carbon tetrachloride, and the Br_2 concentration is kept low by the alkene, the circumstances required for a succinimidyl chain reaction. *The remarkable selectivity of the Ziegler procedure* (CCl_4 *prescribed*) *must be attributable to the low solubility of NBS in this solvent*, so that small amounts of Br_2 can still dominate the chain processes.

While photobrominations employing Br_2 give products by abstraction of H from the weakest bonds, brominations with the new reagent system, NBS in the presence of bromine scavengers, result in less discriminating attack, so that bromination can be carried out even at the primary positions. For example, neopentyl bromide is obtained from neopentane.[8]
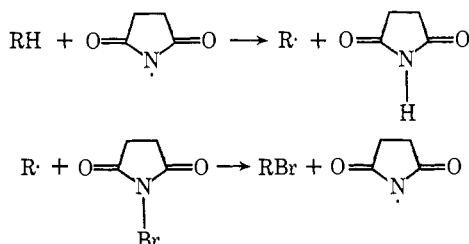
Acknowledgment. We wish to acknowledge support from the Air Force Office of Scientific Research, Grant No. 71-1983.

(8) The succinimidyl radical is sufficiently reactive to abstract hydrogen from cyclopropane; cyclopropyl bromide is reported from NBS bromination of cyclopropane. J. G. Traynham, private communication.

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A Stereochemical Test of Concert in the Thermal Cracking of Cyclobutyl Ketones

Sir:

There have been suggestions that the thermal homogeneous decompositions of cyclobutyl ketones[1,2] and cyclobutanecarboxylic esters[2] follow a concerted rather than a step-wise mechanistic path. We wish to report the results of a test of this proposal involving reaction stereochemistry which bear on the mechanism in question and indirectly on the uncertainty concerning resonance stabilization in carbonyl substituted radicals.

Bicyclic ketones 1–3 were prepared *via* photocycloaddition[3] of 2-cyclopentenone and the 1,2-dichloroethylenes. Their structures including stereochemistry were assigned on the basis of nmr spectral data with reference to the careful analyses previously reported.[3b,4] The structure of 1 is further supported by X-ray diffraction studies.[3b,5] Pyrolyses of 1–3 were carried out in a

(1) R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 381 (1970).

(2) W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *J. Amer. Chem. Soc.*, **94**, 1619 (1972).

(3) (a) P. deMayo, J.-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968); (b) W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, **92**, 1399 (1970).

(4) (a) R. O. Loutfy and P. deMayo, *Can. J. Chem.*, **50**, 3465 (1972); see ref 12. (b) We are grateful to Dr. Dilling and Professor deMayo for helpful discussions regarding the experimental data.

(5) F. P. Boer and P. P. North, *J. Chem. Soc., Perkin Trans. 2*, 416 (1972).

flow (nitrogen) reactor[6] with contact times of about 5 sec. Glc examination of product mixtures with reference to an internal standard indicated about 50% yields of 2-cyclopentenone and the 1,2-dichloroethylenes accompanied by several unidentified materials. Stereochemical data for a large number of runs at moderate to high conversion are compiled in Table I.

Table I. The Stereochemistry of 1,2-Dichloroethylene Product from Pyrolysis of 1–3

Starting ketone	Pyrolysis temperatures (°C)	% conversion	% trans[d]	% cis[d]
1[a]	440–485	31–65	79 ± 2	21 ± 2
2[b]	430–485	44–69	74 ± 2	26 ± 2
3[c]	425–465	27–92	46 ± 4	54 ± 4

[a] >99% 1. [b] 2% 1, 91% 2, 7% 3. [c] 7% 2, 93% 3. [d] The estimated errors are average deviations of duplicate analyses of pyrolyses in triplicate.

The 1,2-dichloroethylenes were configurationally stable under the reaction conditions. Ketones 1 and 2 were not appreciably isomerized in competition with cracking (<2% at about 60% conversion); however the percentage of 2 (originally 7%) rose during cracking of 3 (to 19% at 92% conversion).

Significant loss of stereochemistry in thermal decomposition of 1–3 is apparent. Cracking proceeds with net retention of configuration in product olefin. Stereoselectivities of 79, 81, and 64% (retention) may be calculated for 1–3, respectively, taking into account isomeric contamination in starting ketone and (for 3) a small amount of isomerization (to 2) during cracking.

The results do not support the proposal of classically concerted fragmentation for cyclobutyl ketones. A concerted path sanctioned by transition state aromaticity would require that olefin be produced with predominant inversion of configuration (assuming in the present case that *cis*-cyclopentenone is produced exclusively). Our results parallel quite closely reaction stereochemistries for more simply substituted cyclobutanes[8] and agree more readily with the perception of mechanism as diradical.[9] That these comparison cases of cycloreversion also show largely stereorandom behavior is exemplified by the behavior of 6,7-dimethylbicyclo[3.2.0]heptane.[8a] The trans and cis stereoisomers (analogs of 1 (2) and 3, respectively) fragment with 75 and 50% retention stereoselectivity, respectively. Whether the discreet mechanism for cyclobutane decomposition involves diradical intermediates (*e.g.*, 4), or diradical transition states,[10] or some other mix-

(6) The reactor consisted of a Pyrex tube packed with Pyrex beads which had been aged through numerous pyrolyses with varied systems. Surface catalysis was checked by intermittent pyrolysis of 2,2-diphenyl-3,3,4,4-tetramethyloxetane which cracks with exceeding sensitivity to surface effects (homogeneously to give benzophenone and tetramethylene and heterogeneously to give acetone and 1,1-diphenyl-2-methylpropene).[7] The oxetane monitor indicated that homogeneous conditions prevailed during experiments with 1–3.

(7) G. Jones, II, H. H. Kleinman, M. T. Marton, L. P. McDonnell, S. B. Schwartz, and J. C. Staires, to be submitted for publication.

(8) (a) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969); (b) R. Strinivasan and J. N. C. Hsu, *J. Chem. Soc., Chem. Commun.*, 1213 (1972); (c) J. E. Baldwin and P. W. Ford, *J. Amer. Cehm. Soc.*, **91**, 7192 (1969).

(9) For a review of related systems, see G. Jones, II, *J. Chem. Educ.*, **51**, 175 (1974).

(10) For an elaborate discussion of the diradical problem, see W. von E. Doering and K. Sachdev, *J. Amer. Chem. Soc.*, **96**, 1168 (1974).
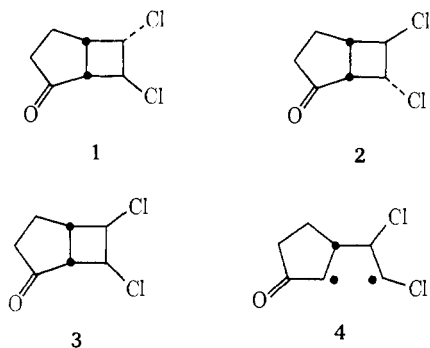
ture of concerted paths cannot be determined by the present examination. However, to be ruled out for fragmentation of 1-3 are simple concerted paths controlled exclusively by either least motion dynamics or orbital symmetry or a mechanism involving a common diradical intermediate (for 2 and 3).

The earlier proposals concerning substituted cyclobutanes[1,2] rested on the observed 5-9 kcal/mol stabilization of the transition state for cracking achieved by substitution of a cyclobutane by acyl or carbomethoxy groups[11] and on the evidence that these groups do not confer that amount of stabilization by delocalization or other means on adjacent radical (and presumably diradical) centers. The latter rests with the determination of bond energies from iodination kinetics data; for example, the α C–H bond dissociation energy for acetone is just that found for the primary C–H bond in propane (i.e., stabilization energy for the acetonyl radical $= 0 \pm 2$ kcal/mol).[14] Analysis of the secondary C–H bond dissociation energy in methyl ethyl ketone likewise reveals a low $(2.7 \pm 1.7 \text{ kcal/mol})$ resonance stabilization for the methylacetonyl radical.[15]

On the other hand these experimentally determined bond dissociation energies for acyl systems may be artificially high since they depend on the virtual equivalency of activation energy and the enthalpy for abstraction (presumed to be homolytic) by iodine at an appropriate hydrogen. That abstraction by halogen atoms (Cl and Br) is in fact electrophilic has been shown by a number of Hammett studies.[16] Considering that abstraction by iodine has similar polar character ($\rho = -1$ to -3), pure homolytic C–H bond dissociation in acetone and analogous systems may be less energetic than previously determined by 2-4 kcal/mol and the attendant stabilization energy in the resulting radical larger by the same amount. This is tantamount to acknowledging that a "repulsion polar effect"[17] (for hydrogen transfer between two electrophilic radicals) may raise the activation energy for reaction of HI and

(11) That the decompositions of 1-3 are accelerated relative to a non-carbonyl substituted model is confirmed by comparison of the Arrhenius parameters for static pyrolysis of 1 ($E_a = 52 \pm 2$ kcal/mol, log $A = 15 \pm 1$) in diphenyl ether solvent at 319-359° with those for cracking of bicyclo[3.2.0]heptane ($E_a = 61.0$ kcal/mol, log $A = 15.02$[12]). This comparison reveals a transition state stabilization of about 7 and 2 kcal/mol for the acyl and chlorine[13] substituents, respectively.

(12) R. J. Ellis and H. M. Frey, J. Chem. Soc., 4184 (1964).

(13) E. N. Cain and R. K. Solly, J. Amer. Chem. Soc., 94, 3830 (1972).

(14) R. K. Solly, D. M. Golden, and S. W. Benson, Int. J. Chem. Kinet., 2, 11 (1970).

(15) R. K. Solly, D. M. Golden, and S. W. Benson, Int. J. Chem. Kinet., 2, 381 (1970).

(16) W. A. Pryor, T. H. Lin, J. P. Stanley, and R. W. Henderson, J. Amer. Chem. Soc., 95 6993 (1973), and references cited therein.

(17) (a) J. A. Kerr and D. M. Timlin, Int. J. Chem. Kinet., 3, 1, 69 (1971); (b) J. C. Amphlett and E. Whittle, Trans. Faraday Soc., 62, 1662 (1966).

the acetonyl radical above the 1 ± 1 kcal/mol assumed in the iodination kinetics treatment.[18] Along with the evidence implicit from the energetics[1,2] and stereochemical losses[19] associated with small ring decompositions, a variety of epr spectral determinations[20] confirm that acyl substituted radicals enjoy significant delocalization stabilization.[21]

Finally, "stereoretention," the olefin product ratio for decomposition of 1-3 which very likely reflects the partition between cleavage and bond rotation in an initially formed diradical intermediate (or the equivalent partitioning of a family of concerted paths), may be compared with the accumulated literature values for systems potentially involving 1,4-diradicals.[9] The present values (3-4) compare favorably with those for systems involving diyls with moderate substituent stabilizing and low ponderal influences at the diradical termini.

(18) D. M. Golden and S. W. Benson, Chem. Rev., 69, 125 (1969).

(19) G. Jones, II, and M. E. Fantina, J. Chem. Soc., Chem. Commun., 375 (1973).

(20) D. M. Camaioni, H. F. Walter, J. E. Jordan, and D. W. Pratt, J. Amer. Chem. Soc., 95, 7978 (1973), and references cited therein.

(21) For further discussion and an interesting survey of substituent effects for thermal chemistry in the bicyclo[2.2.0]hexane series, see E. N. Cain, Tetrahedron Lett., 1865 (1971); E. N. Cain and R. K. Solly, J. Amer. Chem. Soc., 95, 4791 (1973); the assessment in the latter of 1.0 kcal/mol for the resonance energy of the carbomethoxy-methyl radical should be revised upward in light of the recent evaluation[22] of the effect of alkyl group substitution in the same series.

(22) E. N. Cain and R. K. Solly, J. Amer. Chem. Soc., 95, 7884 (1973).

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Transannular Interactions in the Acyloin Reaction.
I. Interactions with the Terminal Methylene Group

Sir:

As part of our investigation of transannular interactions in both the ground and excited states,[1] we have been interested in obtaining 2-hydroxy-6-methylene-cyclononanone (3) and the corresponding dione 4. A previous attempt to synthesize compound 3 via the acyloin reaction of dimethyl 5-methylenenonanedicarboxylate (1a) reportedly[2] did not give the desired product 3 but gave instead a compound tentatively identified as 1-hydroxybicyclo[4.3.1]decan-2-one (2). As we felt this reaction might be modified to give 3, we have undertaken a study of the acyloin reaction of diester 1 and related systems. Our initial studies involving the chlorotrimethylsilane modification[3] of the acyloin reaction of diester 1b showed that neither 2 nor 3 was obtained after hydrolytic work-up but rather hydroxy ketone 5 was the major product (Scheme I). We have now found that 5 is the major product of this

(1) (a) P. Y. Johnson, J. Zitsman, and C. Hatch, J. Org. Chem., 38, 4087 (1973); (b) P. Y. Johnson, Tetrahedron Lett., 1991 (1972); (c) P. Y. Johnson, E. Koza, and R. Kohrman, J. Org. Chem., 38, 2967 (1973).

(2) J. Panzer, dissertation, Cornell University, 1956; Diss. Abstr., 17, 39 (1957). See K. T. Finley, Chem. Rev., 64, 573 (1964).

(3) See J. J. Bloomfield, Tetrahedron Lett., 587 (1958).