

THE DEGENERATE COPE REARRANGEMENT OF
TRICYCLO [3.3.1.0^{4,6}] NONA-2,7-DIENE-9-ONE

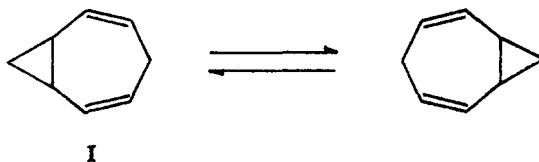
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The discovery¹ that bicyclo [5.1.0] octa-2,5-diene (3,4-homotropilidene, I) undergoes a rapidly reversible, degenerate Cope rearrangement has stimulated considerable theoretical interest. The



generality of such behavior has recently been put to test by the synthesis of tricyclo [3.3.2.0^{4,6}] deca-2,7,9-triene (bullvalene, II)² and of tricyclo [3.3.1.0^{4,6}] nona-2,7-diene-9-one (barbaralone, III).³ All three

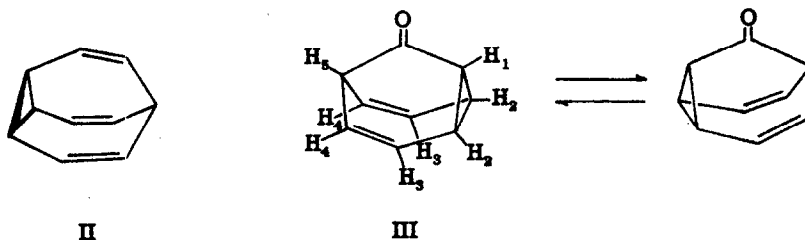
*Contribution No. 3019

¹W. von E. Doering and W. R. Roth, Tetrahedron, 19, 715 (1963).

²G. Schroeder, Angew. Chem., in press.

³W. von E. Doering and B. M. Ferrier, mentioned in a review article by W. von E. Doering and W. R. Roth, Angew. Chem., Inter. Ed., 2, 115 (1963). The synthesis involves treating 7-cycloheptatrienyldiazomethylketone (from cycloheptatriene-7-carboxylic acid by way of the acid chloride) with copper powder.

molecules incorporate the significant structural features of the nonisolable



cis-1,2-divinylcyclopropane, which rearranges to 1,4-cycloheptadiene at temperatures as low as -40° .^{1,4} Molecules I-III furthermore maintain the necessary eclipsed orientation between the allyl components, whereas the vinyl groups in the cyclopropane are subject to free rotation. For rearrangement to occur, the two allyl components also must occupy a position endo with respect to the cyclopropane ring. Therefore, the stable transoid form¹ of I must convert to the cisoid form prior to rearrangement. By means of the bridging groups, molecules II and III maintain the allyl components rigidly in the desirable configuration.

The rapidly reversible Cope rearrangement of bullvalene brings about the equivalence of all carbon atoms in the molecule.¹ Thus at high temperatures the nuclear magnetic resonance (n. m. r.) spectrum exhibits a single peak.² From line shape measurements at various temperatures, Saunders⁵ has calculated that the first-order rate constant is $79,000 \text{ sec}^{-1}$ at 82.7° (1200 sec^{-1} at 10.4°) and the energy of activation is 11.8 kcal/mole.

⁴E. Vogel, K. H. Ott, and K. Gajek, Ann., 644, 172 (1961).

⁵M. Saunders, Tetrahedron Letters, in press.

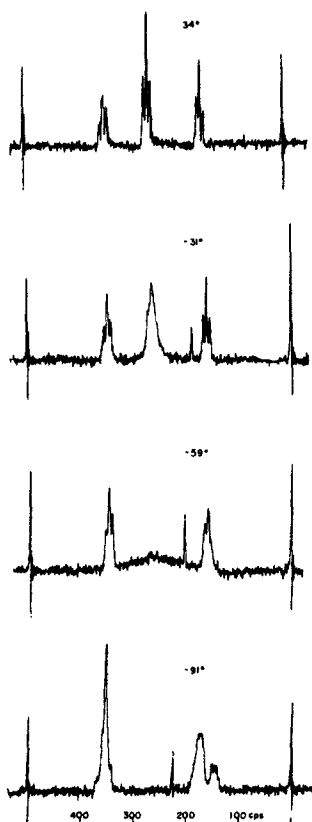


FIG. 1.

The n.m.r. spectrum of III, in acetone- d_6 , calibrated in cps down-field from tetramethylsilane. An impurity near 200 cps and a sideband at 500 cps are present.

multiplier of the room temperature spectrum. The spectrum at -91° is essentially that required of III in the absence of rearrangement. The vinyl

The degenerate Cope rearrangement of barbaralone is easily demonstrated by n.m.r. spectroscopy to be occurring rapidly at 34° (cf. Figure 1). The central triplet (four protons) results from the average of the resonances of the vinyl protons (H_4) and of the allylic cyclopropane protons (H_2). The intensity of the low-field peak shows that only two protons retain vinylic character in the n.m.r. spectrum. The high-field peak results from the average of the resonances of the two protons adjacent to the carbonyl group, H_1 and H_5 .

As the temperature is decreased, the rate of rearrangement is slowed. By -33° , the central triplet has broadened considerably, and by -70° , it has disappeared completely. The high- and low-field multiplets broaden and then gain intensity until, by -91° , the width at half height of the vinyl peak is the same as that calculated from the middle peak of the central

absorption has an intensity of four (H_3 and H_4), and the remaining protons, all of which either are allylic or are adjacent to the carbonyl group, have resonances which fall in the region from 100 cps to 200 cps.

Of compounds I-III, only III has completed averaging of the various protons at room temperature.^{1,2} With respect to I, this is not surprising, but it is less expected that III rearranges at a faster rate than II, which has a statistical factor of three in its favor. This may result from the inductive effect of the carbonyl group or from the larger angle strain, which could be partially relieved in the transition state of the rearrangement.

An approximate determination of the reaction parameters has been made from consideration of line broadening effects. The method of Gutowsky and Holm⁶ is not applicable because the changes in chemical shift below the coalescence temperature (-64°) cannot be measured accurately. The central peak, which disappears at low temperatures, is convenient for the line shape measurements. The presence of spin-spin coupling complicates the situation since the various components of the multiplet broaden at different rates. For this reason, measurements were only made in the temperature range for which a single broad peak was observed. The analysis followed the method of Anbar, *et al.*⁷ Since the populations of the equilibrating species are equal, the rate of reaction is given by:

$$R = \frac{\pi}{2} \frac{\delta^2}{\Delta - \delta_0} \quad (1)$$

where δ is the difference in chemical shift between the low-field and the

⁶H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25, 1228 (1956).

⁷M. Anbar, A. Loewenstein, and S. Meiboom, *J. Am. Chem. Soc.*, 80, 2631 (1958). The rate law, Equation (1), was derived from Equation (2) of this reference.

high-field peaks in the absence of exchange (180.0 cps), Δ is the measured line width at half height, and δ_0 is the natural line width in the absence of exchange effects (6.5 cps). The rate is related to the energy of activation by Equation (2):

$$\log R = \log \nu_0 - \frac{0.4343}{RT} \Delta E \quad (2)$$

A plot of $\log R$ versus $1/T$ (cf. Figure 2 and Table I) therefore permits calculation of the activation energy (from the slope) and the frequency factor (from the intercept at which $\log R$ is zero). Thus, for the degenerate Cope rearrangement of barbaralone, $\Delta E = 8.1$ kcal/mole and $\nu_0 = 1.4 \times 10^{11}$.

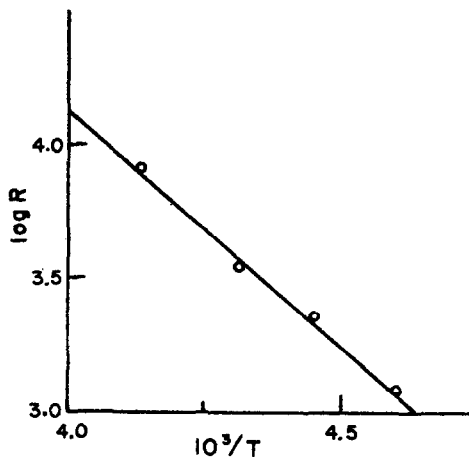


FIG. 2.
Log R vs. $10^3/T$ for III.

TABLE I
Rate Parameters for the
Rearrangement of III

Δ , cps	R, sec ⁻¹	T, °K
12.8	8190	242
19.1	3500	232
27.1	2260	225
48.8	1200	218
$\delta = 180.0$	--	182

All n. m. r. measurements were made on a Varian model 4300B spectrometer operated at 60 Mcps. Calibrations were achieved by the side-band technique.

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