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Cumulated Trienephosphine Oxides. Trapping of an Alkylidenecyclopropylidene

Christiane Santelli-Rouvier* and Maurice Santelli

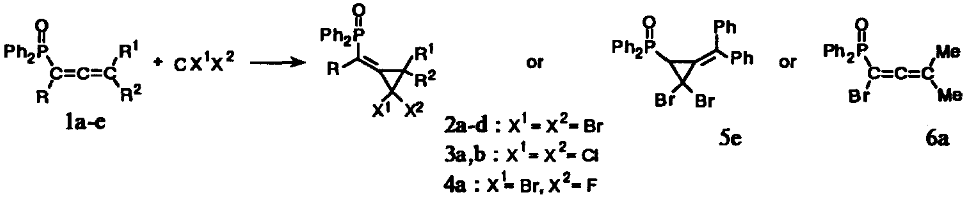
Lab. de Synthèse Organique associé au CNRS, Centre. de St-Jérôme, Av. Esc. Normandie-Niemen, 13397 Marseille Cedex 13 (Fr.)

Abstract: Treatment by BuLi of dibromocarbene adducts on allenic phosphine oxides leads to alkylidenecyclopropylidene that, in one case, is an exceptional stabilized cyclopropylidene: this carbene is trapped by the corresponding cumulated trienephosphine oxide in a bimolecular process.

Allenic phosphine oxides **1** are easily prepared by the method of Boisselle by action of propargylic alcohols on diphenyl phosphine chloride.[1] These compounds are Michael acceptors (several nucleophiles have been added since the first work of Horner: [2] cuprates, [3] alcoholates, [4,5] hydrazine, [4] N-phenyl hydroxylamine lithium salt [6]) and radical acceptors.[7]

To prepare cumulated trienic phosphine oxides that are expected to be versatile reagents, we report the addition of dihalocarbene on phosphine oxides 1 followed by a reduction with BuLi.

The regioselectivity of the addition of dihalocarbene [8] depends on the substituents and is independent of the nature of X: for **1a-d** ($R = R^1 = R^2 =$ alkyl), the addition occurs on the allylic position to phosphine oxide group giving **2a-d**, **3a,b**, **4a**. Only one stereoisomer of **2a-d** (isolated product: 40-50 % yield), **3a,b** (40-50 %) or **4a** is obtained.



1a-e

2a-d : $X^1 = X^2 = Br$
3a,b : $X^1 = X^2 = Cl$
4a : $X^1 = Br, X^2 = F$

5e

6a

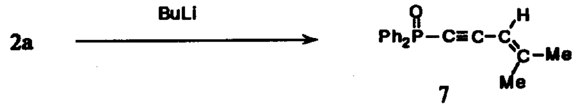
a: $R = H$; $R^1 = R^2 = CH_3$; **b**: $R = CH_3$; $R^1 = R^2 = CH_3$; **c**: $R = CH_3$; $R^1 = CH_3$, $R^2 =$ cyclo-C_3H_5;
d: $R = CH_3$; $R^1 = R^2 =$ cyclo-C_3H_5. **e**: $R = H$; $R^1 = R^2 = Ph$; **f**: $R = Ph$; $R^1 = R^2 = CH_3$.

In contrast for **1e**, the dihalocarbene adds to the vinylic position. When R = Ph (**1f**), the allenic compound is recovered unchanged.

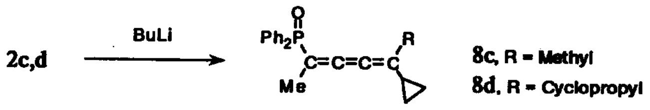
An attempt to add difluorocarbene generated by a phase-transfer catalyzed system (dibromomethane and dibromodifluoromethane)[9] failed, a bromoallene **6a** [10] was obtained.

The comparison between ^{13}C NMR of **2a-d**, **3a,b** and **4a** showed that the only isomer obtained presents the CX_2 group trans to the Ph_2PO one as $J_{PC(X2)} > J_{PC(R^1R^2)}$; $J_{PC(X2)} = 22$ to 24 Hz (δ for $C(X_2)$ in the range 31-81 ppm), $J_{PC(R^1R^2)} = 6$ to 10 Hz (δ for $C(R^1R^2)$ in the range 33-45 ppm).

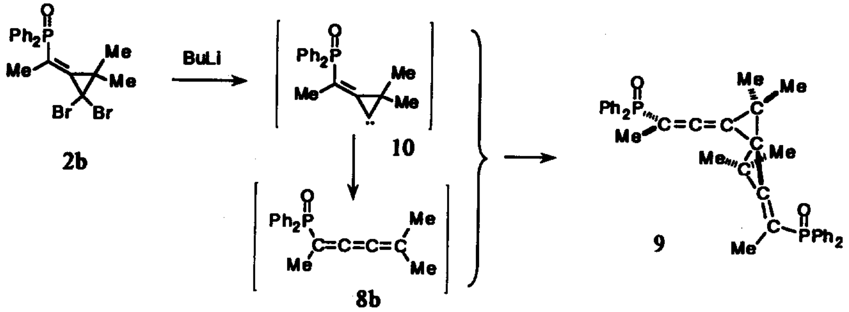
The dibromocyclopropanes were submitted to BuLi (THF, -90°C to 0°C). For **2a**, the reduction gives rise to the enyne 7 (27%).



In contrast, from **2c,d**, we obtained the expected trienic phosphine oxide **8c,d** (30-35 %).



A spectacular result is observed with **2b**: the only product is the spiro adduct **9** (one stereoisomer). The formation of **9** could result from the bimolecular addition of alkylidenecyclopropylidene **10** on the trienic phosphine oxide **8b**.



The IR of the crude product **9** shows a weak absorption at 2060 cm^{-1} indicating the presence of a triene **8b** but the only product isolated is **9** (30%) (IR: 1990 cm^{-1})[11] whatever the conditions of dilution or temperature have been.

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