amine (3 equiv) or tributylamine (10 equiv) had an effect on the rate or yield of the cyclization process. Further, use of the benzenethiol ester instead of I, n = 11, in the above procedure, either in the presence of pyridine (10 equiv) or without pyridine, resulted in the formation of only a trace of lactone.[14]

A subsequent publication will describe application of the cyclization method disclosed herein to the total synthesis of complex, naturally occurring macrolide systems.[15]

(14) Although these observations are consistent with the scheme outlined herein, they do not elevate it beyond the level of a reasonable hypothesis. Further work is required before a more definitive view is possible of the mechanism of the reaction I → IV or of the scope of this approach to the formation of macrocyclic carboxylic acid derivatives.

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E. J. Corey,* Kyriacos C. Nicolaou
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138
Received May 8, 1974

Succinimidyl Radical as a Chain Carrier. Mechanism of Allylic Bromination

Sir:

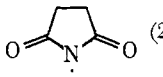
Early mechanisms for allylic brominations with *N*-bromosuccinimide involved a succinimidyl chain reaction (the Bloomfield mechanism).[1] Subsequently a variety of evidence indicated a marked similarity between NBS and Br_2 radical-chain reactions in substitutions at benzylic positions and allylic positions of some highly substituted alkenes, resulting in the general acceptance of the bromine atom chain reaction to explain allylic brominations (the Goldfinger mechanism).[2] Although these considerations brought conviction to many, it must remain a negative argument rather than a positive one. Until one knows the behavior of a succinimidyl radical, one can only say that NBS allylic bromination may occur with a bromine atom chain or with some other chain carrier of similar selectivity, possibly the unexamined succinimidyl radical. We report here the characteristic behavior of succinimidyl radicals, which forces one to conclude it is not an intermediate in the Ziegler allylic brominations.

Succinimidyl radical is a radical of low discrimination in hydrogen abstraction reactions, quite different from bromine atoms. The failure to recognize the behavior of this radical unambiguously is attributable to the domination of reaction paths by even small amounts of bromine, such as is inevitably produced early in most NBS-containing systems.[3] Bromine (Br_2) is much more reactive than NBS in capturing radicals, thus perpetuating a bromine atom chain, the NBS serving only as a reservoir for more Br_2 *via* the rapid reaction of NBS with HBr.[4]

To minimize bromine atom chains, and perhaps eliminate them entirely, the concentration of NBS is increased, and the bromination reactions are carried out in the presence of an alkene which reacts readily by addition of Br_2 and by addition of $Br\cdot$ (no H abstraction). We have found ethylene or *tert*-butylethylene suitable for this purpose.

Carbon tetrachloride and the Freons are very poor solvents for NBS (0.006 and 0.0005 *M*, respectively) so that even minute concentrations of Br_2 are sufficient to dominate the reactions. The solubility of NBS in methylene chloride (0.25 *M*) and acetonitrile (0.8 *M*) are large enough to make NBS the dominant chain carrier in the presence of a bromine scavenger. In the absence of ethylene (or *tert*-butylethylene), irradiation of NBS, in the presence of most hydrogen-containing substances, produces a yellow color quickly (~0.005 *M* Br_2), and from then on the reaction is Br_2 dominated. In the presence of ethylene, the reaction mixtures remain free of discernible bromine. The major negative result of carrying out reactions in the presence of alkenes is that a portion of the NBS goes to production of 1,2-dibromoethane and β-bromopropionyl isocyanate.[5]

For example, bromination of 1-bromobutane in the presence of ethylene results in formation of 1,1-, 1,3-, and 1,4-dibromobutanes in yields of 7, 44, and 18% respectively; the remainder (31%) is attributed to abstraction at the 2-position, which under these circumstances results in formation of 1,2-dibromobutane and products derived from substitution on 1-butene.[6] These proportions contrast sharply with those obtained in the presence of Br_2: 1,3/1,2 = 0.18 and no 1,4 is obtained. In the absence of Br_2, the succinimidyl radical must be the chain carrier (succinimide is the major product); it shows a hydrogen-abstraction selectivity similar to that of Cl atoms.

Abstracting agent	CH_3—CH_2—	—CH_2—	—CH_2Br
$Br\cdot$ (60°)[7]	0	14	85	1
 (25°)	18	44	31	7
$Cl\cdot$ (60°)[7]	23	50	22	5

Bromination of cyclohexene by the Ziegler procedure, in CCl_4, has been reexamined; the only monobromide is 3-bromocyclohexene, without even traces of the 4-bromocyclohexene. Photobromination of cyclohexene with NBS in acetonitrile solvent produces both 3- and 4-bromocyclohexene in 5.6 ratio. In acetonitrile the concentration of NBS is much larger than in

(1) D. H. Hey, *Annu. Rep. Chem. Soc.*, **41** 184 (1944); G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

(2) The bromine atom as the chain carrier in NBS allylic bromination was first suggested by Goldfinger in 1953: P. A. Gosselain, J. Adam, and P. Goldfinger, *Bull. Soc. Chim. Belg.*, **65**, 533 (1956). For general reviews of work pertaining to the mechanism(s) of NBS bromination see W. A. Thaler, *Methods Free Radical Chem.*, **2**, 121 (1969); M. L. Poutsma, *Free Radicals*, **2** 211 (1973).

(3) The suggestion that a hydrogen-abstracting species other than the bromine atom might be involved in NBS bromination has previously been presented. See, for example, J. G. Traynham, E. E. Green, Y. Lee, F. Schweinsberg, and C. Low, *J. Amer. Chem. Soc.*, **94**, 6552 (1972).

(4) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Amer. Chem. Soc.*, **85**, 2850 (1963); K. J. Shea, D. C. Lewis, and P. S. Skell, *ibid.*, **95**, 7770 (1973).

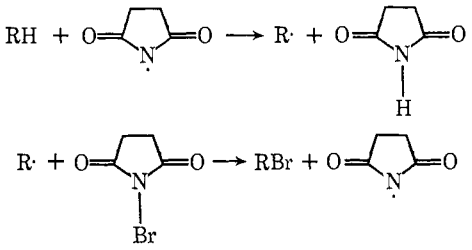
(5) The rearrangement of NBS to β-bromopropionyl isocyanate is enhanced in the presence of olefin. H. W. Johnson, Jr., and D. E. Bublitz, *J. Amer. Chem. Soc.*, **80**, 3150 (1958); J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957); C. Walling, A. L. Rieger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963); R. E. Pearson and J. C. Martin, *ibid.*, **85**, 3142 (1963).

(6) A typical reaction: 17 mmol of 1-bromobutane, 4.3 mmol of NBS, and 2.5 mmol of ethylene in 7 ml of CH_2Cl_2 is irradiated with a medium-pressure mercury vapor lamp, through Pyrex, at 25° for 30–60 min, producing 15–25% C_4 dibromides. The products are separated and identified with the aid of gc procedures. Substitution at C_2 is complicated in the absence of Br_2 by decomposition of the 1-bromo-2-butyl radical to 1-butene (small amounts detected) and ultimately formation of crotyl bromide and 1,4-dibromo-2-butene, in addition to 1,2-dibromobutane. Main product composition does not vary with time or change to CH_3CN solvent.

(7) W. A. Thaler, *J. Amer. Chem. Soc.*, **85**, 2607 (1963).

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.

J. C. Day, M. J. Lindstrom, P. S. Skell*
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802
Received May 3, 1974

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 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-

(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).
(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. 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).