SOLVENT FREE SYNTHETIC PROCEDURE THROUGHOUT REACTION AND SEPARATION: YLIDE REACTION WITH ALKYL ARYL KETONES IN THE ABSENCE OF SOLVENT FOLLOWED BY DISTILLATION TO GIVE 1-ALKYL-1-ARYLOXIRANES

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Abstract- After heating a mixture of trimethylsulphonium iodide, *t* BuOK and an alkyl aryl ketone at 60-70 °C for 1-5 h, vacuum distillation gave the corresponding 1-alkyl-1-aryloxirane. The procedure was accomplished without using any solvent throughout the reaction and the separation.

Methylene transfer reaction from ylides to ketones has been developed as a convenient synthetic method of oxiranes.[1] However, the experimental procedure is a sort of complication. For example, a THF solution of dimethylsulphoniummethanide (**2**) is obtained by treatment of trimethylsulphonium iodide (**1**) with BuLi in THF at 0 °C, and after addition of the ketone the mixture is heated at 50-55 °C under nitrogen to give oxirane. Throughout the reaction and separation of the product, the organic solvent is essential.

We have developed methylene transfers to cyclohexanone derivatives in the absence of solvent [2] Heating a mixture of **1**, solid ground KOH and 4-methylcyclohexanone at 60 °C for 3 h gave the corresponding oxirane derivative in 91% yield. The reaction product was isolated from the reaction mixture by extraction with ether. However, it would be better to avoid any solvent and isolate the oxirane by simple distillation.

This paper is dedicated to the memory of the late Professor Shun-ichi Yamada.

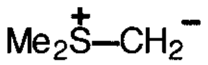
We here report on a novel preparative method by a combination of the methylene transfer reaction to alkyl aryl ketones (**3**) in the absence of solvent at relatively low temperature with the vacuum distillation to give the 1-alkyl-1-aryloxiranes (**4**). Throughout the reaction and isolation of the product, no solvent is necessary. This simple and economical method appears important and valuable also as a pollution free synthetic procedure.

For example, a mixture of propiophenone (**3 a**) (0.5 g), **1** (0.9 g) and powdered *t*BuOK (0.5 g) was heated at 60 °C for 1 h in a flask, and then the reaction mixture was distilled using Kugelrohr at 150 °C under 18 mmHg, to give **4 a** (0.4 g, 75% yield). The spectral data was identical to those reported for **4 a**.[3]

By similar procedure, **4b-f** were prepared from the corresponding ketones (**3b-f**) and the products were isolated by distillation to give the yields in Table 1. The structures of **4b-f** were elucidated by comparison of their ^{1}H NMR spectra with those reported for **4 b**,[4] **4 c**,[5] **4 d**,[5] **4 e**,[6] and **4 f**.[7]


$\mathrm{Me_2\overset{+}{S}{-}Me \cdot I^-}$

1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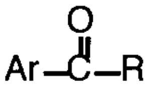
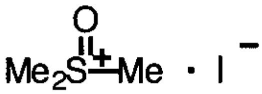
2


$\mathrm{Ar{-}\overset{\overset{O}{\|}}{C}{-}R}$

3

4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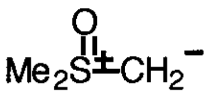
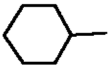
5


$\mathrm{Me_2\overset{\overset{O}{\|}}{S}\overset{+}{-}CH_2^-}$

6

Table 1 Preparation of **4** by the combination of methylene transfer reaction to **3** in the absence of solvent and by Kugelrohr distillation

	Ketone **3**		Reaction Conditions		Product **4**	
	Ar	R	temp (°C)	time (h)		yield (%)
3a	Ph	Et	60	1	**4a**	75
3b	Ph	*i* Pr	70	1	**4b**	89
3c	Ph		70	10	**4c**	91
3d	*p*-MeC_6H_4	Et	70	2	**4d**	86
3e	*p*-BrC_6H_4	Me	70	5	**4e**	64
3f	2-Naphthyl	Me	70	3	**4f**	86

For less volatile oxiranes, it may be useful to distill under high vacuum. For our new technique the reactivity of **2** is fully sufficient. We do not need Corey's more reactive reagent dimethyloxosulphoniumylmethanide (**6**).[1] It does react under our conditions, however, the yields are lower due to decomposition by the reagent. For example, a mixture of propiophenone (**3 a**) (0.5 g), trimethyloxosulphonium iodide (**5**) (1 g) and *t* BuOK (0.5 g) was heated at 50 °C for 3 h and the reaction mixture was extracted with ether. The ether solution was washed with water and dried over $MgSO_4$. Distillation of the product under 18 mmHg gave **4 a** (0.2 g, 34% yield). The same treatment of **3 b** with **5** and *t* BuOK followed by extraction with ether and distillation gave **4 b** in 52% yield.

The methylene transfer reaction in the absence of solvent can also be applied to aromatic aldehydes. For example, treatment with **1** and KOH of benzaldehyde (26%), *o*-tolualdehyde (58%), *p*-tolualdehyde (48%), and 1-naphthaldehyde (50%) followed by extraction of the products with organic solvent gave the corresponding oxiranes in the yields indicated. However, the products can not be isolated directly from the reaction mixture by distillation, because the products decompose under the conditions of the distillation.

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