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A 3+1 CYCLOADDITION (1)

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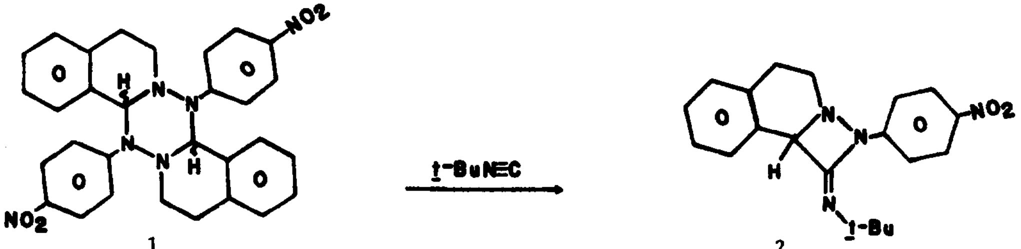
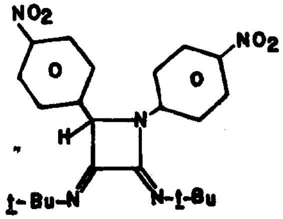
In spite of extensive investigation of cycloadditions, little is known concerning 3+1 cheletropic reactions (2,3). The one reported example, which involves the reaction of ozone with tertiary phosphite esters (4), is clouded with a certain amount of structural ambiguity (5). At least two other workers have considered 3+1 adducts as potential unstable intermediates in multistep chemical conversions (6). In neither case was the adduct isolated nor the arguments for its intermediacy considered compelling. An interest in the potential applications of 3+1 cycloadditions to heterocyclic syntheses has led to the discovery of the unequivocal example which is reported in this communication.



1 2

Reaction of a threefold excess of t-butyl isocyanide with hexahydrotetrazine 1 (7) at 100° for 6 hours yielded 1:1 adduct (8) 2 in 51% yield, melting point 188-190° dec. The nmr spectrum of this material had peaks at δ1.1 and 5.9 ppm (area ratio 9:1). This is in satisfactory agreement with values found for a similar methine and anisotropically shielded t-butyl protons in model compound 3 (9). The infrared spectrum of 2 lacks NH absorption but does show a peak at

1700 cm^{-1}. The latter value is consistent with the four-membered ring structure



3

and is in excellent agreement with values found for 3. Finally the mass spectrum of 2, in addition to a molecular ion of the proper value, also has an extremely intense base peak at 267 which corresponds to loss of t-BuNC from the molecular ion. The facile formation of t-BuNC further substantiates the assigned structure and argues against any rearrangement process in its formation.

Although the formation of 2 clearly results from the reaction between a 1,3-dipolar azomethine imine (formed from 1 (7)) and t-BuNC, it is not yet clear whether the reaction is stepwise or concerted. A search for additional examples of 3+1 cycloadditions and a study of the thermal and photochemical decompositions of these adducts is in progress.

References

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