

occurred, placing it out of conjugation into the $\Delta^{3,4}$ position. The results are summarized in Table I.

The following procedure for the reaction of tri-*n*-butylborane with ethyl 4-bromocrotonate is representative. To a 200-ml three-necked flask equipped with a dropping funnel, a septum inlet, condenser, and magnetic stirring bar was placed 11.4 g (55 mmol) of 2,6-di-*t*-butylphenol in 30 ml of purified tetrahydrofuran (THF). The flask was flushed with nitrogen and 50 ml of 1.0 *M* potassium *t*-butoxide in THF was injected into the flask. The flask was immersed in an ice bath and 12.1 ml (50 mmol) of tri-*n*-butylborane was added, followed by the dropwise addition over 30 min of 9.65 g (50 mmol) of ethyl 4-bromocrotonate in 20 ml of THF. The resulting mixture was allowed to stir for 1 hr at 0°. Glpc analysis, following addition of *n*-octane as an internal standard, indicated a 72% yield of ethyl 3-octenoate. The flask was cooled with a water bath. To destroy residual organoboron intermediates the reaction mixture was treated with 16.5 ml of 3 *M* sodium acetate followed by 12 ml of 30% hydrogen peroxide at a rate sufficient to maintain the temperature below 35°. After stirring for a further 30 min, the reaction mixture was saturated with sodium chloride. The organic phase was separated, dried over sodium sulfate, filtered, and distilled. There was obtained 5.1 g (60% yield) of ethyl 3-octenoate, bp 93–95° (10 mm), n_D^{20} 1.4362.⁹

It is evident that the present reaction provides a highly convenient procedure for achieving a C-4 homologation. At the same time it provides a simple route for the synthesis of $\Delta^{3,4}$ -olefinic esters. Of considerable interest is the unusual migration of the double bond from the conjugated $\Delta^{2,3}$ position to the unconjugated $\Delta^{3,4}$ position achieved in this reaction. Not only does this make these nonconjugated unsaturated esters and acids readily available, but the apparent stereospecificity of the migration would appear to have important theoretical implications.

(9) In all cases glpc examination indicated the presence of only one isomer and the ir spectrum corresponded to the presence of the *trans* isomer. However, glpc examination of the alcohols, obtained by reducing the esters with lithium aluminum hydride, revealed the presence of minor amounts of the *cis* isomer.

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Stereochemistry of the Thermal Fragmentation of β -Lactams. Comparison with the Pyrolysis of 1-Azetines¹

Sir:

Although thermal [2 + 2] cycloaddition reactions of olefins can be symmetry allowed and therefore concerted if the $[\pi 2_s + \pi 2_a]$ combination mode is followed,² only one authenticated example of this phenomenon has been reported to date.³ Presumably this is be-

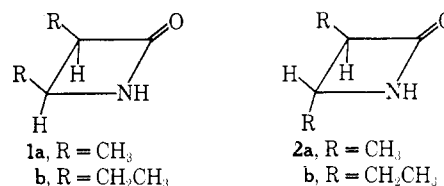
(1) Unsaturated Heterocyclic Systems. LXX. For the previous paper in this series, see L. A. Paquette and J. P. Freeman, *J. Amer. Chem. Soc.*, **91**, 7548 (1969).

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem. Intern. Ed. Engl.*, **8**, 781 (1969).

(3) K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4357, 4723 (1967).

cause steric hindrance and angle strain factors generally develop to rather prohibitive levels as the two π bonds attempt to attain the requisite orthogonality. In contrast, cycloadditions of olefins to allenes,⁴ ketenes,⁵ and reactive isocyanates⁶ are known to proceed with very high degrees of stereospecificity, thereby suggesting that cumulative π -bond systems can function more readily as $\pi 2_a$ donors than isolated double bonds.

If reversal of cyclobutane formation in any of the above examples is to be concerted, the process necessarily must take place *via* the $[\sigma 2_s + \sigma 2_a]$ pathway. Relevant studies on the pyrolysis of simple cyclobutane derivatives have been regarded as uniquely consistent with a stepwise decomposition involving tetramethylene diradicals.⁷ It would appear that the total stereochemical inversion demanded of one of the four-membered ring carbons obtains with significant difficulty. To our knowledge, no information has been available concerning the stereochemical course of retrograde olefin-cumulene cycloadditions. This communication deals with the thermal cleavage of β -lactams **1** and **2**⁸ and contrasts the remarkable stereospecificity noted in these examples with the pyrolytic behavior of the related 1-azetines **5** and **6**.



The four β -lactams were prepared by means of the known⁶ stereospecific addition of chlorosulfonyl isocyanate to the appropriate *cis*- and *trans*-olefins and hydrolysis of the resulting N-(chlorosulfonyl)azetidin-2-ones with aqueous sodium hydroxide in acetone solution. Under conditions where the individual β -lactams were slowly introduced in the gas phase (12 mm, N₂ stream) through a quartz tube packed with glass beads (contact time, ~ 2 sec), these compounds were seen to be stable to 500°. At 600°, however, there resulted virtually complete fragmentation of the four-membered rings, accompanied by the formation of an alkene (>90% yield) and cyanuric acid (80–90%). The olefin composition was analyzed by vpc using either a 100 ft \times 0.02 in. squalane-coated capillary column at 30°^{9a} for the isomeric 2-butenes or a 22 ft \times 0.25 in. column packed with 15% β , β' -oxydi-

(4) See, for example: (a) E. F. Kiefer and M. Y. Okamura, *J. Amer. Chem. Soc.*, **90**, 4187 (1968); (b) J. E. Baldwin and U. V. Roy, *Chem. Commun.*, 1225 (1969).

(5) *Inter alia*, note: (a) R. Montaigne and L. Ghosez, *Angew. Chem.*, **80**, 194 (1968); (b) W. T. Brady, E. F. Hoff, R. Roe, Jr., and F. H. Parry, Jr., *J. Amer. Chem. Soc.*, **91**, 5679 (1969).

(6) (a) E. J. Moriconi and J. F. Kelly, *Tetrahedron Lett.*, 1435 (1968); (b) H. Bestian, H. Biener, K. Clauss, and H. Heyn, *Ann.*, **718**, 94 (1968).

(7) (a) H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 170 (1966). For more recent work, see (b) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969); (c) A. T. Cocks and H. M. Frey, *J. Chem. Soc.*, **A**, 1671 (1969); (d) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

(8) The susceptibility of β -lactams to thermal fragmentation has been noted earlier, but not in stereochemical terms: (a) H. Staudinger, *Ber.*, **44**, 521 (1911); (b) A. M. Van Leusen and J. F. Arens, *Rec. Trav. Chim Pays-Bas*, **78**, 551 (1959).

(9) (a) Employed in conjunction with a flame ionization detector and a calibrated Infotronics CRS-11 HSB Digital Readout system; (b) employed in conjunction with a calibrated thermal conductivity detector (manual integration).

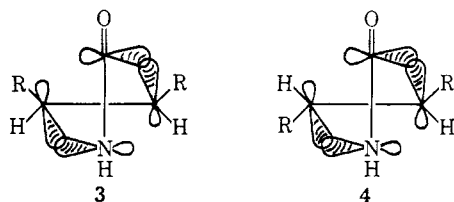
Table I. Composition of the Olefin Fractions Isolated from the Pyrolysis of **1** and **2**

| β -Lactam | Composition, % ^{a,b} | | | |
|-----------------|-------------------------------|--------------|------------|--------------|
| | 2-Butene | | 3-Hexene | |
| | <i>cis</i> | <i>trans</i> | <i>cis</i> | <i>trans</i> |
| 1a | 99.3 | 0.7 | | |
| 2a | 0.4 | 99.6 | | |
| 1b | | | 98.8 | 1.2 |
| 2b | | | 0.5 | 99.5 |

^a Values represent averages of two runs. ^b The four alkenes were stable to the pyrolysis conditions and also at 650°.

propionitrile on Chromosorb P at 45°^{9b} for the isomeric 3-hexenes. The results are summarized in Table I.

Clearly, the thermal fragmentations of **1** and **2** proceed virtually with total retention of stereochemistry. In line with the explanation previously offered,² the high stereochemical purity of the olefins could result from operation of the concerted [$\sigma_2 + \sigma_2$] pathway. The requisite elevated temperatures are not necessarily excessive, particularly since the combination of severe ring distortion, simultaneous stretching of two σ bonds, and disruption of amide resonance which must be achieved in passing to **3** and **4** might well be associated with a high energy of activation. Because the carbonyl group in the β -lactams is functioning



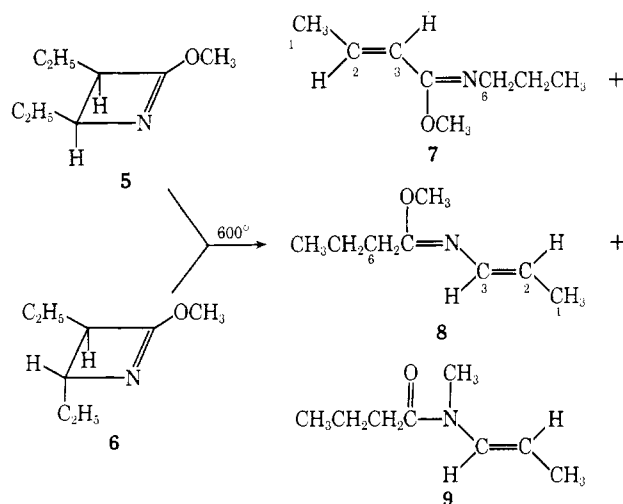
as the antarafacial site, establishment of geometric inversion at this center is not possible and conclusive proof of the [$\sigma_2 + \sigma_2$] path is inaccessible. However, the alternative stepwise mechanism would require that the 1,4-diradical intermediates not lose their stereochemical integrity prior to complete fragmentation. Since the existing analogies⁷ indicate that loss of stereochemistry is rapid relative to cleavage, the highly stereospecific nature of the fragmentation would seem to argue convincingly for the operation of the concerted process.¹⁰

For comparison purposes, the thermal behavior of *cis*- (**5**) and *trans*-3,4-diethyl-2-methoxy-1-azetines (**6**) was examined. The presence of the imino ether linkage in these four-membered rings was expected to reduce significantly their capability for twisting as in **3** and **4**. Azetines **5** [bp 79–80° (26 mm); $\nu_{\text{max}}^{\text{neat}}$ 1620 cm^{-1} ; fluoroborate, mp 92–94°¹¹] and **6** [bp 73–74° (26 mm); $\nu_{\text{max}}^{\text{neat}}$ 1620 cm^{-1} ; picrate, mp 124.5–126°¹¹] were prepared by treatment of **1b** and **2b**, respectively, with

(10) A referee has argued that because thermally generated 1,4-diradicals can cyclize without significant loss of stereochemistry [P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968)], σ -bond rotation need not necessarily be rapid relative to cleavage. We contend that these two reactions are intrinsically different and need not necessarily bear any stereochemical relationship to each other. Thus, cyclization involves bond formation and is most certainly exothermic while the fragmentation to olefins could require the surmounting of a final energy barrier and in so doing be very apt to cause loss of stereochemistry. In this connection, Paquette and Schwartz (submitted for publication) and W. R. Roth and M. Martin (*Tetrahedron Lett.*, 3865 (1967)) have shown that 1,4-cyclohexadienyl radicals are subject to conformational inversion prior to ultimate cleavage.

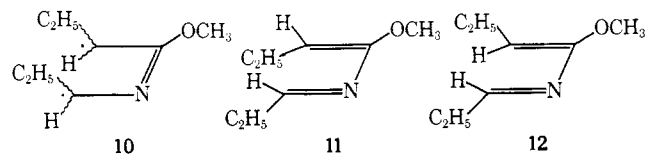
(11) Satisfactorily elemental analyses ($\pm 0.3\%$) were obtained for all new compounds.

trimethyloxonium fluoroborate, followed by drying over pellets of potassium hydroxide.¹² In a typical run, vapor phase pyrolysis of **5** (30.9 mg) under nitrogen at 600° and 23 mm afforded 11.1 mg of pyrolysate which consisted of imideate **7**¹¹ (14%), imideate **8**¹¹ (78%), and N-methylamide **9**¹¹ (8%). Similar thermal decomposition of **6** (363 mg) yielded 261 mg of pyrolysate which contained the same three products in a ratio of 12:77:11. At 700°, **9** was seen to predominate at the expense of **8** in both examples, thereby showing it to be the Chapman rearrangement product¹³ of this imideate. No olefin production occurred under either set of conditions.



The infrared spectrum (neat) of **7**, prepared in unequivocal fashion by reaction of N-propyl crotonamide¹¹ with trimethyloxonium fluoroborate, shows bands of interest at 1680 and 1630 cm^{-1} . Its nmr spectrum consists *inter alia* of absorptions at $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.49 (d of q, H_2 , $J_{2,3} = 16.0$ Hz, $J_{1,2} = 6.5$ Hz), 6.10 (d of q, H_3 , $J_{2,3} = 16.0$ Hz, $J_{1,3} \approx 1.0$ Hz), and 3.33 (t, H_6 , $J = 7.5$ Hz). The 70-eV mass spectrum displays a molecular ion at m/e 141 and other significant peaks at m/e 126 (base peak), 112, 98, 68, 55, 41, and 39. These data contrast well with the spectral properties of **8**: $\nu_{\text{max}}^{\text{neat}}$ 1650 and 1675 (sh) cm^{-1} ; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 6.69 (d of q, H_3 , $J_{2,3} = 13.0$ Hz, $J_{1,3} = 1.8$ Hz), 5.62 (d of q, H_2 , $J_{2,3} = 13.0$ Hz, $J_{1,2} = 6.5$ Hz), and 2.34 (m, H_6); m/e 141, 126, 98, 55, 51 (base peak), and 39.

The nearly identical product distribution realized from the thermal fragmentations of **5** and **6** can be accounted for equally well in terms of a stepwise mechanism involving **10** or conrotatory openings to **11** and **12**, respectively, followed by allylic hydrogen



shifts. Interestingly, the pathway leading to **8** is favored by a factor of 8 over that which gives rise to **7**, perhaps for stereoelectronic reasons.

(12) Prior drying of the azetines in this manner permitted distillation without substantial concomitant decomposition. See also D. Bormann, *Ann.*, **725**, 124 (1969).

(13) For a review, see J. W. Schulenberg and S. Archer, *Org. Reactions*, **14**, 1 (1965).

The results obtained with the β -lactams, when compared with those for the azetines, serve to emphasize that the carbonyl compounds have available to them a reaction path which is inaccessible to **5** and **6**. Although direct comparisons of reaction rates in the two different systems cannot be made in this instance, it is quite possible that such behavior is the result of two distinctly different concerted processes: [$\sigma_2 + \sigma_2$] retrogression in the case of **1** and **2** and conrotatory opening in the case of **5** and **6**.

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(14) (a) National Science Foundation Undergraduate Research Participant, Summers 1968, 1969; (b) Senior Education Awardee, American Cyanamid Company, 1969–1970.

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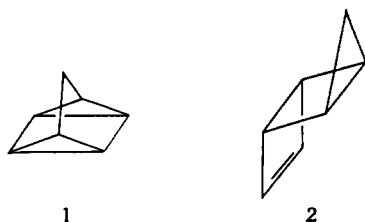
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The Tricyclo[4.1.0.0^{2,5}]hept-3-ene to Quadricyclane Rearrangement. Intramolecular Trapping of a 1,3 Diradical by a Remote Cyclobutene Ring

Sir:

Because the total strain energy in the quadricyclane ring system (**1**) is extremely high (95 kcal/mol),¹ the preparation of such molecules by customary ground-state reactions has not proven feasible, even when symmetry-allowedness is favorable.² Instead, the photorearrangement of norbornadiene derivatives has been frequently utilized as the synthetic entry to quadricyclanes.³ At this time, we wish to report on



an exceptionally facile approach to the *trans*-tricyclo[4.1.0.0^{2,5}]hept-3-ene nucleus (**2**) and also to exemplify the thermal rearrangement of such alicyclic structures to quadricyclane derivatives. The driving force behind such a novel transformation, the result of intramolecular trapping of a 1,3 diradical by a remote cyclobutene ring, is very likely derived from the presence in **2** of strain energy greater than 100 kcal/mol.

Exposure of isopyrazole **3**⁴ to cyclobutadiene (**4**), generated *in situ* from ceric ion oxidation of cyclobutadieneiron tricarbonyl,⁵ afforded in 65% yield the

(1) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968).

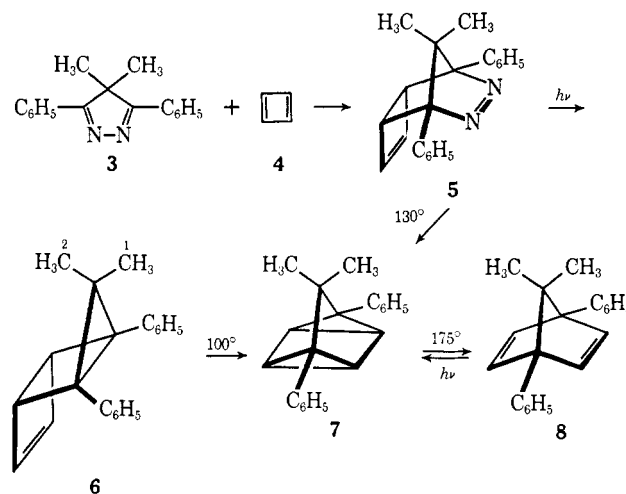
(2) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *ibid.*, **91**, 5668 (1969).

(3) See, for example: (a) S. J. Cristol and R. L. Snell, *ibid.*, **80**, 1950 (1958); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); (c) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Amer. Chem. Soc.*, **83**, 4674 (1961); (d) P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **90**, 7271 (1968); (e) J. R. Edman, *ibid.*, **91**, 7103 (1969), and pertinent references cited therein.

(4) A. B. Evnin and D. R. Arnold, *ibid.*, **90**, 5330 (1968).

(5) (a) L. A. Paquette and L. D. Wise, *ibid.*, **89**, 6659 (1967); (b) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

tricyclic azo compound **5**, mp 153–154°;⁶ $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 343 (ϵ 64) and 353 nm (ϵ 64); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 0.28 (s, 3, -CH₃), 1.04 (s, 3, -CH₃), 3.88 (s, 2, allylic), 6.05 (s, 2, vinyl), and 7.32–7.80 (m, 10, aryl). Irradiation of **5** in ether solution with a 200-W Hanovia lamp (Pyrex



filter) for 3 hr produced **6** in quantitative yield: mp 65.5–67°;⁶ $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 0.88 (s, 3, 1-CH₃), 1.44 (s, 3, 2-CH₃), 3.36 (d, J = 1.5 Hz, 2, allylic), 6.41 (d, J = 1.5 Hz, 2, vinyl), and 7.22 (m, 10, aryl). The *trans* stereochemistry of **6** and the spatial relationships of the two methyl groups were established experimentally by application of nuclear Overhauser effects.⁷ Thus, of the two methyl groups, that labeled 1-CH₃ is sufficiently distant from the allylic and vinyl hydrogens that it should not contribute to the relaxation of either proton type. In line with this consideration, double irradiation of the δ 0.88 singlet did not result in any significant intensity change of either the 3.36 or 6.41 signals. Saturation of the δ 1.44 methyl singlet, however, reproducibly gave evidence of a 7% intensity enhancement in the 3.36 absorption. Accordingly, the 2-CH₃ group and the allylic hydrogens must be proximal, an observation which requires the spatial relationship embodied uniquely in the *trans* isomer. The relatively small NOE effect is due to the mutual relaxation of the two allylic hydrogens such that outside protons contribute less by comparison.

Although nitrogen elimination from **5** has apparently proceeded with retention of configuration, no definite stereochemical conclusions should be drawn at this time in the absence of low-temperature studies (now in progress) which may shed light on the possible intervention of the ephemeral *cis* isomer.⁸

Thermolysis of **6** in tetrachloroethylene solution at 100° could be conveniently monitored by nmr spectroscopy. After approximately 4 hr, quantitative conversion to quadricyclane **7** was observed. Evaporation of the solvent and recrystallization of the residue from ethanol gave long white needles, mp 136.5–

(6) Satisfactory elemental analyses ($\pm 0.3\%$) were obtained for all new compounds.

(7) For a recent review, see G. Moreau, *Bull. Soc. Chim. Fr.*, 1770 (1969). The stereochemistry of **5** was established in a comparable NOE study.

(8) Exceptionally rapid stereomutation of the *cis* isomer can be expected if it does intervene. Compare the ease of equilibration of bicyclo[2.1.0]pentane derivatives: M. J. Jorgenson, R. J. Clark, and J. Corn, *J. Amer. Chem. Soc.*, **90**, 7020 (1968); C. Mackenzie, W. P. Lay, J. R. Telford, and D. L. Williams-Smith, *Chem. Commun.*, 761 (1969).