A Novel Bisacylation *via* Halophilic Reaction of Tri-n-butylarsine. Synthesis of Methane substituted with Four Electron-withdrawing Groups

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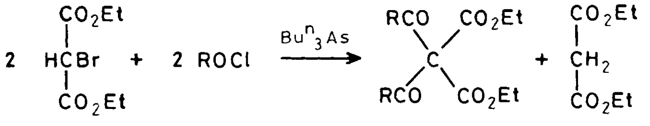
A novel bisacylation *via* halophilic reaction of tri-n-butylarsine and its application to the synthesis of methane substituted with four electron-withdrawing groups are described.

Carbon–carbon bond formation is of great importance in synthetic organic chemistry. Much attention has been paid to the use of heteroelements but there has been no report on the use of organosarsenic compounds as halophiles in organic synthesis. Compounds that contain three electron-withdrawing groups on a single carbon atom are rare,[1] and are usually prepared by acylation at a carbon atom bearing an active hydrogen [reaction (1)].[1] However, no methods have been reported for the synthesis of compounds with four electron-withdrawing groups on a single carbon atom. We now report a novel bisacylation *via* halophilic reaction of tri-n-butylarsine and its application to the synthesis of methane substituted with four electron-withdrawing groups.

The reaction of the bromomalonate (**1**) with aromatic or aliphatic acyl chlorides in the presence of tri-n-butylarsine gave compounds (**3**) in 74—93% yields, (Scheme 1, Table 1).†



(1) **(2)** **(3)** **(4)**

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† In a general procedure the acyl chloride (**2**) (2 mmol) was added slowly to a solution of the ester (**1**) (2 mmol) and tri-n-butylarsine (2 mmol) under nitrogen. The mixture was stirred and heated for several hours (see Table 1) in a capped flask and the disappearance of the starting material and the complete formation of the product monitored by n.m.r. spectroscopy. Chromatography on silica gel with light petroleum (b.p. 60—90 °C)/ethyl acetate (85 : 15) as eluant gave the product (**3**).

Table 1. Synthesis of tetrasubstituted methanes (**3**).

Compound	R	Conditions		M.p., *t*/°C	%
		Time/h	Temp./°C		Yield[a]
(**3a**)	Ph	2.5	80	(165—167/0.1[b])	91
(**3b**)	4-ClC_6H_4	14	80	94—95	85
(**3c**)	4-BrC_6H_4	16	80	97—98	87
(**3d**)	4-$NO_2C_6H_4$	2	80	95—96	93
(**3e**)	2-$NO_2C_6H_4$	2	80	88—89	86
(**3f**)	2,4-$Cl_2C_6H_3$	12	80	(148—149/0.1[b])	80
(**3g**)	4-$MeOC_6H_4$	20	80	86—87	76
(**3h**)	$Me(CH_2)_4$	11	30	(142—144/0.3[b])	74

[a] Isolated yields. All products exhibited n.m.r., i.r., and mass spectra consistent with the assigned structures. [b] B.p./mmHg.

$$\text{Z-CH}_2\text{-Z}' \xrightarrow{\text{base}} \text{Z-}\overset{-}{\text{C}}\text{H-Z}' \xrightarrow{\text{RCOCl}} \text{Z-CH(COR)-Z}' \quad (1)$$

Acyl chlorides[2] or acid anhydrides[3] could acylate isopropyl malonate in the presence of pyridine or triethylamine but monoacylated products were obtained. In our cases bisacylation occurred. In addition this is the first example of the application of halophilic reactions of trialkylarsine in organic synthesis.

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