Title	Carboxylation of nitromethane by carbon dioxide and potassium phenoxide derivatives. substituent effect upon the yield of carboxylate
Sub Title	
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Publisher	共立薬科大学
Publication year	1984
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.29 (1984.) ,p.56- 56
JaLC DOI	
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000029-0056

Carboxylation of Nitromethane by Carbon Dioxide and Potassium Phenoxide Derivatives. Substituent Effect upon the Yield of Carboxylate*

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The carboxylation of nitromethane with carbon dioxide proceeded in the presence of potassium phenoxides in DMF, yielding dipotassium nitroacetate as a precipitate. This reaction proceeded well at 0°C. The substituent effect upon the carboxylation was investigated by using potassium phenoxides with various substituents (*p*-OCH_3, *p*-CH_3, H, *p*-Cl, *m*-Cl, *p*-$COCH_3$, and *p*-NO_2). The reaction was completed in 5 min at 0°C. The maximum yield of carboxylate was obtained when unsubstituted phenoxide was used ; the yield of carboxylate was low when potassium phenoxide with a substituent having a highly negative or highly positive σ value was used.

The mechanism of the carboxylation is discussed. The formation of the carboxylate as a precipitate is considered to be an important factor. Methods for the effective transformation of dipotassium nitroacetate to methyl nitroacetate are briefly surveyed.

* 本報告は *Chem. Pharm. Bull.*, **32**, 2200—2204 (1984) に発表