

The Synthesis of Carboxylic Acids and Esters from Carbon Monoxide and Alkylnitratomercury(II) Complexes

By J. M. DAVIDSON

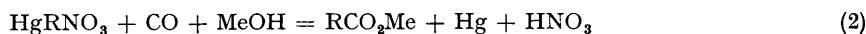
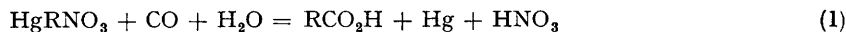
(Department of Chemical Engineering, Pembroke Street, Cambridge)

THERE are a number of syntheses in which carbon monoxide is used in a liquid-phase reaction with an organometallic intermediate¹ and recently² it was shown that benzoic acid derivatives may be prepared from carbon monoxide and complexes

of the type $[\text{Hg}(\text{Aryl})_2]\text{NO}_3\text{OH}$. This Communication concerns similar reactions of alkyl-nitratomercury(II) complexes that yield derivatives of aliphatic acids together with by-products that are indicative of nucleophilic attack at the

α -carbon atom. Arylmercury(II) compounds generally undergo electrophilic attack at the carbon adjacent to mercury.

The examples chosen for study were the n-butyl- and 2-methoxyethyl-nitratomercury(II) complexes (I; HgRNO_3 , $\text{R} = \text{Bu}^n$ or $\text{MeOCH}_2\text{CH}_2$) and these reacted smoothly at 75° in 10% solutions in benzene, water, or methanol using carbon monoxide pressures of 25–250 atmospheres.* Metallic mercury was precipitated quantitatively and in water or moist benzene carboxylic acids were formed (Reaction 1, yield variable 10–50%) but in methanol solution only traces of acids were found and the corresponding methyl ester was obtained (Reaction 2, yield 35–50%).



A carbonate separation afforded a number of neutral by-products that were isolated in a pure state by gas chromatography. Among them were those to be expected from solvolysis of the nitrate-complex.^{3,4} Thus reactions carried out in moist benzene gave small yields of ROH, RNO_3 , and RCO_2R from (I, $\text{R} = \text{Bu}^n$) and RNO_3 from (I, $\text{R} = \text{MeOCH}_2\text{CH}_2$). Presumably the n-butyl-n-valerate was formed according to Reaction 2 with n-butanol in place of methanol. However,

the major by-products were 1-nitrobutane and 1-methoxy-2-nitroethane and these were the only substantial impurities in the methyl esters obtained from methanol solution.

Carboxylic acids have previously been prepared by carbonylation of olefins which were converted into carbonium ions by strong acid catalysts.⁵ Solvolysis reactions of $\text{Hg}(\text{Alkyl})\text{ClO}_4$ have been reported and the mechanism is of the $\text{S}_{\text{N}}1$ type but in the present case the carbonium ion R^+ cannot have been formed since the reaction time for solvolysis of (I, $\text{R} = \text{Bu}^n$) in methanol at 75° is very much greater than the reaction time in the presence of carbon monoxide. Ligand effects indicate that a polar Hg–O bond is important

because donors such as AcO^- , Cl^- , or Br^- that form undissociated HgRX inhibit the reaction, while the corresponding nitrate- or perchlorate-complexes react with carbon monoxide. The alkyl nitrates are not key intermediates since they do not react with carbon monoxide. Perhaps (I) forms an intermediate carbonyl complex that subsequently decomposes either to a nitroalkane or a carboxylic acid derivative.

(Received, February 2nd, 1966; Com. 061.)

* Under similar conditions a solution of 2-hydroxyethylnitratomercury(II) (33 g.) in benzene (50 ml.) underwent a vigorous total decomposition to the constituent elements

¹ C. W. Bird, *Chem. Rev.*, 1962, **62**, 283.

² L. R. Barlow and J. M. Davidson, *Chem. and Ind.*, 1965, 1656.

³ F. R. Jensen and R. J. Ouellette, *J. Amer. Chem. Soc.*, 1961, **83**, 4477, 4478.

⁴ I. Roberts and L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 1063.

⁵ H. Koch, *Brennstoff-Chem.*, 1955, **36**, 321.