Tetrahedron Letters,Vol.27,No.48,pp 5875-5876,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

DIELS-ALDER CYCLOADDITION REACTIONS OF 1,3-DIAZABUTADIENES WITH KETENES

Sujit Nandy Mazumdar, Ibrahim Ibnusaud and Mohinder Pal Mahajan*.
Department of Chemistry, North-Eastern Hill University, Shillong 793 003, Meghalaya, INDIA.

Abstract - Diels-Alder cycloaddition reactions of 1-aryl-4-dimethylamino-2-phenyl-1,3-diazabutadienes with monophenyl and diphenylketenes, resulting in high yields of pyrimidin-6-one derivatives are reported.

Cycloaddition reaction of hetero-dienes have been shown to be of great potential for synthesis in heterocyclic chemistry[1,2]. Dienes containing two nitrogen atoms have attracted the attention of chemists in recent years because of their importance in natural products synthesis[3-5]. There are numerous literature reports concerning the participation of 1,2- and 1,4-diazabutadienes, in which part of the heterodiene is incorporated into either aromatic or heterocyclic systems, as 4π components in Diels-Alder reactions. On the other hand, Diels-Alder reactions of simple 1,3-diazabutadienes are very rare and have not been exploited for the synthesis of heterocyclic compounds. 1-alkyl(aryl)-2,4,5-triphenyl-1,3-diazabutadienes, for example, failed to react with dimethyl acetylenedicarboxylate but affords (2+2) cycloadducts with diphenylketene[6].

We report here (4+2) cycloaddition reactions of 1-aryl-4-dimethylamino-2-phenyl-1,3-diazabutadienes (1)[7] with monophenylketene and diphenylketene resulting in high yields (84-96%) of 1-aryl-2,5-diphenyl-1,6-dihydropyrimidin-6-one (3) and 1-aryl-4-dimethylamino-2,5,5-triphenyl-1,2,5,6-tetrahydropyrimidin-6-one (4), respectively. Cycloadditions were carried out by the dropwise addition of a solution of acid chloride (2.4 mmol) in dry benzene (10 ml) to an ice-water cooled (5-10°C) stirred benzene (20 ml) solution of 1-aryl-4-dimethylamino-2-phenyl-1,3-diazabutadienes (2 mmol) and triethylamine (4 mmol). After the complete addition of acid chloride the reaction mixture was stirred for a further 30 min at the same temperature. It was then washed with cold water, saturated sodium bicarbonate solution and finally dried over anhydrous sodium sulphate. The crude product obtained by removal of benzene under reduced pressure was recrystallised from a mixture (1:1) of benzene and hexane.

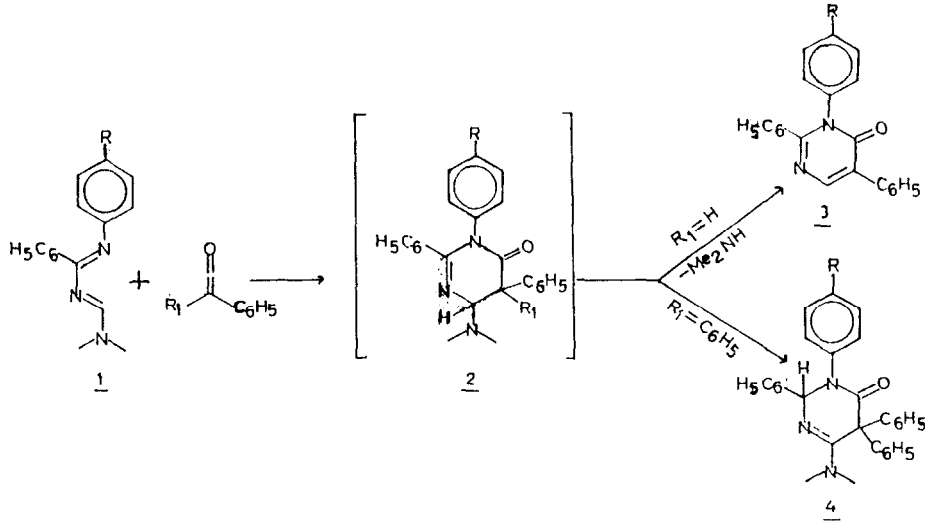

Table 1

Product No.	R	Yield(%)	m.p.(°C)	m/z(M^+)	Product No.	R	Yield(%)	m.p(°C)	m/z(M^+)
3 a.	H	86	166-7	324	4 a.	H	91	164-5	445
3 b.	CH_3	92	196-7	338	4 b.	CH_3	95	148	459
3 c.	Cl	86	163-4	358	4 c.	Cl	85	180	479
3 d.	Br	84	222-3	403	4 d.	Br	96	174-6	524

It seems that the reactions of 1,3-diazabutadienes (1) with monophenylketene and diphenylketene proceed through an intermediate 2. In the case of monophenylketene this undergoes elimination of dimethylamine leading to 3, whereas in the case of diphenylketene it isomerises to 4. The products are assigned structures 3 and 4 on the basis of analytical and spectral (IR, ^{1}H NMR, and MS) data. IR spectra of 3 and 4, for instance, show >C=O stretching around 1675 and 1730 cm^{-1}, respectively, while the ^{1}H NMR spectra of 3 and 4 show the absence and presence of $-N(CH_3)_2$ protons, respectively[8]. In case of diphenylketene the product has been assigned the structure 4 since the methine proton in such an environment is expected around δ 6.7[9] as observed[8], whereas the methine proton in an environment similar to that of 2 is expected around δ 5[10]. The cycloaddition studies of these and other related 1,3-diazabutadienes with various dienophiles and heterodienophiles are under way.

References

1. D. L. Boger, Tetrahedron, 39, 2869 (1983).
2. S. M. Weinreb and R. R. Slaib, Tetrahedron, 39, 3087 (1982).
3. L. E. Overman, C. B. Petty, T. Ban and G. T. Huang, J. Am. Chem. Soc., 105, 6335 (1983).
4. M. L. Bremmer and S. M. Weinreb, Tetrahedron Lett., 261 (1983).
5. D. L. Boger and J. S. Panek, J. Org. Chem., 48, 621 (1983).
6. I. Matsuda, K. Itoh and Y. Ishii, J. Chem. Soc. Perkin Trans 1, 1678 (1972).
7. All 1,3-diazabutadienes reported here were prepared by the reported procedure; M. Nishi, S. Tanimoto, M. Okano and R. Oda, Yuki Gosei Kagaku Kyokai Shi, 27 (9), 754 (1969); Chem. Abstr., 71, 101438v (1969).
8. ^{1}H NMR data (90 MHz) δ downfield from Me_4Si; $CDCl_3$: 3a: 7.4, m, 15H, aromatic, 8.1, s, 1H, vinyl; 3b : 2.3, s, 3H, $-CH_3$, 7.4, m, 14H, aromatic, 8.15, s, 1H, vinyl; 3c: 7.4, m, 14H, aromatic, 8.3, s, 1H, vinyl; 3d: 7.4, m, 14H, aromatic, 8.3, s, 1H, vinyl; 4a: 2.7, s, 6H, $-N(CH_3)_2$, 6.83, s, 1H, methine, 7.3, m, 20H, aromatic; 4b: 2.1, s, 3H, $-CH_3$, 2.6, s, 6H, $-N(CH_3)_2$, 6.9, s, 1H, methine, 7.35, m, 19H, aromatic; 4c: 2.7, s, 6H, $-N(CH_3)_2$,6.86, s, 1H, methine, 7.3, m, 19H, aromatic; 4d: 2.6, s, 6H, $-N(CH_3)_2$, 6.83, s, 1H, methine, 7.4, m, 19H, aromatic. Satisfactory analytical data were obtained for all new compounds.
9. E. G. Tsatsaroni (2), N. G. Argyropolos, N. E. Alexandrou, A. Aoundas and A. Terzis, J. Heterocyclic Chem., 21, 1405 (1984).
10. L. C. Citerio, D. Pocar, M. Saccarello and R. Stradi, Tetrahedron, 35, 2453 (1979).

(Received in UK 8 October 1986)