Tetrahedron Letters No. 49, pp 4761 - 4764.

0040-4039/79/1201-4761$02.00/0

REACTIONS OF CYCLOHEXANONE ENAMINES WITH ASYMMETRIC DIIMIDES

A.Bigotto, M.Forchiassin, A.Risaliti* and C.Russo
Istituto di Chimica, Universitã, 34127 Trieste, Italy

Abstract - Tetrasubstituted enamine derivatives which rearrange into 1,3,4-oxadiazine isomers have been isolated from aryl acyl diimides and 1-morpholinocyclohexenes. The same reactions with 1-pyrrolidinocyclohexenes have led directly to the cyclic derivatives.

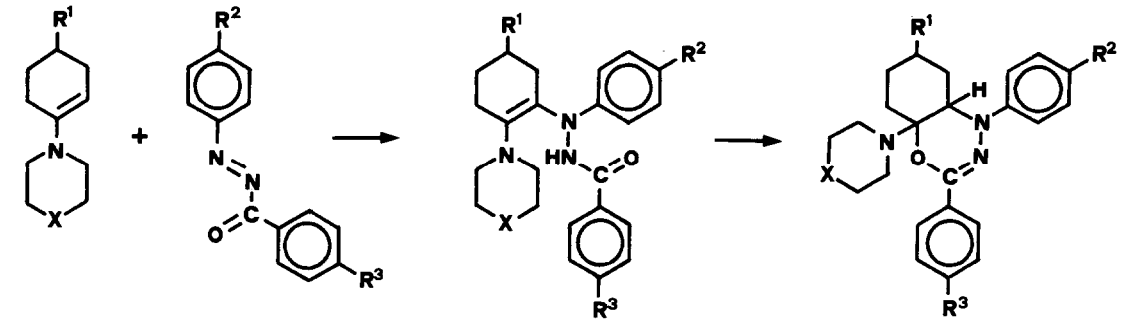
Symmetric diimides such as dialkyl azodicarboxylates and diacyl diimides furnish different 1:1 adducts in the reactions with electron-rich olefins. In particular, azodicarboxylates reacting with cyclohexanone enamines yield only trisubstituted enamine derivatives which do not undergo any further rearrangement,[1] while 1,2-diazetidine or 1,3,4-oxadiazine derivatives are obtained from the same electrophiles and enolethers.[2] On the other hand only 1,3,4-oxadiazines are formed when both enamines and enolethers[3,4] are reacted with diacyl diimides.

Owing to our interest in this field, this variety of results prompted us to investigate the behaviour of asymmetric diimides of type Ar-N=N-CO-Ar, Ar-N=N-CO_2Et, and Ar-CO-N=N-CO_2Et in the reactions with the same substrates.

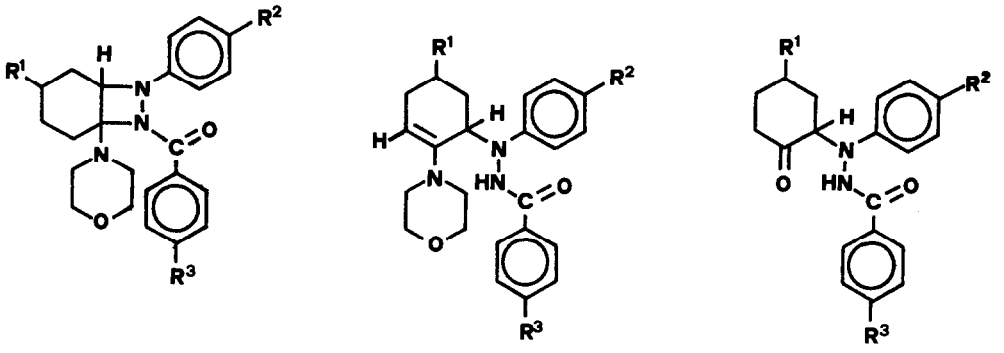
In this communication we wish to report the preliminary results of the reactions between enamines (1) and (2) and aryl acyl diimides (3).

In a typical procedure, dropwise treatment of 1-morpholinocyclohexene (1a) with phenyl benzoyl diimide (3c)[5] (anhydrous ether, 48 hr at 0°C under N_2)[6] afforded a 1:1 adduct (23%) which showed IR absorption bands at 3360 and 1670 cm^{-1}, corresponding to NH and CO stretchings, respectively. The Raman spectrum, besides the CO stretching which appeared as a shoulder at 1666 cm^{-1}, showed a line at 1659 cm^{-1}, attributable to a C=C stretching. The NMR spectrum exhibited the NH signal at δ 10.05 while no proton resonance appeared in the δ 3.5÷6.5 range. These data are inconsistent both with the 1,2-diazetidine (7ac),enamine (8ac), and oxadiazine (5ac) structures, whose N-C=CH and/or N-CH signals should have been present in the δ 3.5÷5.5 range. All the spectral data agree only with a tetrasubstituted enamine structure which is therefore assigned to the adduct (4ac) (Scheme). On treatment with polar solvents even at room temp or on heating in apolar solvents, (4ac) converted quantitatively into the corresponding oxadiazine derivative (5ac), as indicated by the IR spectrum (no NH and CO bands, ring C=N stretching at 1625 cm^{-1}) and NMR spectrum (multiplet at δ 4.2 relative to the proton at C-4a).

S C H E M E



(1) x=O (2) x=- (3) (4) x=O (5) x=O (6) x=-



(7) (8) (9)

a: R^1=H b: R^1=Bu^t c: R^2=R^3=H d: R^2=H, R^3=NO_2 e: R^2=NO_2, R^3=H

Acidic hydrolyses of both (4ac) and (5ac) gave ketone (9ac) [m.p. 170-3°. IR(Nujol) cm^{-1}, 3380 (NH), 1710 (CO), 1680 (CO-NH). NMR($CDCl_3$)δ, 8.45 (s, NH), 4.65 (m, W_H 20 Hz, N-CH)]. When the hydrolysis of (4ac) was run in deuteriated medium (D_2O, traces of CF_3COOD in CD_3COCD_3) the same ketone with a deuterium atom at C-2 was obtained, as shown by the absence of the signal at δ4.65 in the NMR spectrum. This result confirmed the structural assignment for the adduct (4ac).

Similar adducts (4), which gave facile quantitative rearrangement into (5), were obtained from (1a) with (3d)[7] and (3e)[8], and from (1b) with (3c-e) (Table). As for the adduct (4ae), its IR spectrum showed an NH stretching at 3240 cm^{-1} and two bands at 1670 and 1652 cm^{-1}, and its NMR spectrum exhibited a broad signal (0.3 H) at δ 4.75. These spectral data suggested the presence of small amounts of the isomeric enamine (8ae) and/or the 1,2-diazetidine derivative (7ae). Attempts to separate them failed, the only result being the quantitative rearrangement of the mixture into the corresponding oxadiazine (5ae).

TABLE

Compd[a]	mp[b] °C	Yield %	IR(Nujol) $\nu_{max}(cm^{-1})$ NH	CO	C=N	RAMAN[d] $\Delta\nu(cm^{-1})$ C=C	^1H NMR[e] (δ) NH	N-CH(W_H)[f]
(4ac)	123-5	23	3360	1670		1659	10.05	
(5ac)	132-3	51[c]			1625			4.2 (18)
(4ad)	145-7	20	3340	1672			10.42	
(5ad)	159-60	42[c]			1625			4.21(18)
(4ae)	132-40	80	3240	1670			10.6	4.75
(5ae)	170-2	80			1630			4.22(18)
(4bc)	138-40	41	3360	1675		1654	10.1	
(5bc)	173-5	52[c]			1628			4.15(15)
(4bd)	150-2	21	3350	1680			10.4	
(5bd)	175-7	44[c]			1625			4.18(16)
(4be)	158-60	74	3230	1680			10.56	
(5be)	188-90	74			1630			4.28(18)
(6ac)	104-6	47			1620			4.1 (18)
(6ad)	103-5	50			1618			4.18(18)
(6ae)	120-1	65			1630			4.15(18)
(6bc)	114-5	56			1620			4.2 (20)
(6bd)	132-3	54			1618			4.2 (20)
(6be)	105-6	64			1625			4.2 (18)

[a]All compounds gave correct elemental analyses. [b]Compounds (4) were purified on treatment with anhydrous ether, (5) and (6) on crystallization from absolute ethanol. [c]Obtained by rearrangement of the corresponding (4) and by work up of the reaction mother liquor. [d]Excitation: 4880 and 6471 Å. In the derivatives with NO_2 groups a strong fluorescence band was present, hiding most of the details of the spectrum, except for the ν_s vibration of NO_2. [e]Recorded in CD_3SOCD_3 (i.s. sodium 3-(trimethylsilyl)propane sulphonate) for (4), and in $CDCl_3$ (i.s. TMS) for (5) and (6). [f]Values in parentheses are given in Hz.

When the electrophiles (3) were reacted with pyrrolidine enamines (2) under the same conditions or at lower temp, only the oxadiazine derivatives (6) were isolated and no evidence for the formation of enamine derivatives analogous to (4) could be detected (Table).

Formation of tetrasubstituted enamines (4) is a rather surprising result. In fact, the trisubstituted derivatives (8) were to be expected both for steric and electronic reasons, since these were the enamine isomers usually formed in

the reactions between enamines and electrophiles bearing a substituent at the electrophilic center[1,9] Also unusual is the facile irreversible conversion of (4) into the cyclic isomers (5) since only one case of an analogous rearrangement was reported[10] up to date. In that case, however, the reaction was reversible and the equilibrium was solvent dependent.

Work is continuing to determine the factors influencing the formation of adducts like (4) and their subsequent rearrangement into (5), and to examine if this is a general course also for other asymmetric diimides.

This work is being supported by a grant from the CNR (Rome). Thanks are due to Mr. L.Stoppari for recording the NMR spectra.

REFERENCES and NOTES

[1] A.Risaliti and L.Marchetti, Ann.Chim.(Italy), 53, 718 (1963)
[2] J.Firl and S.Sommer, Tetrahedron Letters, 1925, 1929 (1970); ibid., 4713 (1972)
[3] J.Firl and S.Sommer, Tetrahedron Letters, 4193 (1971)
[4] L.Marchetti, J.C.S. Perkin II, 382 (1978)
[5] S.G.Cohen and J.Nicholson, J.Org.Chem., 30, 1162 (1965)
[6] With (3d) and (3e) the reaction was carried out in anhydrous benzene.
[7] C.Gastaldi, Gazz.Chim.Ital., 41, 319 (1911)
[8] H.Bock, E.Baltin and J.Kroner, Ber., 99, 3337 (1966)
[9] A.Risaliti, L.Marchetti and M.Forchiassin, Ann.Chim.(Italy), 56, 317 (1966); A.Risaliti, M.Forchiassin and E.Valentin, Tetrahedron, 24, 1889 (1968); F.P.Colonna, S.Fatutta, A.Risaliti and C.Russo, J.Chem.Soc.(C), 2377 (1970)
[10] G.Pitacco and E.Valentin, Tetrahedron Letters, 2339 (1978)

(Received in UK 30 July 1979)