A Facile Preparation of Chloro-[3]-cumulenes

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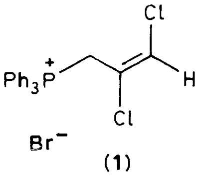
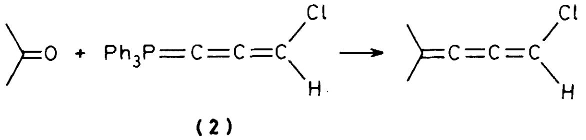
The phosphacumulene ylide derived from 1-(*trans*-2,3-dichloro-2-propenyl)triphenylphosphonium bromide (**1**) reacts with a wide variety of aldehydes and ketones to form substituted chloro-[3]-cumulenes.

Whereas allenes have found wide application in organic synthesis the [3]-cumulenes (buta-1,2,3-trienes) have not been utilised. This is in part due to the lack of good methods for their preparation,[1] particularly those bearing functional groups.[2] In efforts to make substituted [3]-cumulenes available for synthetic purposes we have developed a relatively simple preparation of 1-chloro-[3]-cumulenes by the route shown in Scheme 1.[3] The reagent was prepared from propargyl alcohol by chlorination with copper(II) chloride (4 equiv. in 2 M HCl, 20 °C, 24 h) to give (*E*)-2,3-dichloroallyl

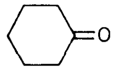
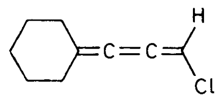
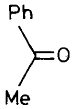
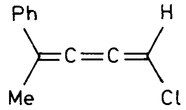
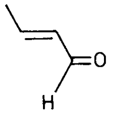
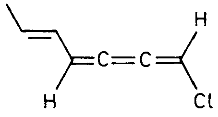
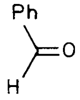
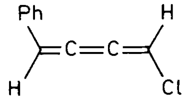
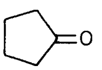
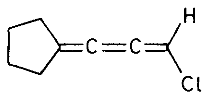
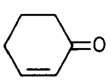
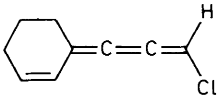
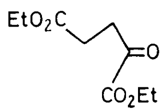
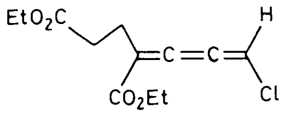


(**1**)



Scheme 1

Table 1. Chloro-[3]-cumulenes obtained by Wittig synthesis.

Carbonyl compound	[3]-Cumulene	Yield (%)
		88, 83[a]
		71[b]
		64[b]
		51[b]
		47
		6[b]
		17[b]

[a] KOBu^t used as base. [b] *Ca.* 1 : 1 (*E*), (*Z*) mixture.

alcohol (56%, b.p. 34°C 0.1 Torr).[4] This was followed by bromination (triphenylphosphine dibromide 1.2 equiv. *N,N*-dimethylformamide, 0°C) and direct reaction with triphenylphosphine (1.5 equiv. benzene, 20°C, 18 h) to give the salt (**1**) [62% m.p. 100°C (decomp.), recrystallised from cold ethanol –diethyl ether]. Conversion into the ylide (**2**) was achieved smoothly with lithium hexamethyldisilazane [$(Me_3Si)_2NLi$] (2 equiv., tetrahydrofuran, −30°C). The carbonyl compound was added (1 equiv., −30°C, 60 min) and dilution with diethyl ether and filtration through florisil followed by chromatography (hexane) over florisil provided the [3]-cumulenes, Table 1. These air sensitive substances were best handled in dilute solutions below 0°C and were characterised by i.r. (2040—2070 cm^{-1}), ^{13}C n.m.r. (145—175 p.p.m.), and mass spectroscopy. As can be seen in Table 1 there is little discrimination of product stereochemistry. In cases where this possibility arose approximately equal quantities of (*E*) and (*Z*) isomers were obtained.

Received, 3rd November 1983; Com. 1438

References

1 Reviewed by: M. Murray in 'Methoden der Organische Chemie,' ed. E. Muller, G. Thieme Verlag, Stuttgart, 1977, vol. V/2a, p. 263; H. Hopf in 'Chemistry of Ketenes, Allenes and Related Compounds,' ed. S. Patai, Interscience, Chichester, 1980, p. 779.

2 Some recent reports include: alkoxy-[3]-cumulenes, R. G. Visser, H. J. T. Bos, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas,* 1981, **100**, 34; dialkylamino-[3]-cumulenes, P. E. Van Rijn and L. Brandsma, *J. Organomet. Chem.,* 1982, **233**, C25; group 4 substituted-[3]-cumulenes, P. J. Stang, *Acc. Chem. Res.,* 1982, **15**, 348, and references cited therein.

3 Only the parent, chlorobutatriene, has been reported: R. Vistin, A. Borg, and T. Lindblom, *Acta. Chem. Scand.,* 1968, **22**, 685. Wittig routes to cumulenes have been used only for aryl substituted systems, *cf.* H. J. Bestmann and G. Schmid, *Tetrahedron Lett.,* 1975, 4025; K. W. Ratts and R. D. Partos, *J. Am. Chem. Soc.,* 1969, **91**, 6112.

4 This is a modification of an earlier method, *cf.* S. Yemura, H. Okazaki, A. Onoe, and M. Okana, *J. Chem. Soc., Perkin Trans. 1,* 1977, 676; G. M. Mkryan, D. G. Rofailyan, and N. A. Papazyan, *Arm. Khim. Zh.,* 1977, **30**, 57 (*Chem. Abstr.,* 1977, **87**, 677946). In our method the salt (**1**) is obtained as a single (*E*) isomer.