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

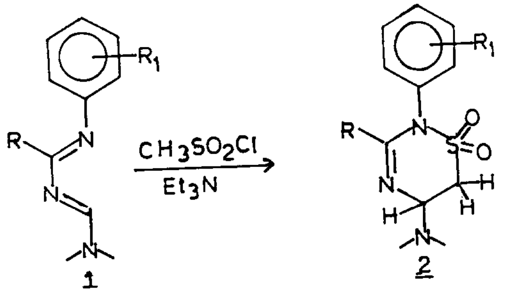
*Sujit Nandy Mazumdar, Manoj Sharma and Mohinder Pal Mahajan**

Department of Chemistry, North-Eastern Hill University,
Shillong 793 003, Meghalaya, India.

Abstract - Diels-Alder cycloaddition reactions of 1-aryl-4-dimethylamino-2-phenyl(thiomethyl)-1,3-diazabutadienes with sulfene resulting in good yields of 1,2,4-thiadiazine-1,1-dioxide derivatives are reported.

The heterodiene Diels-Alder reaction is one of the most versatile routes for the synthesis of heterocyclic compounds[1]. Appropriate selection of heterodienes with dienes and heterodienophiles allows for a wide range of structural and functional variations in the adducts. Although, there are numerous reports concerning the (4+2) cycloaddition reactions of 1,2- and 1,4-diazabutadienes but the reports concerning the Diels-Alder cycloaddition reactions of simple 1,3-diazabutadienes are very rare. Similarly, it was observed that highly reactive heterodienophile simple sulfene either do not add to C=N double bond[2] or had evaded the attention of synthetic chemists. On the other hand, benzoyl sulfene generated from benzoylmethanesulfonyl chloride and triethylamine was reported to react with anils[3,4] and carbodiimides[5] to give the (2+2) and / or (4+2) cycloadducts. Recently we have reported the (4+2) cycloaddition reactions of acyclic 1,3-diazabutadienes with ketenes resulting in good yields of pyrimidine-6-one derivatives[6].

Here we report successful (4+2) cycloaddition reactions of 1-aryl-4-dimethylamino-2-phenyl-1,3-diazabutadienes (1a-1c)[7] with sulfene resulting in high yields of previously unknown 2-aryl-5 - dimethylamino-3-phenyl-4,5-dihydro-1,2,4-thiadiazine-1,1-dioxide derivatives (2a-2c). Cycloaddition reactions were realised by the dropwise addition of a solution of methanesulfonyl chloride (3 mmol) in dry benzene (10 ml) to a cooled (0-5°) 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 methanesulfonyl chloride the reaction mixture was stirred for a further period of 2 hrs at the same temperature. It was then filtered, the filtrate washed with cold water (4x20 ml) and dried over anhydrous magnesium sulfate. The solvent was then removed under reduced pressure and the crude product so obtained was recrystallised from a mixture (1:1) of benzene and hexane.



R=C_5H_5;R_1=H(a);R_1=p-CH_3(b);
R_1=p-Cl(c);
R=SCH_3;R_1=H(d);R_1=p-CH_3(e);
R_1=o-CH_3(f);R_1=p-Cl(g);
R_1=p-OCH_3(h).

In order to further understand the nature of these cycloaddition reactions, we thought it worthwhile to introduce another polarising function at the second position of these 1,3-diazabutadienes. For this purpose, we have synthesised hitherto unknown 1-aryl-4-dimethylamino-2-thiomethyl-1,3-diazabutadienes (1d-1h)[8] and carried out the cycloaddition reactions as described above. The (4+2) cycloaddition reactions in these cases have been found to be much nearer and results in much better yields of 2-aryl-5-dimethylamino-3-thiomethyl-1,2,4-thiadiazine-1,1-dioxide (2d-2h).

TABLE 1

Product No	R	R_1	Yield(%)	mp.(°C)	Product No	R	R_1	Yield(%)	mp.(°C)
2a	C_6H_5	H	64	121-2	2e	SCH_3	p-CH_3	94	161-3
2b	C_6H_5	p-CH_3	70	111-2	2f	SCH_3	o-CH_3	86	86-8
2c	C_6H_5	p-Cl	60	115-6	2g	SCH_3	p-Cl	90	109-10
2d	SCH_3	H	80	111-2	2h	SCH_3	p-OCH_3	82	84-6

The products have been assigned structure 2 on the basis of analytical and spectral (IR, ^1H NMR[9] and MS[9]) data. IR spectra of 2 show characteristic SO_2 stretchings around 1140 and 1340 cm^{-1} and the ^1H NMR spectra of 2 show methine proton as doublet of a doublet around 4.9 δ and methylene protons as a multiplet around 3.4 δ. The cycloaddition reactions of such 1,3-diazabutadienes with various dienophiles and heterodienophiles are under progress.

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7. All 1,3-diazabutadienes (1a-1c) 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. These 1,3-diazabutadienes were prepared by the reaction of N,N-dimethylamino-N^1-arylthiocarbamoyl formamidines with methyliodide in dry acetone at room temperature. The separated hydroiodide salt was basified with 3N KOH. The basified solution was extracted with benzene, washed with water and dried over anhydrous magnesium sulfate. The removal of benzene under reduced pressure resulted in sufficiently pure desired 1,3-diazabutadienes. 1d:IR:3050,2900,1640,1540 cm^{-1}; ^1H NMR (90 MHz),δ $CDCl_3$: 2.3,s,3H,-SCH_3,2.9,s,6H,-$N(CH_3)_2$,7.2,m.5H,aromatic, 8.2,s,1H,vinylic. The thiocarbamoyl formamidines were prepared by the reported procedure Y.Lin, S.A.Lang.Jr and S.R. Petty, J.Org. Chem.,45, 3750(1980).
9. ^1H NMR data (90 MHz)δ downfield from Me_2Si, $CDCl_3$:2a: 2.5,s,6H,-$N(CH_3)_2$3.3,m,2H, -CH_2-,5.0,dd,1H,methine(Jtrans 8-10 Hz,Jcis 3-4 Hz),7.4,m,10H,aromatic; 2d: 2.2,s,3H, -SCH_3,2.4,s,6H,-$N(CH_3)_2$,3.5,m,2H-CH_2-4.9,dd,1H,dd,1H,methine (J trans 8-10 Hz, J cis 3-4 Hz), 7.5,m,5H,aromatic. MS,2a,m/z, 329. Satisfactory analytical data were obtained for all new compounds.

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