1,1-Di-iodoalkenes from Aldehydes and Triphenylphosphine–Carbon Tetraiodide

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The Wittig-like transformation of aliphatic and aromatic aldehydes into 1,1-di-iodoalkenes can be achieved with triphenylphosphine–carbon tetraiodide.

The reaction of aldehydes and ketones with Appel reagents[1,2] (PPh_3–CCl_4 or –CBr_4) has been used as a convenient method for achieving one-carbon homologations. The resulting 1,1-dihalogenomethylene derivatives have found application in the synthesis of acetylenes,[2] allenes,[3] 1,3-diynes, and α,β-unsaturated mono- and di-carboxylic acids.[4] The high versatility that vinyl iodides display in organic synthesis[5] and photochemistry[6] led to us to investigate, as part of a research project related to aryne chemistry,[7] the extension of the above reaction to the case of carbon tetraiodide. We now report the rapid and successful preparation of 1,1-di-iodoalkenes. This class of compounds is almost unknown since as far as we know only di-iodomethylenecyclohexane has been prepared *via* boron intermediates.[8]

Carbon tetraiodide was prepared by a literature procedure[9] and stored under argon at −30 °C. In a typical procedure a solution of triphenylphosphine (4 mmol) and carbon tetraiodide (2 mmol) in dry CH_2Cl_2 (20 ml) was stirred at 0 °C for 15 min. The aldehyde (1 mmol) was then added and the mixture stirred at room temperature for 2—3 h. After consumption of the aldehyde (t.l.c.), Zn powder (2 mequiv.) was added, the mixture stirred for 10 min and filtered, and the residue chromatographed on silica gel (hexane–CH_2Cl_2 as eluant). All compounds reported gave satisfactory spectroscopic data (i.r., n.m.r., and mass) and elemental analyses.

The addition of zinc at the end of the reaction period improves the yields by making the isolation of the iodo-compounds easier, probably by reacting with Ph_3PI_2 to give

Table 1. Yields for the reaction of the aldehydes RCHO with $Ph_3P–CI_4$ to give the di-iodoalkenes $RCH{=}CI_2$[a] and selected n.m.r. data.

R	% Yield (m.p., °C)	N.m.r. δ values[b]		
		$RCH{=}CI_2$ (H)	$RCH{=}CI_2$ (C)	$RCH{=}CI_2$ (CI)
Bu^n	75 (Oil)	6.9 (t, J 7.0 Hz)	153.3	11.2
Ph	87 (Oil)	8.2 (s)	151.0	11.8
p-ClC_6H_4	80 (Oil)	8.1 (s)	149.6	12.9
3,4-$(OCH_2O)C_6H_3$	60 (66.5—67.5)	8.0 (s)	150.2	10.3
3,4-$(MeO)_2C_6H_3$	72 (61—62)	8.1 (s)	150.3	9.0

[a] CH_2Cl_2, room temp.; 2—3 h; then Zn, room temp., 10 min. [b] In $CDCl_3$ at 23 °C. ^1H N.m.r. spectra were recorded at 200.1 MHz and ^{13}C n.m.r. spectra at 50.3 MHz on a Bruker AM-200 apparatus.

ZnI_2 and Ph_3P. Addition of zinc at the beginning of the reaction, as described by Corey,[2] seems not to be beneficial.

As can be seen from Table 1, the present method is applicable to aromatic as well as aliphatic aldehydes, but so far it does not appear to be applicable to ketones.

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