MESOIONIC SIX-MEMBERED HETEROCYCLES, VI[1]. REACTIONS OF 6-OXO-6H-1,3-OXAZIN-3-IUM-4-OLATES WITH CARBODIIMIDES

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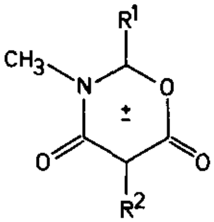
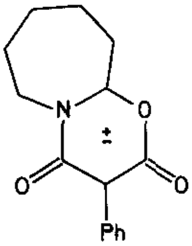
Abstract - 6-Oxo-6H-1,3-oxazin-3-ium-4-olates (1, 2) react with carbodiimides (3) to give 2,3-dihydro-2-imino-4-oxo-1,3-oxazin derivatives (4).

There are a number of examples where mesoionic six-membered heterocycles of type 1[2] react with 2π-components to give products which may be envisaged as results of cycloadditions. As we now have found carbodiimides (3)[3] react (toluene, several hours of reflux) both with mono- (1) and bicyclic (2) oxazinium olates to give compounds (4) which can formally be derived from ketene tautomers (B) of these heterocycles (eq.(1)). Whether such open chain tautomers are involved[4] or whether these reactions are initiated by a nucleophilic attack of A (Scheme 1)[7] is open to question[8]. *A primary adduct (C) may yield - via D - compound E*[9] which after ring opening[10] to



1a, b

a: $R^1 = C_6H_5CH_2$, $R^2 = Ph$
b: $R^1 = C_6H_4(4\text{-}OCH_3)$, $R^2 = C_6H_5CH_2$



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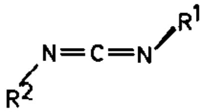
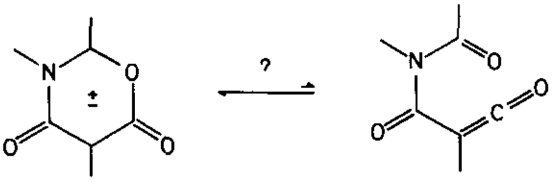


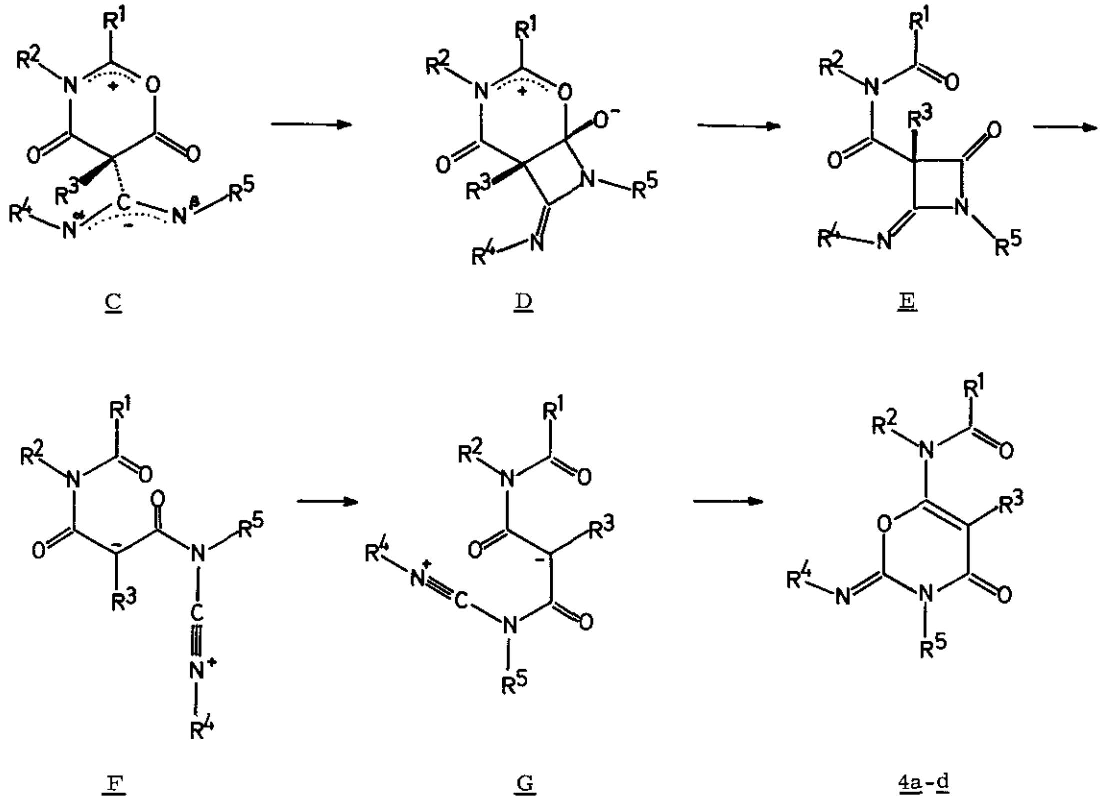
3a, b

a: $R^1 = R^2 = $ Cyclohexyl
b: $R^1 = $ Ph, $R^2 = $ Cyclohexyl



A B (1)

F (G) may suffer from a ring closure to give the observed product (4). The structures of 4a - d



	R^1	R^2	R^3	R^4	R^5
a:	$C_6H_5CH_2$	CH_3	Ph	Cyclohexyl	Cyclohexyl
b:	C_6H_4(4-OCH_3)	CH_3	$C_6H_5CH_2$	Cyclohexyl	Cyclohexyl
c:	-$(CH_2)_5$-		Ph	Cyclohexyl	Cyclohexyl
d:	$C_6H_5CH_2$	CH_3	Ph	Cyclohexyl	Ph

Scheme 1

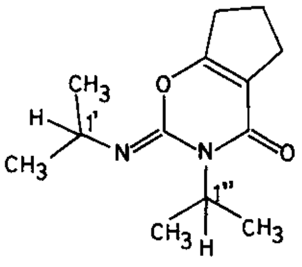
have been determined spectroscopically (Table). The IR spectra compare well with the known[6c] compound 5 (IR(film): 1646, 1653, 1688, 1699 cm^{-1}. - ^{1}H-NMR ($CDCl_3$): δ = 1.10 (d, 2 CH_3, J = 6.0 Hz), 1.42 (d, 2 CH_3, J = 6.7 Hz), 1.8-2.25 (m, 2 H), 2.5-2.76 (m, 4 H), 4.90 (sept., H(1″), J = 6.0 Hz), 5.10 (sept., H(1′), J = 6.7 Hz)). The ambiguity concerning the positions of R^4 and R^5 in 4d is easily removed by an inspection of the ^{1}H-NMR spectrum: The signal of H(1′) is observed as a triplet of triplets in the expected region.

It is of interest to note that the unsymmetrical carbodiimide 3b yields one isomer (4d) predominantly or exclusively. If the course of the reaction is determined by the electron distribution in the

Table: Spectroscopic Data of 1, 3-Oxazinones (4)

4	mp (^{o}C)	IR (cm^{-1}), KBr	^{1}H-NMR (CDCl$_3$), δ in ppm[a]
a	131	1645, 1660, 1704	1.1-2.0 (m, 18 H), 2.37, 2.60 (AB-q, J = 11.5 Hz, H($2'_a$), H($6'_a$)), 3.02 (s, N-CH$_3$), 3.48 (m, H(1'')), 3.55 (s, CH$_2$), 4.70 (tt, H(1'), J$_1$ = 11.4 Hz, J$_2$ = 3.5 Hz), 7.0-7.45 (m, 10 H)
b	125	1603, 1648, 1655, 1703	1.0-2.0 (m, 18 H), 2.32, 2.54 (AB-q[b], J = 13.5 Hz, H($2'_a$), H($6'_a$)), 3.10 (s, N-CH$_3$), 3.36 (s, CH$_2$), 3.42 (bs, H(1'')), 3.80 (s, OCH$_3$), 4.58 (tt, H(1'), J$_1$ = 11.4 Hz, J$_2$ = 3 Hz), 6.78, 7.44 (AB-q, 4 H, J = 9 Hz), 7.22 (m, 5 H)
c	151	1645, 1660, 1687, 1704	1.04-2.0 (m, 26 H), 2.3-2.7 (m, 3 H), 3.3-3.48 (m, 2 H), 3.58 (bs, 1 H), 4.69 (tt, H(1'), J$_1$ = 12 Hz, J$_2$ = 3 Hz), 7.30 (s, 5 H)
d	106-8	1635, 1665, 1695[c]	1.05-2.18 (m, 8 H), 2.46, 2.66 (AB-q[b], J = 10.8 Hz, H($2'_a$), H($6'_a$)), 2.84 (s, N-CH$_3$), 3.42 (s, CH$_2$), 4.84 (tt, H(1'), J$_1$ = 11.5 Hz, J$_2$ = 3.2 Hz), 6.7-7.47 (m, 15 H)

[a] Numbering as depicted in H; [b] With further splitting; [c] Shoulder



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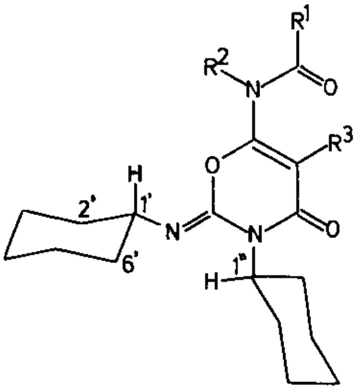

H

diazaallyl anion moiety of C, then the observed product is to be expected; even simple HMO and ω - calculations[12] reveal a slightly higher electron density at N(β). But as the difference in the electron densities is only small the preponderance for 4d may be accidental; in other cases both isomers should be observed.

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