Novel Degenerate Sigmatropic Rearrangements of Amidines

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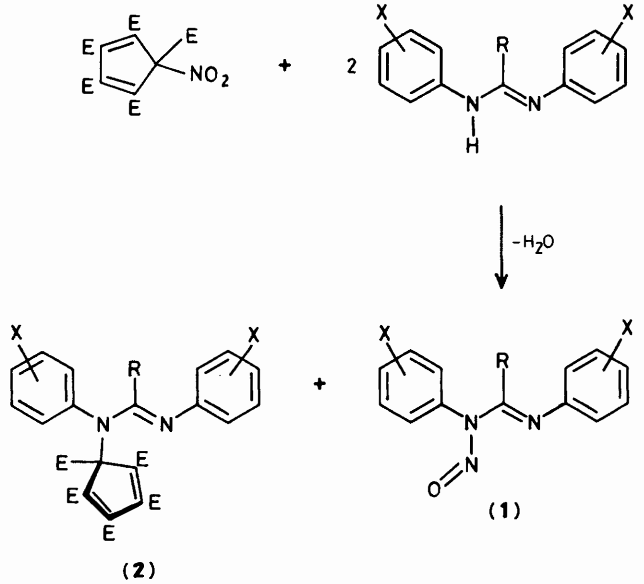
N-Nitroso-*N*,*N'*-diarylamidines (**1**) and *N*-(1,2,3,4,5-pentakismethoxycarbonylcyclopentadienyl)-*N*,*N'*-diarylamidines (**2**) prepared by the reaction of *N*,*N'*-diarylamidines with 5-nitro-1,2,3,4,5-pentakismethoxycarbonylcyclopentadiene show fluxional behaviour arising from degenerate sigmatropic 1,3-shifts of the nitroso group in (**1**) and 3,3-shifts of the amidinyl moiety in (**2**).

Two novel degenerate intramolecular rearrangements were found to occur in the products of the reaction of 5-nitro-1,2,3,4,5-pentakismethoxycarbonylcyclopentadiene[1] and *N*,*N'*-diarylamidines. The reaction proceeds smoothly upon storage for 2—3 days of solutions in benzene or *o*-dichlorobenzene of the reactants in a 1 : 2 molar ratio, giving the *N*-nitroso (**1**) and the pentakismethoxycarbonylcyclopentadienyl-amidines (**2**) (Scheme 1).[†]

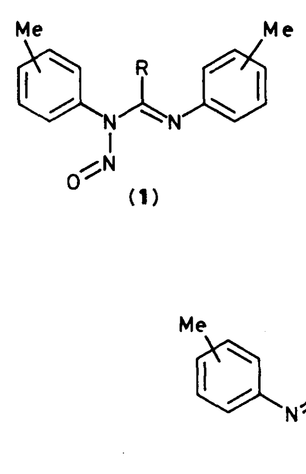
The ^1H n.m.r. spectra of compounds (**1**) are temperature-dependent and the methyl proton peaks reversibly broaden and coalesce upon raising the temperature of perchlorobutadiene solutions to 90—95 °C. These spectral effects unambiguously show that rapid 1,3-shifts of the nitroso group in the amidine triad are occurring. No concentration effects on the rate of the rearrangement were observed and no intermediate radical type species were detected by e.s.r. spectroscopy. This indicates that the degenerate rearrangement of (**1**) is intramolecular. According to previous MINDO/3 calculations[2] the symmetrical C_s structure (**3**) (Scheme 2) represents an energy-rich intermediate rather than a transition state structure of the rearrangement. Thermodynamic and kinetic data are in Table 1.



E = CO_2Me
a; R = Ph, X = *p*-Me
b; R = 1-naphthyl, X = *p*-Me
c; R = 1-naphthyl, X = *m*-Me

Scheme 1

[†] Compounds (**1**) are oils which are difficult to crystallize. 40—50% yields were obtained after by column chromatography (neutral alumina). Compounds (**2**) form deeply coloured crystals: m.p.s (**2a**), 142—143 °C; (**2b**), 140—141 °C; (**2c**), 126—127 °C, and were obtained in almost quantitative yields. Compounds (**1**) and (**2**) all gave satisfactory elemental and spectral analyses.



Scheme 2

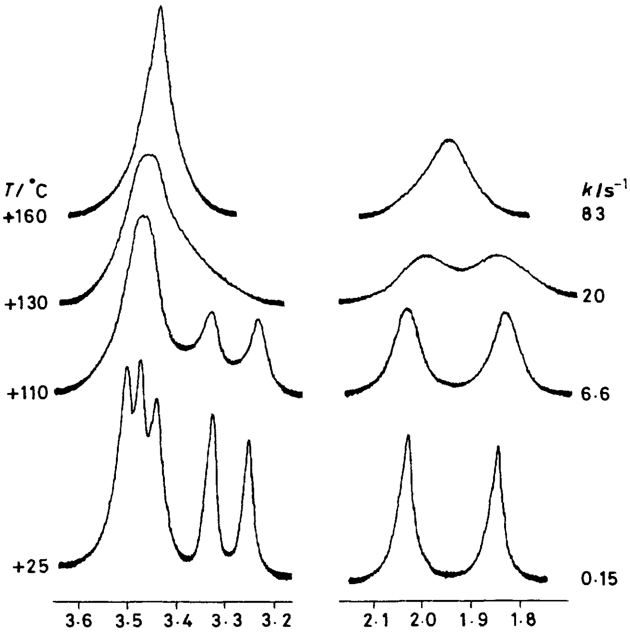
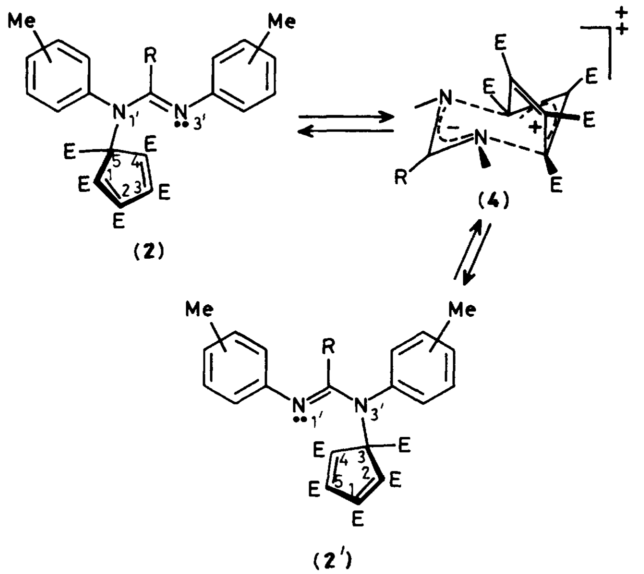


Figure 1. Temperature-dependent ^1H n.m.r. spectra of the amidine (**2c**) in perchlorobutadiene solution in the methyl (δ 1.84, 2.02) and methoxy proton region. Rate constants were obtained by computer simulation of spectral line-shapes.

A comparison of the kinetic data in Table 1 with those obtained for degenerate 1,3-shifts of other main-group element migrants[3] shows the following order of migratory aptitudes in the series of amidine derivatives: $C_6H_3(NO_2)_2$-2,4 < C(O)R < P(O)(OR)$_2$ < PAr_2 < NO < $S(O)C_6H_4$-4 < $SC_6H_3(NO_2)_2$-2,4 < $C_6H_2(NO_2)_3$-2,4,6 < $SiMe_3$ < $^+PAr_3$.

The cyclopentadienyl amidines (**2**) also undergo fast degenerate rearrangement (Scheme 3), as shown in their ^1H n.m.r. spectra by a simultaneous averaging of both methyl and methoxy resonances on raising the temperature of their solutions in perchlorobutadiene. Kinetic parameters for the rearrangement calculated by total line-shape analysis using both groups of indicator signals are the same within error limits.



Scheme 3

Table 1. Kinetic and thermodynamic data for the amidines (**1**) and (**2**).

Compound	k(90 °C)/s^{-1}	$\Delta H^{\ddagger}$/ kcal mol^{-1} [a]	$\Delta S^{\ddagger}$/ kcal mol^{-1}	$\Delta G^{\ddagger}$(90 °C)/ kmol^{-1} [b]
(**1a**)	5.1	—	—	20.2
(**1b**)	57	14.4 ± 0.4	−11.5 ± 0.9	18.5
(**1c**)	103	17.3 ± 0.5	−2.0 ± 1.0	18.0
(**2a**)	0.17	22.5 ± 0.4	−1.5 ± 0.5	22.7[c]
(**2b**)	3.9	15.1 ± 0.3	−14.7 ± 0.7	20.4
(**2c**)	2.0	15.7 ± 0.4	−14.3 ± 0.9	20.9

[a] cal = 4.184 J. [b] Rate constants and free energy activation parameters were calculated on the basis of total line-shape analysis of the temperature-dependent spectra. Coalescence of the methyl resonances and total averaging of the ^1H n.m.r. (100 MHz) spectra of compound (**1a**) were observed in perchlorobutadiene or 1,1,2,2-tetrachloroethane solutions above 100 °C when (**1a**) began to decompose extensively. [c] For compound (**2a**), slow *Z–E* isomerization, as shown by doubling of the methyl resonances in the ^1H n.m.r. spectrum, occurred upon prolonged storage of its *o*-dichlorobenzene solution at ambient temperature or on heating the solution at 80 °C. The equilibrium content of *Z*-(**2a**) in *o*-dichlorobenzene solution at 80 °C is 70 ± 5%. Another example of uncatalysed slow *Z–E* isomerization of amidine derivatives has been reported recently.[5]

These spectral changes indicate a hitherto unknown[4] low energy barrier hetero-Cope rearrangement in the NCN system.

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