

Conversion of Aldehydes and Ketones into Chloro-olefins and Acetylenes Using Chloriodomethane as a Chloromethylene Source

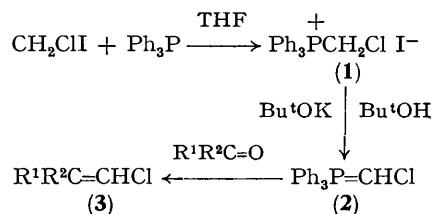
By SOTARO MIYANO,* YU IZUMI, and HARUKICHI HASHIMOTO

(Department of Applied Chemistry, Faculty of Engineering, Tohoku University, Aramaki-Aoba, Sendai 980, Japan)

Summary Chloriodomethane smoothly reacts with triphenylphosphine to yield chloromethyltriphenylphosphonium iodide (**1**), which in turn can be utilized for the conversion of aldehydes and ketones into chloro-olefins and acetylenes upon treatment with potassium *t*-butoxide.

WITTIG chloromethylenation of carbonyl compounds has been reported using chloromethylenetriphenylphosphorane (**2**),^{1,2} but the preparation of the requisite precursor chloromethyltriphenylphosphonium salts is rather complicated. We report here a convenient method for the synthesis of the phosphonium iodide (**1**) and its use for chloromethylenation (Scheme 1).[†]

The phosphonium iodide (**1**) was obtained as a white precipitate in 60–70% yield by heating a solution in tetrahydrofuran (THF) of triphenylphosphine and chloriodomethane³ (slight excess) under reflux for *ca.* 10 h [m.p.



SCHEME 1

BPh_4^- salt 190–193 °C (decomp.)¹].[‡] Potassium *t*-butoxide seemed to be the most suitable base for the deprotonation of (**1**) to give (**2**), the formation of which was shown by the appearance of a characteristic orange-red colour. Addition of an aldehyde or a ketone led to conversion into the corresponding chloro-olefin (**3**) in reasonable yield (Table), after purification by preparative g.l.c.

[†] Recently another method for the preparation of chloromethyltriphenylphosphonium chloride has appeared: R. Appel and W. Morbach, *Synthesis*, 1977, 699.

[‡] Satisfactory elemental analyses were obtained for all compounds.

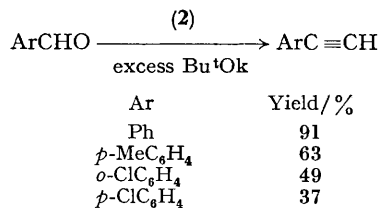
TABLE

Chloromethylenation of aldehydes and ketones (Scheme 1).^a

| R ¹ | R ² | Yield/% ^b of (3) | E:Z ratio |
|---|----------------|-----------------------------|--------------------|
| -[CH ₂] ₅ - | | 94 | |
| -[CH ₂] ₆ - | | 86 ^c | |
| -[CH ₂] ₄ CHMe- | | 89 | 92:8 |
| Ph | Me | 75 | 56:44 ^d |
| <i>p</i> -ClC ₆ H ₄ | Me | 59 | 52:48 |
| <i>p</i> -MeC ₆ H ₄ | Me | 65 | 57:43 |
| Ph | H | 81 | 46:54 |
| <i>p</i> -ClC ₆ H ₄ | H | 68 | 37:63 |
| Me[CH ₂] ₇ | H | 45 | 44:56 |

^a Compound (1) (25 mmol) was treated with Bu^tOK (30 mmol) in 50 ml of Bu^tOH for 1.5 h at ambient temperature, the carbonyl compound R¹R²C=O (20 mmol) was added, and the mixture was kept for 4 h under nitrogen. In the case of acetophenones, the olefin R¹R²C=CH₂ was also detected in 10–15% yield. ^b G.l.c. yield based on R¹R²C=O. ^c 10 mmol of R¹R²C=O. ^d Z-isomer: δ(CCl₄) 2.00 (3H, d, Me), 5.96 (1H, q, =CClH), and 7.18 (5H, s, Ph); E-isomer: δ 2.11 (3H, d, Me), 6.15 (1H, q, =CClH), and 7.15 (5H, s, Ph).

In the presence of excess of potassium t-butoxide (2.5 equiv.), prolonged reaction of aromatic aldehydes (8 h) gave phenylacetylenes, the procedure giving a route for the one-step conversion of the formyl group into an acetylenic function⁴ (Scheme 2).



SCHEME 2

(Received, 14th March 1978; Com. 280.)

¹ D. Seyferth, S. O. Grim, and T. O. Read, *J. Amer. Chem. Soc.*, 1960, **82**, 1510; 1961, **83**, 1617.² M. Schlosser and V. Ladenberger, *Chem. Ber.*, 1967, **100**, 3901.³ S. Miyano and H. Hashimoto, *Bull. Chem. Soc. Japan*, 1971, **44**, 2864.⁴ Cf. E. J. Corey and P. L. Fuchs, *Tetrahedron Letters*, 1972, 3769; J. Villieras, P. Perriot, and J. F. Normant, *Synthesis*, 1975, 151.