction.

d. Yields refer to pure, isolated compounds, characterized by comparison with authentic samples (i.r., ¹H-n.m.r., t.l.c., g.l.c.).

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REFERENCES AND FOOTNOTES

⁺ In a typical procedure, TBAPI (0.01 moles) and phenylacetic acid (1a) (0.01 moles) were refluxed in 1,4-dioxane. When the reaction was complete (12h), the reaction became dark from the formation of iodine. The product was recovered by evaporation of the solvent and extraction of the residue with diethyl ether. In this solvent tetrabutylammonium salts are insoluble and following evaporation of the solvent afforded nearly pure (2a), which was then distilled (yields indicated in Table).

1. C.A. Bunton, in "Oxidation in Organic Chemistry", W.A. Wiberg Ed., Academic Press, N.Y., 1965, p. 388.
2. E. Santaniello, A. Manzocchi and C. Farachi, *Synthesis*, in the press.
3. Reactions can also be carried out in dichloromethane or chloroform in screw-cap test tubes at 100°C.
4. Not completely satisfactory yields may be explained through some side product formation; this remains with the tetra alkylammonium salts and is not extracted in the isolation procedure.
5. F. Kaberia and B. Vickery, *J. Chem. Soc., Chem. Comm.*, 459 (1978).

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