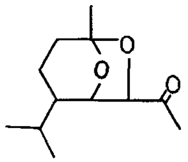
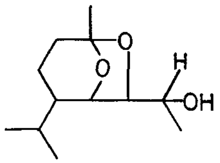
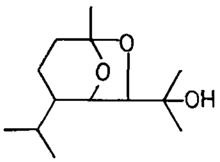


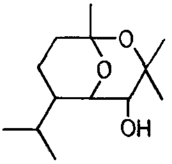
*1*



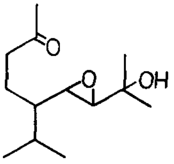
*2*



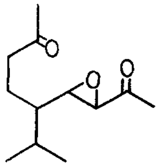
*3*



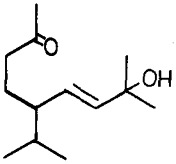
*4*



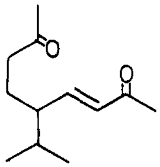
*5*



*6*



*7*



*8*

REFERENCES

[1] a) *E. Demole & D. Berthet*, Helv. *55*, 1866 (1972); b) *iidem*, ibid., p. 1898; c) *E. Demole*, (Mrs) *C. Demole & D. Berthet*, Helv. *56*, 265 (1973).
[2] *U. Scheidegger, K. Schaffner & O. Jeger*, Helv. *45*, 400 (1962); *E. Demole & H. Wuest*, Helv. *50*, 1314 (1967).
[3] *H. H. Wasserman & E. H. Barber*, J. Amer. chem. Soc. *91*, 3674 (1969).
[4] *J. M. Coxon, M. P. Hartshorn & W. H. Swallow*, Chem. Commun. *1973*, 261.

---

# 20. Synthesis and Ring Opening of 1,4-Dicyanobicyclo[2.2.0]hexane. Radical Stabilization Energy of a Cyano Group[1]

Preliminary Communication

by **Daniel Belluš** and **Günther Rist**

Central Research Laboratories, Ciba-Geigy AG, 4000 Basel

(22. XII. 73)

*Summary.* 1,4-Dicyanobicyclo[2.2.0]hexane (**2**) was prepared by (2+2)-photocycloaddition of ethylene to 1,2-dicyanocyclobutene. **2** isomerizes cleanly to 2,5-dicyanohexadiene-1,5 (**3**) with a very low activation energy of 21.7 ± 1.4 kcal/mol. From comparison with the reported rates of isomerization of bicyclo[2.2.0]hexane, the radical stabilization energy of the cyano group is shown to be about 7.3 kcal/mol.

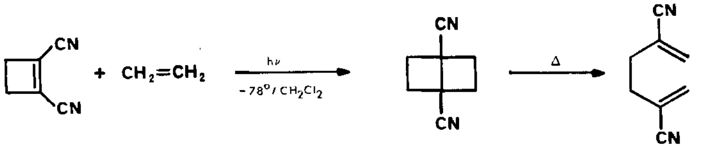
---

[1] Synthesis and Reactivity of Compounds with Cyclobutane Ring(-s). Part IV. For Part III see [1].

In view of the steadily growing interest in mechanistically uncertain thermolyses of bicyclo[2.2.0]hexanes, we wish to report the results on the thermal reaction of 1,4-dicyanobicyclo[2.2.0]hexane (**2**).

The thermally induced (2+2)-cycloreversions of molecules with bicyclo[2.2.0]hexane structures are essentially stereospecific [$\sigma 2_s + \sigma 2_a$] cleavages, involving the C(1)–C(4) and C(2)–C(3) bonds [2]2). However, there exists strong evidence for a 1,4-biradical intermediate in the thermal isomerization of bicyclo[2.2.0]hexanes. *E.g.*, the experimental activation energies depend on the kind of substituents in position 1 and 4, and *vice versa*, the radical stabilization energies of these substituents can be conveniently determined by ring opening of suitably substituted bicyclo[2.2.0]hexanes [4].

Compound **2** was prepared by benzophenone-sensitized (2+2)-photocycloaddition of ethylene to 1,2-dicyanocyclobutene (**1**) [5] at –78°3).



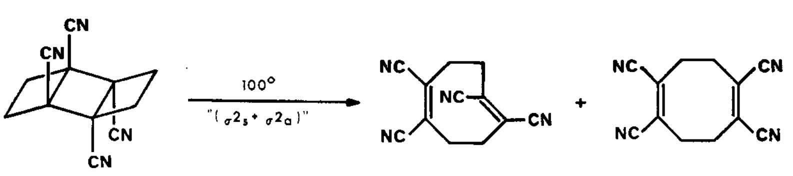
**1** **2**, 57% **3**, 100%

In crystalline state at 0° compound **2** is reasonably stable. In solution, first order kinetics corresponding to clean isomerization to 2,5-dicyanohexadiene-1,5 (**3**)3) were observed. NMR. measurements in deuteriochloroform (over the temperature range +20° to +50°) yield the following activation parameters: $E_a = 21.7 \pm 1.4$ kcal/mol; $\log A = 11.6 \pm 1.0$; $\Delta H^{\neq} = 20.0 \pm 1.4$ kcal/mol and $\Delta S^{\neq} = -5.6 \pm 4.6$ cal/deg. mol at 308° K4).

The activation energy of the thermal isomerization of bicyclo[2.2.0]hexane was reported to be 36 [2b], 36.2 [6] and 36.8 kcal/mol [7]. Compared with the mean value of 36.3 ± 0.5 kcal/mol for the parent hydrocarbon, the activation energy for the isomerization of **2** is reduced by 14.6 ± 1.9 kcal/mol. Thus, *one* cyano group in the bridge-

---

2) The unprecedented solid state isomerization of 1,2,5,6-tetracyano-*anti*-tricyclo[$4.2.0.0^{2,5}$]octane (**4**) to the stable 1,2,5,6-tetracyano-(*E,Z*)-cyclo-octadiene-1,5 (**5**) represents another example [3]:



**4** **5**, 97% **6**, trace

3) New compounds **2** and **3** gave satisfactory analytical data. Experimental details, including synthetic and isolation procedures, will be reported in a full paper. Selected IR. ($cm^{-1}$) and NMR. (δ) data for these compounds are listed below. **2**: M.p. 81–82°. – IR. (KBr): 2230, 1442, 1280, 1268, 1245, 1230, 1065, 940, 896 and 760. – NMR. ($CDCl_3$): 2.3–3.0/*m*. – **3**: B.p. 75–78°/0.01 Torr. – IR. ($CHCl_3$): 2225, 1632, 1440, 1405 and 945. – NMR. ($CDCl_3$): 2.57/*s*, 4H, 2× $-CH_2-$; 5.82 and 5.92/2× *s*, 4H, 2× $-(CN)C{=}CH_2$.

4) The error limits are standard deviations from the least-squares calculations.

head position of bicyclo[2.2.0]hexane decreases the activation energy by 7.3 ± 1.0 kcal/mol. This value may lie very close to the actual radical stabilization energy per cyano group with respect to the hydrogen atom and agrees excellently with values of 6–10 kcal/mol per cyano group, obtained in gas-phase thermolyses of five cyano-substituted, four-membered ring compounds [8] [5]).

The good agreement between the experimental and expected ($E_{\text{expected}} \simeq 36.3 - 2 \times 8 \simeq 20.3$ kcal/mol) activation energy of the thermolysis of **2** supports the assumption of the 1,4-biradical mechanism [6]). We hope, that the ring opening experiments with 2,3-substituted derivatives of **2** will help to distinguish between biradical and concerted isomerization of 1,4-dicyanobicyclo[2.2.0]hexanes.

## REFERENCES

[1] *D. Belluš, H.-C. Mez & G. Rihs,* J. chem. Soc. Perkin II, in press.

[2] a) *L. A. Paquette & J. A. Schwartz,* J. Amer. chem. Soc. *92,* 3215 (1970); b) *M. J. Goldstein & M. S. Benzon,* ibid. *94,* 5119 (1972); c) *A. Sinnema, F. Van Rantwijk, A. J. De Koning, A. M. Van Wijk & H. Van Bekkum,* J.C.S. Chem. Commun. *1973,* 364.

[3] *D. Belluš,* Abstracts of Papers, 3rd. Int. Symposium on Synthesis in Organic Chemistry, Oxford, 10–13 July 1973, p. 40. Publication in preparation.

[4] *E. N. Cain & R. K. Solly,* J. Amer. chem. Soc. *95,* 4791 (1973) and references cited therein.

[5] *D. Belluš, K. von Bredow, H. Sauter & C. D. Weis,* Helv. *56,* 3004 (1973).

[6] *C. Steel, R. Zand, P. Hurwitz & C. G. Cohen,* J. Amer. chem. Soc. *86,* 679 (1964).

[7] *R. Srinivasan,* Int. J. Chem. Kinet. *1,* 133 (1969).

[8] *S. F. Sarner, D. M. Gale, H. K. Hall, Jr. & A. B. Richmond,* J. phys. Chemistry *76,* 2817 (1972).

[9] *P. E. Eaton & G. H. Temme* III, J. Amer. chem. Soc. *95,* 7508 (1973).

---

[5]) This comparison is made, however, without considering the differences in *Arrhenius* pre-exponential factors. For an excellent discussion of this aspect see [4].

[6]) Although the experimental activation energy for the isomerization of **2** is lower than that reported for the first-order ring opening of a very strained [2.2.2]propellane ($E_a \simeq 22$ kcal/mol [9], **2** does not react with bromine at 0–10°. The [2.2.2]propellane reacts instantly with bromine, even at −70° [9], thus reflecting different $sp^{<3}$ hybridization of the bridgehead carbon atoms.

---

## 21. Pyrolyse du Diméthylidène-2,3-oxa-7-bicyclo[2.2.1]heptane

par **Pierre Vogel et Michèle Hardy**

Institut de chimie organique de l'Université, 2, rue de la Barre, CH-1005, Lausanne

(3. XII. 73)

*Summary.* Benzocyclobutene **10** and 3-oxabicyclo [3.2.0]hepta-1,4-diene **11** are formed by gas-phase pyrolysis of the title compound **9**. The results are discussed with reference to the estimated reaction parameters. It is found that the activation due to oxygen in **9** is relatively weak in comparison to its effect on the reactivity of oxaquadricyclanes **1**.

La plupart des oxaquadricyclanes **1** s'isomérisent thermiquement en oxépines **2** à la suite de la scission des liaisons *b* [1]. Cette isomérisation est formellement un réarrangement $3\,\sigma \rightarrow 3\,\pi$ [2]. Les quadricyclanes **3**, quant à eux, s'isomérisent par chauffage généralement en norbornadiènes **4**, suite à la rupture des liaisons *a* ($2\,\sigma \rightarrow 2\,\pi$) [3].