

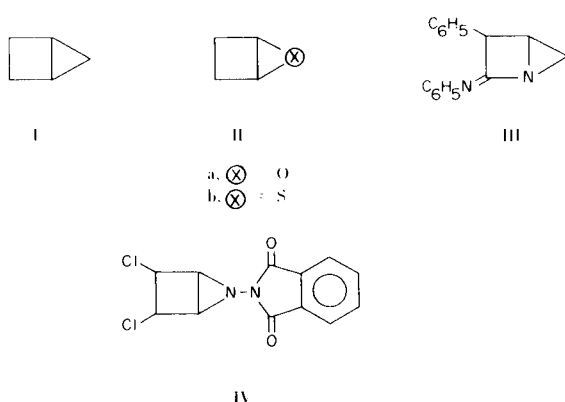
The Synthesis of 2-Phthalimidyl-4,5-dichloro-2-azabicyclo[2.1.0]pentane

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Sir:

The strained (2) bicyclo[2.1.0]pentane molecule (I) was first prepared relatively recently by Criegee and Rimmelin (3). Subsequently the analogous cyclobutene epoxide (IIa) (4) and episulfide (IIb) (5) structures and one compound having a bridgehead nitrogen (III) were synthesized (6). We now report the first example (IV) of the nitrogen analog of II.

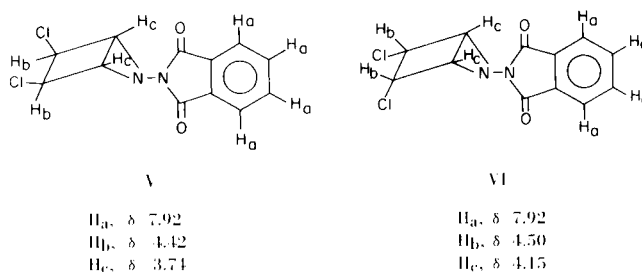


Compound IV was obtained (0.11 g., 6.2%) as pale yellow crystals, m.p. 165-170° dec., from the reaction of 3,4-dichlorocyclobutene (7) (1.54 g., 12.5 mmoles) with *N*-aminophthalimide (8) (1.0 g., 6.25 mmoles) and lead tetraacetate (2.76 g., 6.25 mmoles) in dry dichloromethane (20 ml.), with subsequent addition of potassium carbonate (2.4 g.). The final separation of IV was effected by thin layer chromatography on silica gel with 3:1 petroleum ether-acetone. The molecular weight (mass spectrum) was 281.99440 (calcd. 281.99622). The ultraviolet spectrum (acetonitrile) showed λ_{max} (log ϵ) at 231 (3.4), 295 (2.15), and 305 (2.11) μ . Infrared absorption was recorded (dichloromethane) at 3.50, 5.63, 5.81, 6.22, 6.35, 6.83, 7.41, 7.93, 8.85, 9.09, 9.30, 9.80, 10.0, 10.42, 11.11, 11.43, 12.34 and 12.70 μ . The absorptions at 5.63 and 5.81 μ were found to correspond in position and relative shape to those reported for *N*-aminophthalimides (9) but not for phthalhydrazides (10).

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{Cl}_2\text{N}_2\text{O}_2$: C, 50.91; H, 2.85; N, 9.90. Found: C, 51.08; H, 3.01; N, 9.60.

Analysis of the nmr spectrum (hexadeuterioacetone) (peaks at δ (ppm) 7.92 (s), 4.50 (m), 4.42 (m), 4.15 (m) and 3.74 (m)) revealed the presence of both the *exo*

(V) and *endo* (VI) isomers in a ratio of 4:1 with the assignments as shown. This was confirmed by a spin decoupling experiment wherein irradiation at δ 3.74 (*exo* absorption) produced a singlet at δ 4.42 but did not affect the corresponding peaks of the *endo* isomer. Also in agreement was the finding that the nmr spectrum of *N*-aminophthalimide had a singlet at δ 7.8 whereas that of phthalhydrazide showed a multiplet at δ 7.6-8.2.



Compound IV slowly decomposes on standing at room temperature, but 28% was recovered unchanged after it was heated (steam bath) in glacial acetic acid for twenty-four hours. Further studies on this and related compounds are in progress.

Rees and coworkers had previously found that *N*-amidyl- and *N*-imidyl nitrenes react with olefins to form the corresponding aziridines rather than the isomeric diazetidines (11). The above results provide an additional example of this mode of reactivity. To our knowledge, however, only one other highly strained bicyclic nitrogen heterocycle, 3-phenyl-1-azabicyclo[1.1.0]butane (12) has been formed *via* a nitrene intermediate.

REFERENCES

- (1) NDEA Title IV Fellow, 1967-1969.
- (2) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr. and M. Pomerantz, *J. Am. Chem. Soc.*, **90**, 4315 (1968) have calculated a strain energy of 54.1 kcal/mole by a semi-empirical method.
- (3) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).
- (4) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **80**, 5505 (1958); R. Criegee and K. Noll, *Ann. Chem.*, **627**, 1 (1959); W. R. Moore and C. H. Beede, Abstracts, 144th National Meeting, American Chemical Society, Los Angeles, Calif., April, 1963, p. 11M; A. Padwa, *J. Am. Chem. Soc.*, **87**, 4205 (1965);

- J. L. Ripoll and J. M. Conia, *Bull. Soc. Chim. France*, 2755 (1965).
- (5) E. Block and E. J. Corey, *J. Org. Chem.*, **34**, 896 (1969).
- (6) F. P. Woerner, H. Reimbinger, and D. R. Arnold, *Angew. Chem. Intern. Ed. Engl.*, **7**, 130 (1968).
- (7) M. Avram, I. Dinulescu, M. Elian, M. Farcasin, E. Marica, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 372 (1964).
- (8) H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, **16**, (1937).
- (9) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 98 (1957).
- (10) F. C. Brown, C. K. Bradsher, B. F. Moser and S. Forrester, *J. Org. Chem.*, **24**, 1057 (1959); J. U. N. Cheinker, T. V. Gortinskaia and T. P. Sycheva, *J. Chim. Phys.*, **55**, 217 (1958).
- (11) D. J. Anderson, T. L. Gilchrist, D. C. Horwell, and C. W. Rees, *Chem. Commun.*, 146 (1969); R. S. Atkinson and C. W. Rees, *ibid.*, 1230 (1967).
- (12) A. G. Hortmann and J. E. Martinelli, *Tetrahedron Letters*, 6205 (1968).

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