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Cycloaddition Reactions of (Diethylphosphono)ketenes

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Methyl- and chloro(diethylphosphono)ketenes were found to add to cyclopentadiene or imines in unusual manner in the certain cases. Some chemical conversions and the Horner-Wittig reaction of the cycloadducts were examined.

Ketenes have been well recognized as the sysnthetic tools for the construction of four-membered carbo- and heterocycles owing to the ability of $(2\pi+2\pi)$ cycloaddition.$^{1)}$ From the synthetic points of view, there are many chemical modifications of ketenes,$^{2)}$ which opened new routes to complex molecules. Of these ketenes, some ketenes bearing heteroatom substituents$^{3)}$ have been so far developped and effectively functionalized four-membered compounds were synthesized by their cycloaddition reactions. In spite of numerous applications of modified ketenes, investigation of phosphonoketenes was almost limited to some electrophilic reactions only for the comfirmation of their generation. Kolodyazhnyi and his co-workers$^{4)}$ isolated (diethylphosphono)phenylketene but no cycloaddition reaction was reported. We now wish to report in this paper the cycloadditions of phosphonoketenes and some chemistries of cyclobutanones and β-lactams with phosphoryl substituents.

Methyl- and chloro(diethylphosphono)ketenes (**1a** and **1b**) were generated *in situ* from the corresponding acid chlorides$^{5)}$ and triethylamine. The characteristic absorption band of ketene of **1a** was observed at 2130 cm^{-1} in the IR spectrum of its reaction mixture. In the presence of excess cyclopentadiene or imines, both ketenes gave cycloadducts, cyclobutanone **2a** and **2b**, or β-lactams **3a**-**c**, respectively. The results are summarized in Table 1.

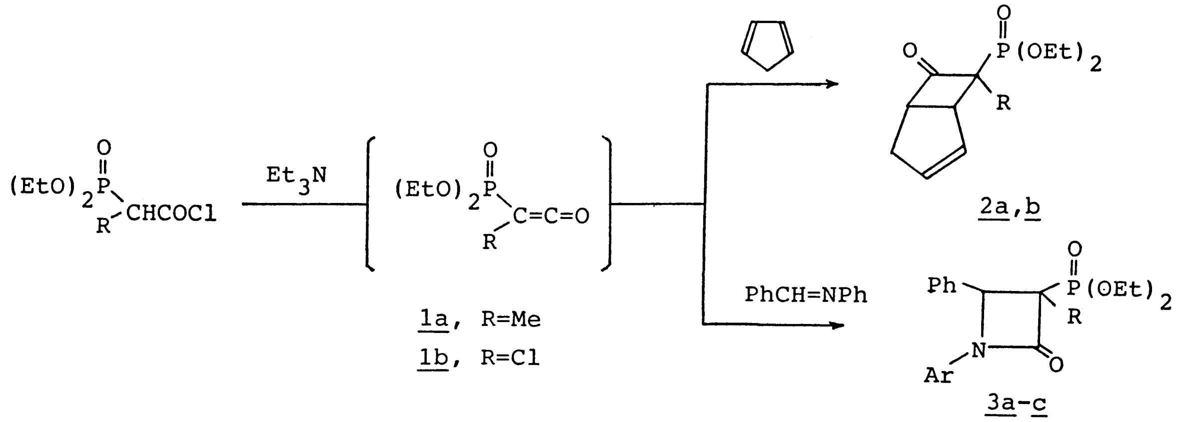


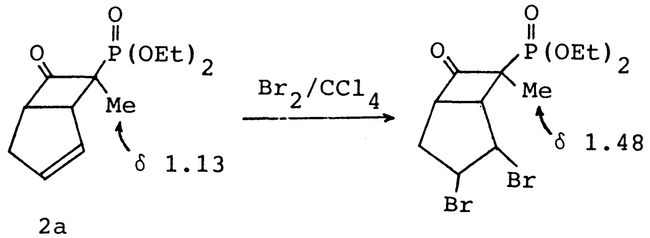
Table 1. Cycloadditions of Ketenes 1a and 1b

Products	R	Ar	Reaction condn.[a)] Solvent	Temp / °C	Yield/%[b)]	IR $\nu_{C=O}/cm^{-1}$	MS m/e(M^+)
2a	Me	-	Benzene	50	50	1765	258
2b	Cl	-	Benzene	0→50	64	1775	278
3a	Me	Ph	$CHCl_3$	r.t.	26	1730	373
3b	Cl	Ph	$CHCl_3$	0→r.t.	65	1770	393
3c	Cl	p-MeO-C_6H_4-	$CHCl_3$	0→r.t.	48	1760	423

a) 10 equiv. of cyclopentadiene or 2 equiv. of imines were employed, respectively. b) Yields after isolation by column chromatography.

Ketenes 1a and 1b added also to ethyl vinyl ether with complex side-products, while no reaction was observed when cyclohexene or styrene was employed as a reactant. On the other hand, alternatively prepared diethylphosphonoketene (1c, R=H) reacted only with benzylidenaniline to give a β-lactam in a very low yield (7%) as an isolable product.

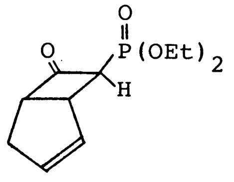
Of these adducts, the stereochemistry of 2a[6)] was clarified according to Brady's procedure.[7)] Namely, the signal of methyl group of 2a at δ 1.13 ppm shifted to the lower field at δ 1.48 ppm when the unsaturated moiety of 2a was brominated to exclude the shielding corn of π-electrons. This showed not only that methyl group of 2a occupied the endo position but also that the cycloaddition occurred in regioselective manner. Additionally, by comparing 2b[8)] and its dechlorinated product 4 (vide infra), we could also find that the chloro-substituent of 2b was in the endo position.[9)] These observations that the larger



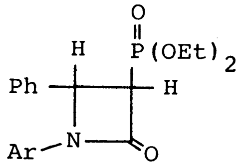
2a

substituents, phosphoryl groups, occupy the exo posotions contrasted with the modes observed in other ketene-cyclopentadiene adducts in which the larger substituents predominantly occupied the endo positions.[10)] However, there is an exception in the literature[2a)] that (carbomethoxy)chloroketene added to cyclopentadiene with the ester group in the exo position. The phosphoryl group of 1a and 1b might behave like the electron rich ester group of (carbomethoxy)-chloroketene compensating the steric repulsion. Although the stereochemistry of β-lactams 3a-c could not be determined, only one doublet of methine protons (J_{PH}=6.0-6.5 Hz) in their ^{1}H-NMR spectrum suggests that only cis or trans isomer was isolated in each case.

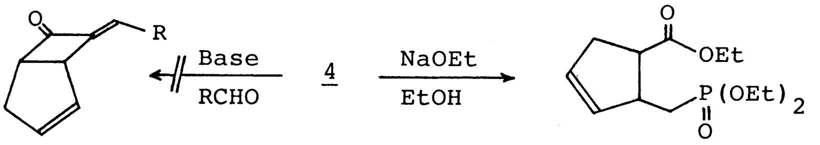
To explore the utility of the introduced phosphoryl groups, dechlorination of the adducts was performed. The treatment of 2b with zinc metal in acetic acid gave cyclobutanone 4, and the β-lactams 5a or 5b was obtained by the treatment of 3b or 3c with zinc metal in refluxing methanol in the presence of ammonium chloride, respectively. The small coupling constants between two methine protons (J_{HH}=3.6 Hz for 5a and J_{HH}=2.4 Hz for 5b) clearly showed that these β-lactams were trans isomers. In various conditions, the Horner-Wittig reaction of 4 did not proceed but the ring-opened product 6 was formed when sodium ethoxide was used as a base. We would like to explain this result as follows: in the anion 4 the phosphoryl group still occupies the exo position, so the carbonyl compounds must approach from the endo side where it is too crowded with the rigid cyclopentene ring and the corn of π-electrons for the reactants to close. In contrast to 4, β-lactams 5a and 5b reacted smoothly with carbonyl compounds by the action of sodium hydride at 0 °C to afford α-ylidene-β-lactams 7a-7d. 7b was found to be a mixture of E and Z isomers in the ratio of ca. 3:1 by ^{1}H-NMR spectrum, but in the case of 7a the ratio of mixture could not be determined because of overlapping of the olefinic proton with aromatic protons.



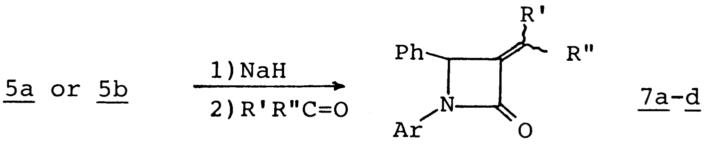
4 70%



5a, Ar=Ph 70%
5b, Ar=p-MeO-C_6H_4- 60%



6 71%



7a, R'=Ph, R"=H, Ar=Ph 80%
7b, R'= *iso*-Pr, R"=H, Ar=Ph 85%
7c, R'=Me, R"=Me, Ar=Ph 40%
7d, R'=Me, R"=Me, Ar=p-MeO-C_6H_4- 20%

Thus, we showed the first cycloadditions of (diethylphosphono)ketenes and some chemical conversions of their adducts.

References

1) W. T. Brady, "The Chemistry of Ketenes, Allenes and Related Compounds," ed by S. Patai, John Wiley & Sons, New York (1980), Chap. 8.

2) For recent examples, see: a) S. Goldstein, P. Vannes, C. Houge, A. M. Frisque-Hesbain, C. Wiaux-Zamar, and L. Ghosez, J. Am. Chem. Soc. 103, 4616 (1981); b) A. E. Greene, F. Charbonnier, M. J. Luche, and A. Moyano, ibid., 109, 4752 (1987).

3) For the recent review, see: M. Reichen, Chem. Rev., 78, 569 (1978); for the recent references which describe ($2\pi+2\pi$) cycloadditions of the ketenes with heteroatom substituents, see: M. Ishida, T. Minami, and T. Agawa, J. Org. Chem., 44, 2067, (1979); P. Michel, M. O'Donnel, R. Binaname, A. M. Hesbain-Frisque, and L. Ghosez, Tetrahedron Lett., 1980 2577; T. Agawa, M. Ishida, and Y. Ohshiro, Synthesis, 1980, 933.

4) O. I. Kolodyazhnyi, Zh. Obshch. Khim., 49, 716 (1979); O. I. Kolodyazhnyi, V. N. Yakovlev, and V. P. Kuhhar, ibid., 49 2485 (1979); O. I. Kolodyazhnyi and V. N. Yakovlev, ibid., 50, 55 (1980).

5) (Diethylphosphono)chloracetic chloride was prepared from ethyl (diethylphosphono)acetate by saponification, chlorination with sulfuryl chloride and then reaction with phosphorus pentachloride.

6) The ^{1}H-NMR spectrum of 2a: (CCl_4) δ 1.13 (d, 3H, endo-CH_3, J_{PH}=16.5 Hz), 1.33 (t, 6H, $C\underline{H}_3CH_2O$, J_{HH}=6.8 Hz), 2.2-2.8 (m, 2H, CH_2,) 3.6-4.3 (m, 6H, CH , $CH_3C\underline{H}_2O$), 5.5-6.0 (m, 2H, vinyl protons).

7) W. T. Brady and M. Holifield, Tetrahedron Lett., 1966, 5511.

8) The ^{1}H-NMR spectrum of 2b: ($CDCl_3$) δ 1.36 (t, 6H, $C\underline{H}_3CH_2O$), 2.48-2.78 (m, 2H, CH_2), 3.73-4.53 (m, 6H, CH, $CH_3C\underline{H}_2O$), 5.63-6.05 (m, 2H, vinyl protons).

9) While large difference of chemical shifts of vinyl protons between 2b and 4 could not be observed, the drastic change in the pattern of signal appeared. This can be also explained by occupation of chloro-substituent in the endo position.

10) W. T. Brady, F. H. Parry, III , R. Poe, Jr., and E. F. Hoff, Jr., Tetrahedron Lett., 1970, 819.

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