3-Cyano-3-methoxycarbonyl-2,4,4,5-tetraphenylpyrrolidine as a Precursor of Benzylidenammonium Benzylide

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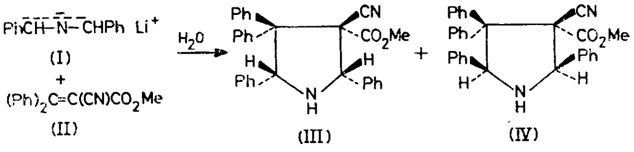
Summary On being heated in refluxing toluene, 3-cyano-3-methoxycarbonyl-2,4,4,5-tetraphenylpyrrolidine undergoes a retro-1,3-dipolar cycloaddition to yield benzylidenammonium benzylide, which is trapped by some dipolarophiles.

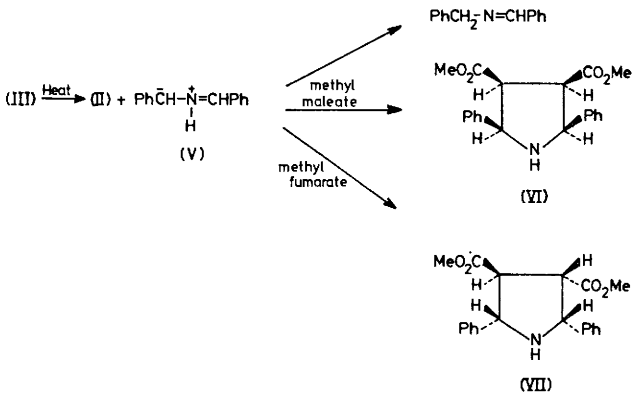
During the course of our work on the [3⁻ + 2] anionic polar cycloaddition of the lithium salt (I) with activated double bonds[1] we have studied the addition of (I)[2] to methyl α-cyano-β-phenylcinnamate (II) in tetrahydrofuran (THF) at −70 °C. Quantitative conversion takes place to give, after hydrolysis, the pyrrolidines (III) (80%) and (IV) (20%) (Scheme 1). From this mixture we could separate (III), m.p. 191 °C (from MeOH), in 75% yield (n.m.r. data and elementary analysis are in agreement with the proposed structure). This result shows that electron-withdrawing groups are not unsuitable for anionic cycloaddition.[3]



Scheme 1

TABLE. N.m.r. data for (VI) and (VII); δ values; $CDCl_3$ solution; Me_4Si internal standard

	M.p.°/C	NH	2-H	3-H	4-H	5-H	CO_2Me
(VI)	158	3·25	4·54q	3·70q	3·70q	4·54q	3·25
(VII)	174	2·41	4·38d	3·60m	3·60m	4·66d	3·12—3·60



SCHEME 2

When (III) was heated in refluxing toluene under nitrogen for 24 hours, we observed a retro-cycloaddition leading to the alkene (II) and the azomethine ylide (V) which forms benzylidenebenzylamine. In order to trap this ylide we ran the reaction in the presence of dipolarophiles such as methyl maleate or fumarate (Scheme 2) and we observed the formation of the corresponding pyrrolidine (VI) or (VII) quantitatively. Assignment of the stereochemistry of (VI) and (VII) is based on n.m.r. analysis (Table).

The addition is stereospecific and only the *cis–cis* or *trans–trans* form of the ylide reacts. The same reaction is observed with (*Z*)- or (*E*)-methyl cinnamate. It is important to mention that the addition of the anion (I) to methyl maleate or fumarate does not lead to pyrrolidines but to the corresponding diastereoisomeric imines $PhCH{=}N{-}CH(Ph)CH(CO_2Me)CH_2CO_2Me$.[1]

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[1] S. Sinbandhit, thèse de 3ème cycle, Rennes 1977, unpublished results.

[2] (I) was first prepared by T. Kauffmann, *Angew. Chem. Internat. Edn.*, 1974, **13**, 627, by reaction of lithium di-isopropylamide with benzylidenebenzylamine in THF–ether (9:1). We used n-butyl-lithium in THF.

[3] T. Kauffmann, H. Ahlers, A. Hamsen, H. Schulz, H.-J. Tilhard, and A. Vahrenhorst, *Angew. Chem. Internat. Edn.*, 1977, **16**, 119.