An Unusually Fast Chapman-like Thermal Rearrangement in the Solid State

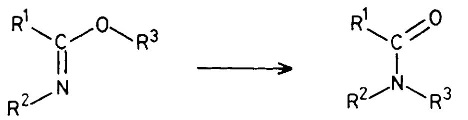
Michèle Dessolin and Michel Golfier*

Laboratoire de Chimie Organique de Synthèse, Bâtiment 420, Université de Paris-Sud, 91405-ORSAY Cedex, France

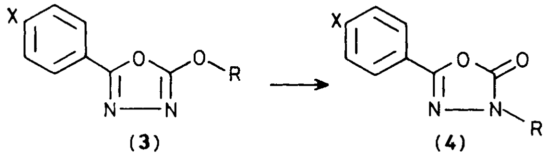
Some 5-methoxy-2-aryl-1,3,4-oxadiazoles undergo a 1,3 O-to-N thermal rearrangement of the methyl group, which takes place unusually easily, and much faster in the solid state than in the melt.

Thermal solid-state organic reactions are more numerous than is generally believed, but few of them have been thoroughly studied,[1] and they often concern single compounds. We have encountered a remarkable example of a *family* of products (prepared in connection with other studies[2]) that undergo a Chapman-like thermal rearrangement[3] of type (**1**) → (**2**) (R^3 = alkyl), which occurs much faster in the crystal than in the melt.

The Chapman-like rearrangement is always difficult and requires temperatures higher than 200 °C.[3] In the case of 5-alkoxy-2-aryl-1,3,4-oxadiazoles (**3**) (R = alkyl), this reaction occurs slightly more easily and begins near 180 °C in the



(1) (2)



(3) (4)

a: R = Me, X = H
b: R = Me, X = Cl
c: R = Me, X = OMe
d: R = Me, X = NO_2
e: R = CD_3 X = OCD_3

Table 1. Ratio of the predicted half-lives in the two states, at the melting point.

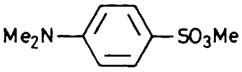
Compd.	M.p., t/°C	$t_{\frac{1}{2}}$(melt)/$t_{\frac{1}{2}}$(solid)[c]
(**3a**)	50[a]	—
(**3b**)	116[a]	384
(**3c**)	122[b]	218
(**3d**)	184[a]	2.3

[a] Determined by extrapolation of the results of a differential scanning calorimetry study. [b] Taken on a Kofler hot-stage. [c] At the melting point; half-lives extrapolated values.

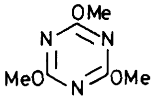
neat molten compounds[2a] (no reaction occurs in solution, at the same temperature). In contrast, this rearrangement takes place exceptionally easily when R = Me. Not only does it occur, in the melt, at 120—140 °C, but the reaction also takes place even more readily in the crystalline state. On storage for more than two years in the dark, at room temperature, analytical samples of compounds (**3b**)—(**3d**) are more or less rearranged into compounds (**4b**)—(**4d**), without apparent change in the crystalline state [percentage of rearranged product (**4**) in parentheses]: (**3b**) (85%), (**3c**) (90%), (**3d**) (9.5%); (**3a**) is unchanged.

Kinetic measurements were carried out at different temperatures, with neat, molten compounds (**3a**)—(**3d**), as well as with neat, polycrystalline (**3b**)—(**3d**) [owing to its low melting point, (**3a**) is rearranged only in the melt]. The reaction was very clean and could be followed up to 90—95% completion; starting materials (**3**) and products (**4**) were in each case the only observed compounds. The fraction α of rearranged product (**4**) was determined by ^{1}H n.m.r. spectroscopy.

As is generally observed with a reaction in the solid state,[4] it was not possible to find a single rate law for the whole of each reaction. For solid or molten (**3b**), a first-order law [$-\ln(1-\alpha) = kt$] was obeyed up to 70% completion. In all other cases, a linear law ($\alpha = kt + \mathrm{b}$) was obtained up to 50—60% completion [an induction period was observed with solid or molten (**3d**) and with molten (**3a**)]; no simple kinetics were observed with solid (**3c**) and the reaction rate coefficient k was determined using the value of the initial rate.



(5)



(6)

The Arrhenius equation was obeyed well over the range of temperatures used, and the following apparent activation energies (kcal mol^{-1}; 1 cal = 4.184 J) were determined: reaction in the solid state: (**3b**), 24; (**3c**), 18; (**3d**), 56; reaction in the melt: (**3a**), 28; (**3b**), 31; (**3c**), 28; (**3d**), 31. These figures show that: (a) there is no appreciable difference between the apparent activation energies for the reactions in the melt; (b) the mechanism of the rearrangement in the solid state might be different for the nitro-compound (**3d**) compared with the chloro- (**3b**) or the methoxy-compound (**3c**); (c) the activation energies for the rearrangement of (**3b**) and (**3c**) are significantly smaller in the solid state than in the melt.

Each reaction gave a fairly good linear plot of ln $t_{1/2}$ *vs.* T^{-1}. Assuming that all these linear relationships could be extrapolated to the melting point, a predicted ratio of the half-lives for the rearrangement in the two phases was calculated for (**3b**)—(**3d**) (Table 1). This ratio gives a rough but striking illustration of the fact that *the rearrangement is much faster in the solid-state than in the melt.*

It was shown earlier[2a] that the rearrangement in the melt was intermolecular. By rearranging a 50 : 50 (w/w) mixture of (**3c**) with the deuteriated compound (**3e**), a mixture of the four possible products (**4**) (R = CH_3 or CD_3, X = CH_3O or CD_3O) was obtained for the reaction in the solid-state as well as in the melt. This result confirms our previous observation and proves that the rearrangement in the solid-state is also *intermolecular.*

This unexpectedly fast Chapman-like rearrangement in the solid state is probably the consequence of a favourable geometry in the crystal packing, analogous to that observed with compound (**5**).[5] The same kind of rearrangement seems also to occur, in the solid state, with some methyl cyanurates such as (**6**).[6] Crystallographic studies of compounds (3) and (4) are in progress.

Received, 8th August 1985; Com. 1189

References

1 (a) I. C. Paul and D. Y. Curtin, *Acc. Chem. Res.*, 1973, **6**, 217; (b) A. Gavezzotti and M. Simonetta, *Chem. Rev.*, 1982, **82**, 1.
2 (a) M. Golfier and R. Milcent, *Tetrahedron Lett.*, 1973, 4465; (b) G. Aranda, M. Dessolin, M. Golfier, and M. G. Guillerez, *Org. Magn. Reson.*, 1982, **18**, 159; (c) M. Dessolin, M. Golfier, and T. Prangé, *J. Org. Chem.*, 1985, **50**, 4461.
3 (a) J. W. Schulenberg and S. Archer, *Org. React.*, 1965, **14**, 24; (b) G. D. Lander, *J. Chem. Soc.*, 1903, **83**, 406.
4 C. H. Bamford and C. F. H. Tipper, 'Comprehensive Chemical Kinetics, 22. Reactions in the Solid State,' Elsevier, Amsterdam, 1980, p. 77.
5 C. N. Sukenik, J. A. P. Bonapace, N. S. Mandel, R. G. Bergman, P. Y. Lau, and G. Wood, *J. Am. Chem. Soc.*, 1977, **99**, 851.
6 M. L. Tosato and L. Soccorsi, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1321, and references cited therein.