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Relational Action (1990) Actio	
Title	Carboxylation of nitromethane by carbon dioxide and potassium phenoxide derivatives. substituent effect upon the yield of carboxylate
Sub Title	
Author	森, 久和(Mori, Hisakazu) 大窪, 睦子(Okubo, Mutsuko) 桶, 美子(Oke, Yoshiko) 野口, 信子(Noguchi, Nobuko) 福田, 美保(Fukuda, Miho) 石原, 政雄(Ishihara, Masao)
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

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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-OCH₃, p-CH₃, H, p-Cl, m-Cl, p-COCH₃, and p-NO₂). 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