

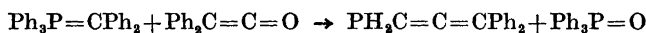
Study of the Applicability of the Wittig Reaction in Syntheses of Allenes

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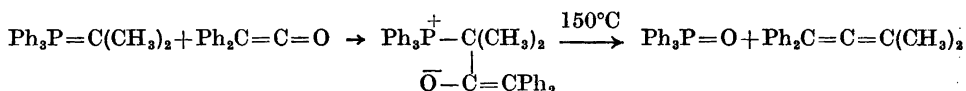
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The Wittig reaction has been of little importance in allene syntheses. Its limited success seems to be due to the stability of the betaine intermediate and instability of the allene formed. It is shown that substituents in the phosphorane and ketene which counteract both these effects give rise to good yields of allene derivatives.

Luscher¹ observed that tetraphenylallene was formed quantitatively when benzhydrylidene triphenylphosphorane and diphenylketene were heated to approximately 140°C:



In 1949 Wittig and Haag² isolated the betaine intermediate formed between isopropylidene triphenylphosphorane and diphenylketene. The betaine was shown to have a remarkable high stability; heating to 150°C *in vacuo* was necessary to obtain a moderate yield of diphenyl dimethylallene:



An attempt of the same authors to isolate diphenyl methylallene from ethylene triphenylphosphorane and diphenylketene failed.

Lately Birum and Matthews¹⁴ have isolated the allene derivative, 1,1-diphenyl-4,4-bis(trifluoromethyl)butatriene from the reaction between 2,2-bis(trifluoromethyl)vinylidene triphenylphosphorane and diphenylketene.

From the reaction between diphenylketene and the anion of phosphonate ester, Wadsworth and Emmons³ isolated the following allene derivative:

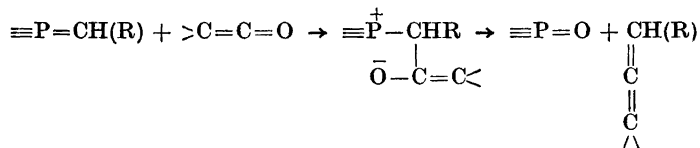


The present authors have studied the reaction between diphenylketene and methylene triphenylketene. When the crystalline betaine formed between these reactants was subjected to heating no diphenylallene could be obtained.

The negative result stimulated us to study the substituent effect in this type of Wittig reaction. According to our working hypothesis, the failure of the allene synthesis was caused by two effects: 1) the high stability of the betaine intermediate formed between phosphorane and ketene and 2) the instability of the allene formed.

Luscher¹ as well as Wittig and Haag² had shown that heating of the phosphorane and ketene to approximately 150°C was necessary for allene formation. Under this condition, polymerization of the allene may be difficult to avoid, especially if unsubstituted hydrogen atoms are linked to the allenic double bonds. With regard to the aforementioned formation of carboethoxy diphenylallene from diphenylketene and phosphonate anion, this compound contains a hydrogen atom linked to one of the allenic double bonds. But the stability of the allene is in this particular case greatly increased due to conjugation with the carbonyl group.

Kinetic studies of the Wittig reaction of stabilized phosphoranes (phosphoranes containing a C=O group in conjugation with the ylene bond) and ketones^{4,5} have shown that the decomposition of the betaine intermediate is so rapid that such intermediates have never been isolated.⁶ Given that the first step between stabilized phosphoranes and ketene, the formation of the betaine, is sufficiently rapid at room temperature, the reaction might prove suitable for allene synthesis since high reaction temperature can then be avoided.



Experiments proved the correctness of this assumption. In Table 1 is recorded various reactants and products from the present study. In addition to the allenes shown in Table 1, several other allenes made from other stabilized phosphorane and ketenes were identified in the reaction solution by following the disappearance of the infrared ketene absorption band at 2100 cm⁻¹ and appearance of the allene band at approximately 1950 cm⁻¹. Many of these allene compounds were, however, difficult to isolate in pure form due to decomposition during distillation.

In order to avoid the distillation procedure, allenes containing a carboethoxy group were subjected to acid hydrolysis. But after working up of the reaction product the corresponding allenic carboxylic acid could not be isolated. Maitland and Mills⁷ have reported that treatment of tetraphenylallene with acid gives an indene derivative:

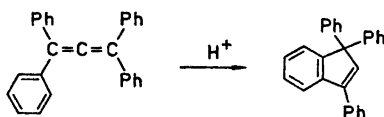


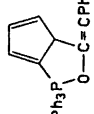


Table 1. Products from reaction between stabilized phosphoranes and ketenes.

No.	Reactants		Allene	Product formed						IR allene band (cm ⁻¹)
	Phosphorane ^a	Ketene ¹⁰⁻¹²		Analysis of products						
				% C		% H				
	(C ₆ H ₅) ₃ P-R	R ₁ R ₂ C=C=O	R ₁ R ₂ C=C=CR ₃ R ₄	calc.	found	calc.	found	calc.	found	
1	$\bar{R} = \bar{C}HCH(O)CH_3$	R ₁ =phenyl R ₂ =mesityl	R ₁ =phenyl, R ₂ =mesityl R ₃ =H, R ₄ =-C(O)CH ₃	85.08	84.34	7.29	7.24			1940
2	$\bar{R} = \bar{C}(CH_3)C(O)CH_3$	R ₁ =phenyl R ₂ =mesityl	R ₁ =phenyl, R ₂ =mesityl R ₃ =CH ₃ , R ₄ =-C(O)CH ₃	86.85	86.75	7.63	7.88			1930
3	$\bar{R} = \bar{C}(CH_3)C(O)OEt$	R ₁ =phenyl R ₂ =phenyl	R ₁ =R ₂ =phenyl R ₃ =CH ₃ , R ₄ =-C(O)OEt	81.06	81.92	6.52	6.12			1950
4	$\bar{R} = \bar{C}HCH(O)OEt$	R ₁ =phenyl R ₂ =mesityl	R ₁ =phenyl, R ₂ =mesityl R ₃ =H, R ₄ =-C(O)OEt	82.32	82.78	7.23	7.00			1950
5	$\bar{R} = \bar{C}HCH(O)OEt$	R ₁ =phenyl R ₂ =phenyl	R ₁ =R ₂ =phenyl R ₃ =H, R ₄ =-C(O)OEt	—	—	—	—			1950
			This allene was characterized as its acid hydrolysis product:							
6	—			81.33	80.75	5.23	5.32			1765 (C=O)
7	R = 	R ₁ =phenyl R ₂ =phenyl	gives no allene, but the betaine:	85.38	85.52	6.27	6.19			—
				% P calc.: 5.51, found: 5.76						

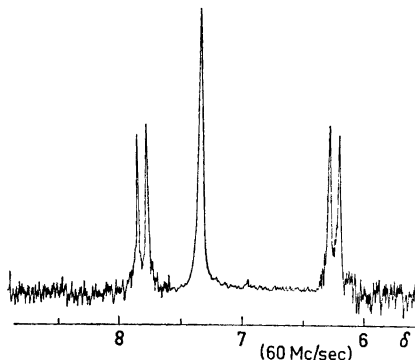
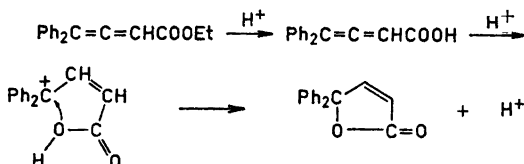
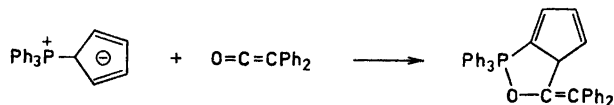


Fig. 1. The NMR spectrum of the cyclic unsaturated anhydride (No. 6, Table 1). The doublets at approximately 6.25 δ and 7.80 δ are due to the β -, respectively, α -vinyl protons. The phenyl hydrogens are seen as an unresolved peak at 7.35 δ . The absorption of the phenyl hydrogens have been damped relative to the vinyl protons.

IR and NMR spectra of the product from the acid hydrolysis of compound No. 5, Table 1, carbethoxy diphenylallene, excluded the indene structure in this case. The compound had a strong infrared band at 1765 cm^{-1} which pointed to a C=O group in a ring. The NMR spectrum (Fig. 1) revealed the presence of two equivalent phenyl groups. From the spectra and elementary analysis the compound was shown to be an unsaturated cyclic anhydride (compound No. 6, Table 1). The mechanism of its formation is probably as follows:

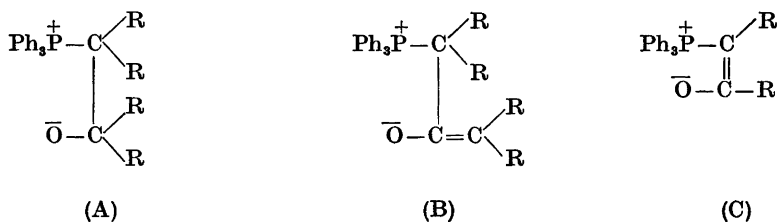


The very stable cyclopentadienyliene triphenylphosphorane is so far the only stable phosphorane which has not given allenic product with ketene. This phosphorane reacts, however, with diphenylketene, but the product formed contains phosphorus and no allenic IR band at 1950 cm^{-1} appeared. The isolated product melted at 248°C, it was sparingly soluble in carbon tetrachloride and toluene, but even less soluble in polar solvents. These findings argue against the dipolar betaine structure. Most reasonable the compound has arisen from an electrophilic attack of the ketene on the pseudoaromatic cyclopentadienyl ring:



A correspondingly electrophilic attack on cyclopentadienyliene triphenylphosphorane is observed with diazonium salt.⁸

With regard to the stability of different phosphonium betaines it is interesting to compare the following series of compounds:



When R is alkyl or phenyl groups (A) decomposes at room temperature, (B) at approximately 150°C, and (C) at 250°C. Two effects may contribute to the observed results: 1) The stability of the betaines increases from (A) to (C) because the charge on oxygen can be successively reduced through conjugation, making oxygen less nucleophilic and phosphorus less electrophilic. 2) The betaine (A) has two sp^3 -hybridized carbon atoms, the betaine (B) has one sp^3 - and one sp^2 -hybridized carbon atom, and betaine (C) has two sp^2 -hybridized carbon atoms in the four-membered ring intermediate. The net result is a successive increase of the P—C—C and C—C—O angles, making the closure of the four-membered ring correspondingly difficult.

EXPERIMENTAL

Materials. The phosphoranes⁹ and ketenes¹⁰⁻¹² used in this study were made according to description in literature.

Synthesis of allenes (see Table 1). Equimolecular amounts of ketene and phosphorane in dry benzene (approximately 0.3 M) were mixed together with rapid stirring. A considerable increase of temperature of the reaction mixture was usually observed. When the exothermic reaction was ended, the infrared spectrum of the reaction mixture was recorded. The product was worked up without further heating if no sign of the characteristic infrared ketene band at 2100 cm^{-1} was observed. The allene formation was always recognized on the strong band at approximately 1950 cm^{-1} . Most of the benzene in the reaction mixture was evaporated *in vacuo* whereafter the triphenylphosphine oxide was allowed to crystallize. After standing for 24 h the triphenylphosphine oxide was filtered off. Since the allene derivatives studied were very high boiling oils which did not crystallize, the problem of purification was difficult. The allene compounds recorded in Table 1 were distilled according to Kolf's "ruhenden Sumpf" method.¹⁵ In this method registration of distillation temperatures is so uncertain that boiling points of the allenes have been omitted in Table 1.

The cyclic compound (No. 7, Table 1) obtained from cyclopentadienylidene triphenylphosphorane and diphenylketene was sparingly soluble in the reaction solution. It was filtered off and recrystallized several times from toluene, yellow solid, m.p. 248°C. Analytical data are recorded in Table 1.

The cyclic anhydride (No. 6, Table 1) was obtained by treating diphenylcarbethoxyallene with excess half concentrated hydrochloric acid. The compound was recrystallized from ether, m.p. 133°C. Lit.¹³ m.p. 130–31°C. Its NMR spectrum is recorded in Fig. 1, and analytical data are given in Table 1.

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