J.C.S. Снем. Сомм., 1978

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

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Summary Chloroiodomethane 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 tbutoxide.

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 chloro-iodomethane³ (slight excess) under reflux for *ca.* 10 h [m.p.



 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).8

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R¹	\mathbb{R}^2	Yield / % ^b of (3)	E:Z ratio
$-[CH_2]_5$	-	94	
$-[CH_2]_6$ $-[CH_2]_4$	- CHMe	89	92:8
Ph	Me	75	$56:44^{d}$
φ-ClC ₆ H₄	Me	59	52:48
φ-MeČ ₆ H₄	Me	65	57:43
Ph [°]	H	81	46:54
p-ClC ₆ H ₄	н	68	37:63
Me[CH ₂] ₇	H	45	44:56

^a Compound (1) (25 mmol) was treated with Bu^tOK (30 mmol) ^a Compound (1) (25 mmol) was treated with Bu OK (30 mmol) in 50 ml of Bu OH for 1.5 h at ambient temperature, the car-bonyl compound $R^1R^2C=O$ (20 mmol) was added, and the mixture was kept for 4 h under nitrogen. In the case of aceto-phenones, the olefin $R^1R^2C=CH_2$ was also detected in 10—15% yield. ^b G.l.c. yield based on $R^1R^2C=O$. ^c 10 mmol of $R^1R^2-C=O$. ^d Z-isomer: $\delta(CCl_4)$ 2.00 (3H, d, Me), 5.96 (1H, q, =CCIH), and 7.18 (5H, s, Ph); E-isomer: δ 2.11 (3H, d, Me), 6.15 (1H, q, =CCIH), 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).



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

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 ⁴ Cf. E. J. Corey and P. L. Fuchs, Tetrahedron Letters, 1972, 3769; J. Villieras, P. Perriot, and J. F. Normant, Synthesis, 1975, 151.