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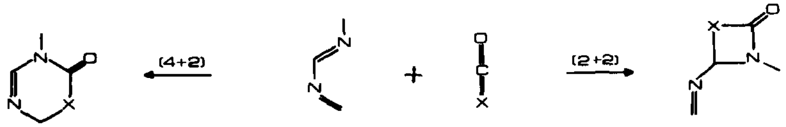
[2+2]- AND [4+2] CYCLOADDITION REACTIONS OF 1,3-DIAZABUTADIENES WITH DIPHENYLKETENE

Peter Luthardt and Ernst-Ulrich Würthwein*
Organisch-Chemisches Institut der Westfälischen Wilhelms-
Universität Münster, Orléansring 23, D-4400 Münster

Abstract: 1,3-Diazabutadienes react with diphenylketene in [2+2] - and [4+2] cycloaddition reactions, depending on the substitution pattern. Spectroscopic data (IR, ^{1}H- and ^{13}C-NMR) and results of quantummechanical model calculations (ab initio 3-21G) are presented.

Reports on syntheses and reactions of 1,3-diazabutadienes 1 are rare 1). Occasionally they have been postulated as reactive intermediates 2,3) or as substructures of heterocyclic imines 4). However, the chemistry of 4,4-bis-trifluoromethyl-1,3-diazabutadienes 5) is well developed, but these substances are not particularly representative for the parent system. Easy access to substituted derivatives of 1,3-diazabutadienes is possible via hydrogen migrations of 2,4-diazapentadienes-1,4 6), or - more generally - by condensation reactions of N-silylimines with imidoyl halides 7), and by reactions of appropriate amidine derivatives with carbonyl compounds 8).

As hetero-substituted butadienes, these reactive N-methylene amidines are of considerable synthetic interest for open chain and heterocyclic compounds. In terms of perturbation theory, one of the perturbating nitrogen atoms (in the 1-position) is situated in a favourable position of the wave function, whereas the other nitrogen atom is placed in an unfavourable site of the butadiene π-system (compare: chemistry of 2-aza-butadienes); thus, charge alternation and pronounced electron deficiency govern their reactivity.

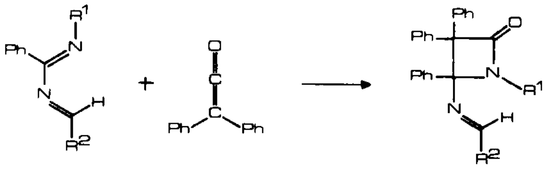


3 1 2

Cycloadditions of 1,3-diazabutadienes with heterocumulenes were investigated by Matsuda, Yamamoto and Ishii 7). As the first example of a [4+2] cycloaddition reaction they found the formation of dihydrotriazinones as products from an isolated 1,3-diazabutadiene derivative and isocyanates. With diphenylketene [2+2] cycloaddition was observed; the resulting azetidinones were unambigously characterized by IR- and ^{1}H-NMR spectroscopy. They explained the preference for [2+2] over [4+2] cycloadditions by steric factors.

Very recently Mazumdar, Ibnusaud and Mahajan 9) claimed the first isolation of a Diels-Alder cycloaddition reaction product of 1,3-diazabutadiene 1a with diphenylketene; they presented IR- and ^{1}H-NMR data as support for their six-membered ring structure.

In connection with our investigations on the chemistry of molecules containing two-coordinated nitrogen atoms 10) we are studying inter alia the reactions of 1,3-diazabutadienes; according to our IR- and ^{13}C-NMR measurements the product of the reaction of diphenylketene with 1-aryl-4-dimethylamino-2-phenyl-1,3-diazabutadiene 1a does not adopt the claimed six-membered ring structure (substance 4 in 9)); on the basis of the published IR absorption (given in 9): 1730 cm^{-1}, conformed by us) and numerous reports on IR data of ß-lactams, we assign the azetidinone structure 2a to the cycloadduct, well in line with the much earlier investigations by Matsuda et al. 7). Further support for the four-membered ring structure is obtained from the ^{13}C-NMR data (see. Tab.); the absorption of the imino carbon atom at 168.0 ppm is very indicative for the formulated ß-lactam structure. Obviously the three vicinal phenyl groups in 2a are not prohibitive for such a [2+2] cycloaddition reaction. Another example for the same type of reaction is our compound 2b, also definitely a four-membered ring system. On the other hand, the reported pyrimidinone derivative (3 in 9)), prepared form 1a and monophenylketene, has definitely the assigned six-membered ring structure (IR-, ^{13}C-NMR data).



1a,b

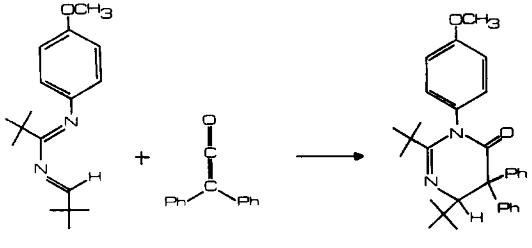
2a,b

1a,2a: $R^1 = Ph$ $R^2 = N(CH_3)_2$

1b,2b: $R^1 = R^2 = tBu$

However, it is possible to react 1,3-diazabutadienes with diphenylketene in a [4+2] Diels-Alder type reaction as well. The sterically strained tert.-butyl derivate 1c forms readily the dihydropyrimidinone system 3; first evidence for this structure is obtained from the IR spectra (1653 and 1695 cm^{-1} for C=N/C=O), which is supported again by ^{13}C-NMR data (see Tab.). As anticipated, the doublet for carbon 4 is found at 69.0 ppm.

The alternative [2+2] cycloaddition of 1c with diphenylketene would give rise to a azetidinone with one tert.butyl and two phenyl groups in vicinal positions, undoubtedly suffering from severe steric hindrance. Thus we confirm Matsudas et al. explanation that steric reasons are decisive for the mode of the cycloaddition.



1c 3

Table: Physical and spectroscopic properties of compounds **2** and **3**.

	R^1	R^2	mp (°C)	Yield (%)	IR (CN/CO) (cm^{-1})	^{1}H-NMR (-CH-) (ppm)	^{13}C-NMR (ppm)
2a	Ph	N(CH3)2	162 164-165[8]	74 91[8]	1645(s), 1730(s)	6.83	79.6(C-3),86.0(C-4), 152.2(CH),168.0(CO)
2b	tBu	tBu	155	34	1628(m), 1667(s), 1672(s), 1743(s)	7.47	78.0(C-3),89.3(C-4), 170.5(CO),172.2(C-H)
3	-	-	255	52	1653(s), 1695(s)	4.48	65.8(C-5),69.0(C-4), 156.0(C-2),173.7(CO)

The cycloaddition chemistry of ketenes[11] is dominated by [2+2] type reactions ; however, if electron-deficient dienes are used, Diels-Alder reactions with invers electron demand became feasible. Certainly 1,3-diazabutadienes, as indicated above, fulfill these requirements.

We complete our experimental results by ab initio 3-21G model calculations for the parent compounds[12,13]; the best conformer of 1,3-diazabutadiene was found to be the s-trans form with Z-configuration at the C=NH-unit (E(RHF) = -185.85376 au, E_{rel} = 0.00 kcal/mol); a gauche minimum ($\Theta_{C=N-C=N}$ = 60°) is 2.75 kcal/mol higher in energy. For the isomers with E-C=NH-unit a gauche conformer ($\Theta_{C=N-C=N}$ = 30°) is predicted to be the global minimum (E_{rel} = 1.31 kcal/mol); the s-trans form corresponds to a local minimum, 3.48 kcal/mol higher in energy (E_{rel} = 4.79 kcal/mol). Both s-cis-conformers are maxima (transitions states of the C-N-rotation). - Since the barriers for the rotation around the C-N-bond for both series are small (4-6 kcal/mol; maxima at ca. Θ = 110 and 120°), sterically and electronically favourable arrangements for [2+2] and [4+2] cycloaddition reactions can be expected.

The formation of the azetidinone is a kinetically governed process, because this ß-lactam derivative (E(RHF)= -336.78369 au) is predicted to be ca. 32

kcal/mol higher in energy than the corresponding 4,5-dihydro-6-pyrimidinone system (E(RHF)= -336.83447 au). From this data and from the total energy of ketene (E(RHF)= -150.87653 au) heats of reaction for the formation of the four-membered ring of ca. -34 kcal/mol and for the six-membered ring of -66 kcal/ mol are predicted, both reactions being fairly exothermic processes.

Because of the substantial differences in electronegativity of the reacting atoms we propose a non-synchronous concerted or even stepwise mechanism for both cycloaddition reactions 14). The [2+2] cycloaddition of 1,3-diazabutadiene along the 3,4-N=C-double bond with ketenes would lead to a regioisomer of <u>2</u>; such a N-substituted ß-lactam (according to AM1 15)) is ca. 6 kcal/mol higher in energy than the observed product. Similarly, other possible four- and six-membered isomers within the $C_4H_5N_2O$ group of substances were calculated to be more energy rich using the AM1 method.

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