β-Elimination of some Solid ββ'-Dihalogenoadipodinitriles with Gaseous Ammonia. An Example of a Non-topochemically Controlled Reaction

By Gad Friedman, Edna Gati, Meir Lahav,* Dov Rabinovich,* and Zippora Shakked
(*Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel*)

Summary The stereocourse of the reaction of solid dihalogenoadipodinitriles with gaseous ammonia has been investigated in terms of the conformation of the reacting molecules in the crystal; under the heterogeneous conditions of the reaction, in certain systems, an equilibrium between different rotamers occurs before an *anti*-type elimination takes place.

We have recently reported the stereospecific *β*-elimination from the solid dimethyl-(**1**) and dibenzyl-(**2**) ester of *meso*-*ββ'*-dihalogenoadipates with dry gaseous ammonia or vapours of volatile organic amines,[1] and shown that the process is controlled by the conformation of the dihalogenobutane in the reacting crystal.[2] Here we describe the reactions of the nitriles (**3**)—(**6**), two of which, (**3**) and (**4**), behave differently from (**1**) and (**2**). We interpret this difference in terms of a mechanism involving pre-reaction equilibration of rotamers in the solid.

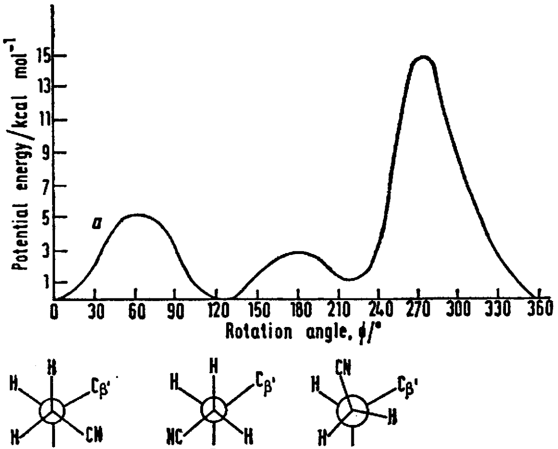
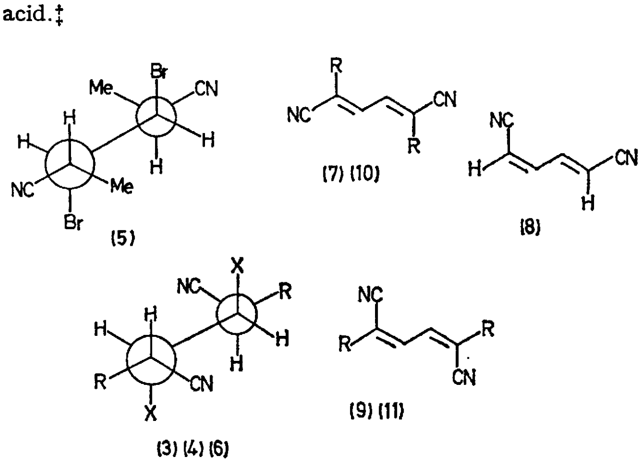


Figure. The energy variation of (**4**) as a function of the rotation angle about C_α–C_β, in an isolated molecule.

Crystalline powders or single crystals of *meso*-2,3-dihalogeno-1,4-dicyanobutanes, (**3**)—(**6**), were exposed to dry ammonia at room temperature.† (**3**), m.p. 118—121 °C[3] (PriOH), yields a mixture of (**7**), (**8**), and (**9**) in the ratios of 3:5:2. No melting was observed during the reaction and no mono-olefin was isolated from the mixture. The corresponding reaction in solution in various solvents yields a complex mixture of unidentified brown material containing no more than 10% of a mixture of the dienes. (**4**), m.p. 130—132 °C, is dimorphic (form A separated by slow cooling from chloroform, and form B by slow cooling from benzene), and each crystalline modification was treated separately with ammonia; both yielded the three dienes (**7**), (**8**), and (**9**) in the ratio 3:5:2. (**5**) is dimorphic; both plates (A) and needles (B) were separated from benzene, and here both forms were converted into the diene (**10**), m.p. 187—190 °C (decomp.) [*τ*, 2·70 (2H, s, =CH), 8·05 (6H, s, C–CH_3)]; its structure was established by comparison with a sample prepared from *αα'*-dimethyl-*cis,cis*-muconic acid. (**6**) reacts quantitatively yielding the diene (**11**), m.p. 139—140 °C, [*τ* (Me_2SO) 2·71 (2H, s, =CH)], identical with a sample obtained from *αα'*-dimethyl-*trans,trans*-muconic acid.‡



(3) R = H; X = Cl (7) R = H
(4) R = H; X = Br (9) R = H
(6) R = Me; X = Br same conformation in form [A] and [B] (10) R = Me
(11) R = Me

Scheme. The Newman projections of the molecules in their crystals, and geometries of the products after elimination.

Three-dimensional *X*-ray analyses of the structures of (**3**), (**4**) (form A), (**5**) (forms A,B), and (**6**) have been performed.[4] The Newman projections of the molecular structures from the above analyses are in the Scheme. All the molecules have a hydrogen antiperiplanar to the leaving halogen atom, and in (**5**) and (**6**) these hydrogens are eliminated. Thus the reactions of (**5**) and (**6**) under these heterogeneous conditions clearly proceed by an *anti*-type elimination mechanism. The question of how charge separation occurs in the solid state without the aid of solvation of the leaving group by solvent molecules remains to be answered.

The role played by the conformation of (**3**) and (**4**) on the stereo-course of the elimination is more complex. Topochemically controlled *anti*-elimination from these compounds, such as is displayed by the reactions of (**5**) and (**6**), would lead to the formation of *cis,cis*-muconnamed nitrile. The

---

† Samples of 1·0—10 g were used and elimination was completed after 15—75 h. Product ratios were determined by g.l.c. with columns of 5% B.D.S. and 2% QF1 on chromosorb G.

‡ Experiments on (**5**) and (**6**) with NaOAc in ethanol indicate that the reaction in solution proceeds *via* anti-elimination.

unexpected formation of all three geometrical isomers, with more *trans*- than *cis*-double bonds, suggests that rotation occurs around the C_α–C_β single bond at some stage in the reaction. Such a rotation apparently does not occur in (**1**) and (**2**).

In order to examine more quantitatively the difference between the behaviour of the diester (**1**) and that of the nitrile (**4**), we have calculated the energy variations of the isolated molecules as functions of the rotation angle about the single bond C_α–C_β (Figure).§ In (**4**), the two *gauche* conformations *a* and *b* which would yield, *via* an *anti*-type elimination, *cis*- and *trans*-double bonds respectively, are almost energetically identical and conversion from one into the other involves an energy barrier of only *ca.* 5 kcal mol^{-1}.[7] Rotation around the C_α–C_β bond in the dihalogenoadipate esters which contain two α-hydrogens is much less favourable, since it has to be accompanied by an additional rotation around the C_α–(C=O) single bond to avoid strong steric repulsions between the methoxycarbonyl group and the C_β substituents. Using similar calculations we estimate the barrier for this rotation in an isolated molecule to be at least 10 kcal mol^{-1}.[8] These calculations refer to the free molecules; the rotational barriers in the ordered crystal are much higher. It is still uncertain which barriers are pertinent to our reaction conditions; however if, as we believe, the reaction occurs at structurally defective sites in the crystal (*e.g.* surfaces and dislocations),[9] then we may expect the rotational barriers to be higher than those of the free molecules but lower than those for the ordered crystal.

We suggest that, because of the difference in the rotational barriers at the site of reaction, the course of the reaction in the adipates (**1**) and (**2**) is determined by the initial molecular conformation whereas in the nitriles (**3**) and (**4**) equilibrium of the rotamers is established before the transition states of the reactions are reached.

The *X*-ray structure analyses and detailed calculations referred to above will be published elsewhere.

We thank Professor M. D. Cohen for interesting discussions and Sun Oil Company for the generous gift of αα'-dimethyl *cis,cis*-muconic acid.

(*Received, 18th February* 1975; *Com.* 206.)

---

§ The calculations included only non-bonded and torsional energy contributions. The potential functions used were those given for saturated molecules.[5] The parameters for the non-bonded potential involving Br atoms were taken from ref. 6.

[1] For previous paper in series, 'Heterogeneous Reactions with Organic Solids,' see: G. Friedman, M. Lahav, and G. M. J. Schmidt, *J.C.S. Perkin II*, 1974, 428.

[2] H. Kaufman, D. Rabinovich, and G. M. J. Schmidt, *J.C.S. Perkin II*, 1974, 433.

[3] H. F. Pipenbrink, *Annalen*, 1951, **1**, 572.

[4] Z. Shakked, Ph.D. Thesis, Weizmann Institute of Science, 1974; D. Rabinovich and Z. Shakked, to be published.

[5] A. Warshel and M. Karplus, *J. Amer. Chem. Soc.*, 1972, **94**, 5613.

[6] T. Kawaguchi, K. Takashina, T. Tanaka, and T. Watanabe, *Acta Cryst.*, 1972, **B28**, 967.

[7] For similar rotations in the plastic phase of succinonitrile see: D. E. Williams and C. P. Smith, *J. Amer. Chem. Soc.*, 1962, **84**, 1808; S. G. Powels, A. Begum, and M. O. Norris, *J. Mol. Phys.*, 1969, **17**, 489; H. Fontaine, W. Longueville, and F. Wallart, *J. Chim. Phys.*, 1971, **68**, 1593.

[8] At room temperature a barrier of 16—20 kcal mol^{-1} between rotational isomers is usually required to permit their isolation, see 'Stereochemistry of Carbon Compounds,' E. L. Eliel, McGraw-Hill, New York, 1962, p. 156.

[9] S. P. Desvergne and J. M. Thomas, *Chem. Phys. Letters*, 1973, **23**, 343.

Printed by Heffers Printers Ltd Cambridge England