

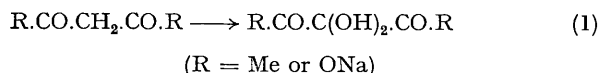
Reaction of some Arylacetic Acids and Related Compounds with Alkaline Sodium Hypochlorite Solution

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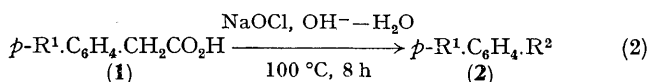
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Summary Arylacetic acids react with alkaline sodium hypochlorite solution to yield the next lower aldehyde and/or carboxylic acid. _____

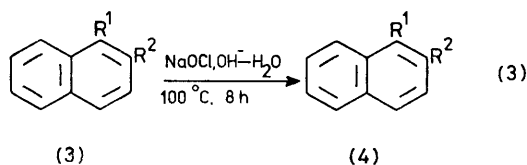
In an earlier paper¹ we reported the reactions of some molecules having reactive methylene groups with alkaline sodium hypochlorite solution [reaction (1)]. We thought



that similar oxidations, probably to give 2-ketoacids, might take place in phenylacetic acid, and in its derivatives having electron withdrawing groups on the benzene nucleus. The expected reactions did not however take place, and the products were found to be an aldehyde and/or a carboxylic acid having one carbon atom less than the starting material [reactions (2) and (3)].



	Yield of (2)/%
a; R ¹ = H; R ² = CHO	40
b; R ¹ = F; R ² = CHO	35
c; R ¹ = Cl; R ² = CO ₂ H	89
d; R ¹ = Br; R ² = CO ₂ H	67
e; R ¹ = NO ₂ ; R ² = CHO or CO ₂ H	75 or 60



	R ¹	R ²	R ¹	R ²	Yield /%
a;	CH ₂ CO ₂ H	H	a;	CHO	40
b;	H	CH ₂ CO ₂ H	b;	H	6+65
				CHO and CO ₂ H	

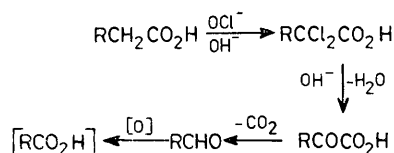
In order to identify the factors which activate the methylene group in these reactions we also treated but-3-enoic acid and cyclohexylacetic acid with alkaline sodium hypochlorite. The former gave propenal (acrolein) while the latter did not react.

When the electron releasing -OH group was *para* to the -CH₂CO₂H group, no reaction took place. Also no corresponding reaction took place with 3-indolylacetic acid, but a small amount of the decarboxylation product 3-methylindole was obtained.

In the reaction of 4-nitrophenylacetic acid with alkaline hypochlorite we found that the product obtained was dependent upon the concentration of the sodium hypochlorite. If the latter were <2% w/v the aldehyde was obtained; if >2% w/v the acid was produced. 1-, and 2-naphthylacetic acids differed in their behaviour towards alkaline sodium hypochlorite solution (4% w/v); the 1-isomer gave only the 1-aldehyde, whilst the 2-isomer gave a mixture of the 2-aldehyde and the 2-acid. Variation is possibly due to the difference in steam volatility between 1- and 2-naphthaldehyde. The 1-isomer appears to be

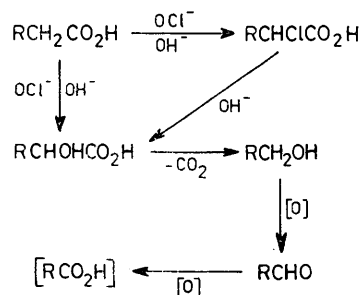
readily steam volatile, and during the reaction some collects in the condenser where it cannot be further oxidised to 1-naphthoic acid; the 2-isomer is less steam volatile and remains in solution and is further oxidised to 2-naphthoic acid.

We have considered two possible reaction pathways in these reactions: (i) whilst it is known that alkaline sodium hypochlorite is able to introduce two chlorine atoms into the methylene group of 2,4-dinitrophenylacetic acid (Scheme 1),¹ we found that 2-oxo-2-phenylacetic acid could not be



SCHEME 1

converted into benzaldehyde by alkaline sodium hypochlorite solution indicating that this mechanism is not applicable to the benzaldehyde synthesis. (ii) We found that both 2-hydroxy-2-phenylacetic acid and benzyl alcohol were readily converted into benzaldehyde by alkaline sodium hypochlorite (Scheme 2), suggesting that



SCHEME 2

the reaction takes place by this route. We have not as yet been able to establish conclusively whether the 2-chloro acid is involved, or whether the methylene group is directly oxidised to a secondary alcohol group by the alkaline sodium hypochlorite.

In the reactions where the product is a 4-substituted benzoic acid, we have found that in all cases the corresponding 4-aldehyde is readily converted into the 4-acid with alkaline sodium hypochlorite.

While it is known that *N*-bromosuccinimide can convert 2-hydroxycarboxylic acids into the next lower aldehyde,² we believe that we report the first example of the reaction of a substituted acetic acid to give an aldehyde with one carbon atom less.

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¹ B. Vickery and F. Kaberia, *Chem. and Ind.*, submitted for publication.

² M. Z. Barakat and M. F. A. El-Wahab, *J. Amer. Chem. Soc.*, 1953, **75**, 5731.