

$$G/G_{\infty} = f \left[ 1 - 0.18 \left( \frac{1-f}{1-0.9661f} \right)^2 - 0.82 \left( \frac{1-f}{1-0.6761f} \right)^2 \right] \quad (3)$$

Equation (3) is plotted in Fig. 2. It is seen that, for this case, there is a significant correction to the usual assumption that  $G/G_{\infty} = f$ .

The degree to which the example above approximates any real system is uncertain. It is likely that the probability that a given base be paired is influenced significantly by the presence or absence of pairs among neighboring bases. The result would be that the distribution of sequence lengths would not be random as assumed above. Any attempt to account for this in the type of calculation performed here must introduce structural parameters which are not known at present. An indication of the nature of this effect has been given by theoretical treatments of the thermal denaturation process for two-stranded nucleic acids,<sup>5</sup> where it has been shown that the process occurs via states involving a significant proportion of base pairs in relatively short sequences. For this case it appears likely that the sequence length distribution is weighted more heavily in the long sequences than is the random distribution, as a result of the cooperative nature of the denaturation. This effect would decrease the correction necessary in the assumption of  $G/G_{\infty} = f$ . In the case of ribonucleic acid, thermal denaturation occurs over a much broader range than in deoxyribonucleic acid,<sup>2</sup> suggesting that the destruction of base pairs is more nearly random in the former, in which case the above example would apply to a better degree of approximation. The example serves at least to place an upper limit on the correction necessary to the calculation of  $f$  from the hypochromism in cooperative melting. In denatured DNA, on the other hand, where a partial restoration of hypochromism occurs on reversal of the denaturing conditions, it appears that the cooperative nature of the base pairing has been destroyed, as evidenced by the broadening of the transition.<sup>2</sup> It is expected that the example used here would be a reasonable approximation to this case.

One significant result of these observations is the possible necessity to reinterpret the melting temperature,  $T_m$ , for nucleic acids. This has been defined<sup>2</sup> as the temperature at which  $G/G_{\infty} = 0.5$ . This definition remains adequate for most purposes, where  $T_m$  is required only as an operational quantity. However, a melting temperature of simpler thermodynamic significance would be defined as the temperature at which  $f = 0.5$ . At this temperature  $T_m'$ ,  $\Delta F^0$  for the transition is zero, and  $T_m' = \Delta H^0/\Delta S^0$ . From Table I it is seen that  $G/G_{\infty} = 0.18$  at this temperature for the present example. For the broad thermal transitions in ribonucleic acids, it appears<sup>2</sup> that  $T_m'$  might be around 10° higher than  $T_m$ , although this is assumed to be an approximate upper limit.

DEPARTMENT OF CHEMISTRY  
COLUMBIA UNIVERSITY  
NEW YORK 27, NEW YORK

JON APPLEQUIST

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(5) B. H. Zimm, *J. Chem. Phys.*, **33**, 1349 (1960), and references cited therein.

### TRANSANNULAR AND HYDROGEN-REARRANGEMENT REACTIONS IN CARBENOID DECOMPOSITION OF DIAZOCYCLOALKANES

Sir:

Diazo compounds decompose to carbenes which give olefins by hydrogen-migration and cyclopropanes by 1,3-intramolecular insertion<sup>1</sup>; carbon-skeleton rearrangement does not occur extensively in carbenoid systems of the neopentyl type.<sup>1a</sup> Rearrangements of carbon-skeleton<sup>2</sup> are major reactions, however, in thermal decomposition of diazocyclopropane,<sup>3</sup> cyclopropyldiazomethane,<sup>4</sup> and diazocyclobutane<sup>4</sup> in that allene (ring opening), cyclobutene (ring expansion), and methylenecyclopropane (ring contraction), respectively, are the principal products.

Intramolecular 1,2-, 1,3-, 1,5- and 1,6 hydride shifts occur extensively in carbonium ion reactions of medium-sized saturated rings; transannular alkylations to give bicyclic products occur only to a limited extent.<sup>5</sup> A study has now been made of decomposition of homologous C<sub>5</sub> through C<sub>10</sub> diazocycloalkanes in order to determine the kind and extent of transannular and rearrangement reactions which simple cyclic carbenes give. Diazocyclopentane<sup>6</sup> and diazocyclohexane<sup>6</sup> decompose thermally to cyclopentene (100%) and cyclohexene (100%), respectively; there were no detectable quantities of hydrocarbons derived from transannular insertion or ring contraction in these systems. The decomposition of diazocyclohexane to cyclohexene is contrasted with the quantitative

(1) (a) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (b) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); (c) 1,5- and 1,6-intramolecular insertion occurs in decomposition of 2-(β-phenylethyl)-phenyldiazomethane to 2-phenylindan and of 2-(γ-phenylpropyl)-phenyldiazomethane to 2-benzylindan and 2-phenyltetralin: C. D. Gutsche and H. E. Johnson, *J. Am. Chem. Soc.*, **77**, 5933 (1955); C. D. Gutsche, E. F. Jason, R. S. Coffey and H. E. Joanson, *ibid.*, **80**, 5756 (1958).

(2) Carbon-skeleton rearrangement of a carbene is equivalent to intramolecular insertion of the carbenic center across a carbon-carbon bond.

(3) (a) Private communication by S. S. Rawalay of this laboratory. Diazocyclopropane was generated as a presumed intermediate in reaction of N-cyclopropyl-N-nitroso-p-toluenesulfonamide and lithium ethoxide in diethyl Carbitol. (b) See also W. M. Jones, *ibid.*, **82**, 6200 (1960).

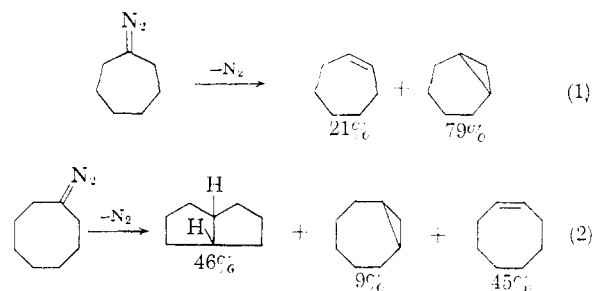
(4) L. Friedman and H. Shechter, *ibid.*, **82**, 1002 (1960).

(5) (a) Solvolysis of cyclodecyl arylsulfonates,<sup>5a</sup> diazotization of cyclodecylamine,<sup>5d</sup> and formolysis of cycloheptene oxide,<sup>5e</sup> *cis*- and *trans*-cyclodecene oxides,<sup>5f,6</sup> *cis*- and *trans*-cyclononene oxides,<sup>5h</sup> and *cis*-cyclodecene oxide<sup>5i</sup> involve marked transannular hydride shifts; no bicyclic products were reported. (b) *cis*- and *trans*-decalins<sup>5j</sup> are minor products in acid-catalyzed isomerization of *trans*- to *cis*-cyclodecene. Formolysis of *trans*-cyclodecene oxide yields *trans*-1-decalol<sup>5k</sup> (see footnote 13b), a transannular alkylation product (21%), along with cyclodecanone, 1,6-cyclodecanediol and other products. (c) H. J. Urich and V. Prelog, *Helv. Chim. Acta*, **40**, 477 (1957). (d) V. Prelog, H. J. Urich, A. A. Bothner-By and J. Wursch, *ibid.*, **38**, 1095 (1955). (e) A. C. Cope, T. A. Liss and G. W. Wood, *J. Am. Chem. Soc.*, **79**, 6289 (1957). (f) A. C. Cope, J. M. Grisar and P. E. Peterson, *ibid.*, **81**, 1640 (1959). (g) A. C. Cope, A. Fournier and H. E. Simmons, *ibid.*, **79**, 3905 (1957). (h) V. Prelog, K. Schenker and W. King, *Helv. Chim. Acta*, **36**, 471 (1953). (i) V. Prelog and K. Schenker, *ibid.*, **35**, 2044 (1952). (j) A. C. Cope, D. C. McLean and N. A. Nelson, *J. Am. Chem. Soc.*, **77**, 1628 (1955).

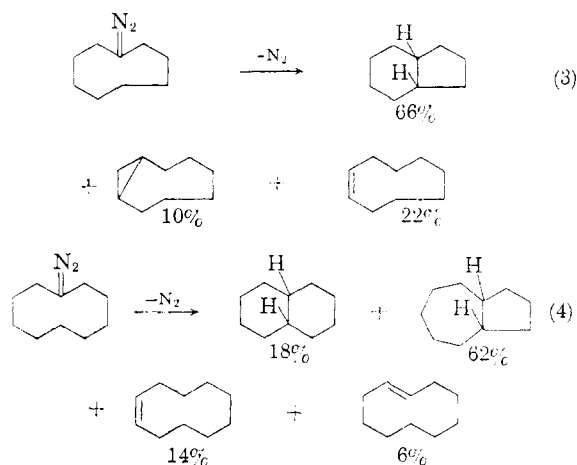
(6) (a) The diazocycloalkanes were generated by decomposing tosylhydrazones of the cycloalkanonones with sodium methoxide (1.2 equivalents) in diethyl Carbitol. The yields of hydrocarbons are 60–70%. The percentages reported are product compositions of the mixture of hydrocarbons formed as determined by gas chromatography. (b) The C<sub>8–10</sub> cycloalkanonone tosylhydrazones (analytical samples) melted at 180–181, 155–156, 144–146, 140–141, 135–136, and 137–138°, respectively.

conversions of 2-diazocamphane and 2-diazonorborene to tricyclene and nortricyclene, respectively. These results illustrate the differences in carbenic reactions of 6-membered rings in their chair and rigid-boat forms.

Decomposition of diazocycloheptane<sup>6</sup> (Equation 1) yielded bicyclo[4.1.0]heptane (18%) by 1,3-transannular insertion and cycloheptene (82%) by 1,2-rearrangement of hydrogen. Thermolysis of diazocyclooctane<sup>6</sup> (Equation 2) gave *cis*-bicyclo[3.3.0]octane (46%), bicyclo[5.1.0]octane (9%)<sup>7</sup> and *cis*-cyclooctene (45%)<sup>7</sup>. Diazocyclononane<sup>8</sup> (Equation 3) yielded *cis*-hydrindane (66%), bicyclo-



[6.1.0]nonane<sup>9</sup> (10%), and *cis*-cyclononene (22%). Diazocyclodecane<sup>3</sup> (Equation 4) gave a greater variety of transannular reactions than its lower homologs: *cis*-bicyclo[5.3.0]decane (62%) and *cis*-decalin (18%)<sup>10</sup> result from transannular insertion and *cis*-cyclodecene (14%) and *trans*-cyclodecene (6%) are formed by hydrogen rearrangement.



Carbenoid decomposition of C<sub>7</sub> through C<sub>10</sub> diazocycloalkanes is thus characterized by extensive 1,3-, 1,5- and 1,6-transannular insertion along with rearrangement of  $\alpha$ -hydrogen. It is also

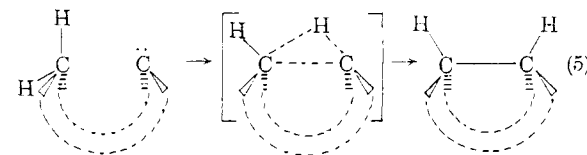
(7) Also prepared from cycloheptene, methylene iodide and zinc-copper: b.p. 141.5–142° (760 mm.),  $n_D^{20}$  1.4601 (analytical sample).

(8) Essentially identical results have been obtained independently by A. C. Cope, M. Brown and G. L. Woo for decomposition of *p*-tosylhydrazones of cyclooctanone and cyclodecanone and will be reported separately by them. A preliminary account of this work was given by A. C. Cope in a lecture at the Robert A. Welch Foundation Conferences on Chemical Research in Houston, Texas, November 7, 1960.

(9) Also synthesized from *cis*-cyclooctene, methylene iodide and zinc-copper: b.p. 43° (8 mm.),  $n_D^{20}$  1.4622 (analytical sample).

(10) A saturated hydrocarbon also was obtained (~1%) which has been assigned tentatively as bicyclo[7.1.0]decane.

apparent that bicyclic products are formed much more efficiently by carbenic rather than cationic insertion processes.<sup>5,11</sup> The absence of 1,4-insertion products presumably stems from improper stereochemistry during decomposition of the medium-sized diazocycloalkanes. It is of interest that the insertion processes are stereoselective in that only *cis*-bicyclic hydrocarbons are formed. The extensive transannular insertion and the stereochemistry of decomposition of the diazocycloalkanes thus parallel reactions of lithium diethylamide with *cis*-cyclodecene oxide and *cis*-cyclooctene oxide to give *cis-cis*-1-decalol and *endo-cis*-bicyclo[5.3.0]decan-2-ol, and *endo-cis*-bicyclo[3.3.0]octane-2-ol, respectively, by processes involving simultaneous  $\alpha$ -elimination and carbenic insertion.<sup>12</sup> The stereospecific transannular insertions of carbenic systems to give *cis*-bicyclic derivatives is a necessary consequence of transfer of axial hydrogen in ring systems (Equation 5<sup>12a-c</sup>) and is consistent with the principle that carbenic insertions occur with retention in configuration.<sup>13d</sup>



(11) In base-catalyzed decomposition of C<sub>7</sub>-C<sub>10</sub> cycloalkane tosylhydrazones in protonic solvents, processes which are in part cationic, the ratios of olefin to bicyclic products are considerably greater than those obtained from reactions under optimum carbenic conditions.

(12) (a) A. C. Cope, G. A. Berchtold, P. E. Peterson and S. H. Sharman, *J. Am. Chem. Soc.*, **82**, 6370 (1960). (b) Reactions of lithium diethylamide with *trans*-cyclodecene oxide and *trans*-cyclooctene oxide, presumably  $\alpha$ -elimination carbenic processes, yield *cis-trans*-1-decalol and *exo-cis*-bicyclo[3.3.0]octan-2-ol, respectively: A. C. Cope, M. Brown and H. H. Lee, *ibid.*, **80**, 2855 (1958), and A. C. Cope, H. H. Lee and H. E. Petree, *ibid.*, **80**, 2849 (1958).

(13) (a) On the basis of stereochemical criteria, it is also expected that the bicyclic products of kinetic control produced from transannular reactions of monocyclic derivatives via alkylation of the carbonium ion type or by nucleophilic displacement will be of *cis*-structure. (b) Formolysis of *trans*-cyclodecene oxide is reported to yield *trans*-1-decalol, m.p. 93°, as a transannular product. D. J. Cram in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 286, suggests that the product is *trans-trans*-1-decalol. The present authors assign the structure of the transannular product as *cis-cis*-1-decalol, see W. Hüchel, R. Dannell, A. Gross and H. Naab, *Ann.*, **502**, 99 (1933), and ref. 12. (c) The present authors wish to acknowledge the contributions of P. B. Sargeant, S. Ranganathan, D. C. Berndt and S.-Y. Lee to these stereochemical conclusions.<sup>12b</sup> (d) W. von E. Doering, 139th Meeting of the American Chemical Society, St. Louis, Mo., March 30, 1961.

CHEMISTRY DEPARTMENT  
THE OHIO STATE UNIVERSITY  
COLUMBUS 10, OHIO

LESTER FRIEDMAN  
HAROLD SHECHTER

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#### SELECTIVE HYDROGENATION OF AN AROMATIC RING IN A NITRO COMPOUND<sup>1</sup>

Sir:

We wish to report an instance of the selective hydrogenation of the benzene ring in a compound (I) that also contains a nitro group, the selectivity evidently resulting from a combination of steric and electronic factors that protect the nitro group and facilitate attack on the aromatic system.

(1) Support of this work by a grant (G-6223) from the National Science Foundation is gratefully acknowledged.