very unstable (*e.g.*, it detonated with a flash on being rubbed), but could be stored in ether solution at 0°. A satisfactory elemental analysis or mass spectrum could not be obtained for this reason, but the assigned structure follows from the method of synthesis, the spectral data, and the fact that catalytic hydrogenation in ethyl acetate over platinum gave cyclotetracosane (mass spectrum, m/e 336).

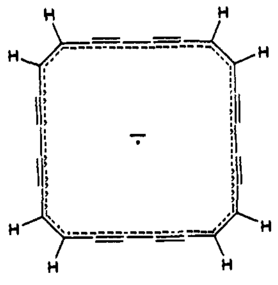
The octadehydro[24]annulene (**5**) is formally derived from cyclooctatetraene by insertion of four 1,3-diyne rods, and, like this substance, appears to be nonplanar. This follows from the general similarity of the electronic spectrum to that of the precursor **4a** (both in λ_{max} and ϵ values, taking into account that **5** is made up of two units of **4a**), and especially from the fact that the position of the proton resonance in the nmr spectrum (τ 3.85 in THF-d_8) is not shifted upfield compared with linear models (*e.g.*, **3a**, τ 4.11 in CCl_4; **4b**, τ 4.06 in THF-d_8). This is in contrast to the presumably more planar 1,7,13,19-tetradehydro[24]annulene[11] and 1,3,9,11,17,19-hexadehydro[24]annulene,[12] in which the outer protons are shifted appreciably upfield due to a paramagnetic ring current. The fact that **5** is nonplanar is probably due to the presence of four cis double bonds and the comparative rigidity imposed by the four 1,3-diyne units.

Contact of a solution of the octadehydro[24]annulene (**5**) in THF-d_8 with a potassium mirror at room temperature *in vacuo* resulted in the immediate disappearance of the nmr signal. The esr hyperfine spectrum of the deep blue solution in THF consisted of nine equally spaced lines, and these had the approximate relative intensities expected for the hyperfine splittings of a symmetrical radical anion with eight equivalent protons. The line width was about 0.15 G,[13] and a value of 1.66 G was found for a^H, the hyperfine interaction. The small value of a^H compared to that observed for the cyclooctatetraenyl radical anion (3.21 G)[13] indicates that the electron spends part of the time on the acetylenic carbon atoms.

Contact of **5** in THF-d_8 with the potassium mirror (with occasional shaking) for 2 hr resulted in the appearance of a new singlet at τ 3.88[14,15] (*i.e.*, at approximately the same position as that of **5**), which we attribute to the dianion. This signal slowly decreased in intensity on further contact with potassium. Quenching this solution with water gave only some **5** and a considerable amount of polymer.

The course of the reduction of **5** in THF with a potassium mirror could be followed most conveniently by examination of the electronic spectrum. After shaking for 1 min, the spectrum showed λ_{max} (>380 nm) 389 (relative optical density 0.39), 428 (0.35), 441 (0.36), 446 (0.37), 468 (0.33), 564 (0.04), 582 (0.03), 595 (0.02), and 638 nm (0.07), as well as maxima due to **5**. After 10 min, the spectrum was similar but the optical densities of the new bands were greater. The 468-nm maximum then increased in intensity at the expense of the other bands and gradually moved to higher wavelength, until after ~1 hr the spectrum (>300 nm) consisted simply of one maximum at 476 nm. The spectrum after 1 min is considered to be due to mainly the radical anion, and the final spectrum to the dianion.[16]

The simple esr spectrum of the radical anion demands that the molecule has a high degree of symmetry, and this is most readily accommodated by the planar delocalized structure **6**, formally derived from the cyclooctatetraenyl radical anion[13] by elongation of alternate bonds. The proton chemical shift of the nmr spectrum of the dianion is at lower field than would be expected for a localized system having two excess electrons,[17] and is indicative of the planar delocalized structure **7**. The coincident position of the nmr signals of **5** and **7** is attributed to the balance between the deshielding effect of the diamagnetic ring current and the shielding due to the excess electron density, as has previously been observed for cyclooctatetraene and its dianion.[18]



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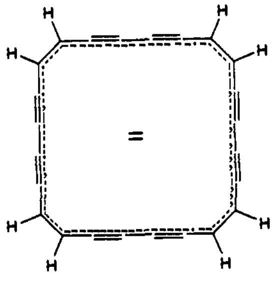

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(13) For the method of measurement and its significance, see H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 2360 (1963).

(14) Measured from the low-field band of THF, taken as τ 6.40.

(15) At the concentrations required for the nmr experiments, the formation of a black insoluble polymer occurred in a number of cases, and no new signal was observed.

(16) The fact that the electronic spectra of this type of radical anion is more complex than that of the corresponding dianion has been observed before (see N. S. Hush and J. R. Rowlands, *Mol. Phys.*, **6**, 317 (1963).

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* Address correspondence to this author.

R. M. McQuilkin, P. J. Garratt, F. Sondheimer*
Chemistry Department, University College
London W.C.1, England

Received August 10, 1970

Photodecomposition of *cis*- and *trans*-2,4-Dimethylcyclobutanones in the Gas Phase. Stereochemical Inversion in the Decarbonylation Process and Unimolecular Lifetime of the Hot Ground State[1]

Sir:

We have recently reported one aspect of the stereochemistry in the thermal and photolytic decomposition of *cis*- and *trans*-2,3-dimethylcyclobutanones (DMCB).[2]

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(1) This research has been supported by National Science Foundation Grant No. GP 11390.

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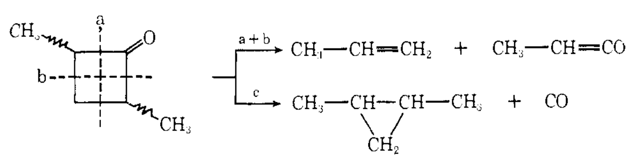
Our more recent study of the other position isomers, *cis*- and *trans*-2,4-DMCB, provides a significant additional feature of the stereochemistry which could not be resolved in the earlier study of the 2,3-DMCB isomers, and we wish now to present and discuss the results.

The product distribution pattern, as expected from the parallel studies,[2] is shown in Scheme I. The noteworthy results are: (1) pyrolysis of *cis*- and *trans*-2,4-DMCB at 330–335° gives propylene (and methylketene) only by the ring-fission paths a and b, indicating an absence of the decarbonylation process c; (2) the $^3B_{1u}$ benzene-sensitized decompositions of these stereoisomers give only *cis*- and *trans*-1,2-dimethylcyclopropanes (DMCP) with a trans/cis ratio of 1.24; (3) direct photolysis of *cis*- and *trans*-DMCB at 325.0 nm (He–Cd laser) and at low pressure gives predominantly the ring-fission product over the decarbonylation product in the following proportions: c = 0.115(a + b) and c = 0.125(a + b), respectively; (4) the DMCP isomer quantum yields are pressure independent and the trans/cis ratio of DMCP is 2.20 for *cis*-DMCB and 1.06 for *trans*-DMCB in the 325.0-nm photolysis; (5) the propylene yield in the 325.0-nm photolysis decreases with increasing pressure (>0.1 Torr), leveling off at ~10 Torr, and the pressure-unquenchable amount of propylene (at a limiting low pressure) corresponds to 17.6% of the total propylene for *cis*-DMCB and 10.0% for *trans*-DMCB; and (6) the half-quenching pressure ($P_{1/2}$) of the pressure-quenchable portion of the propylene yield due to the decomposition of the vibrationally hot 2,4-DMCB (S_0*) is ~0.9 Torr of the parent DMCB.

Scheme I

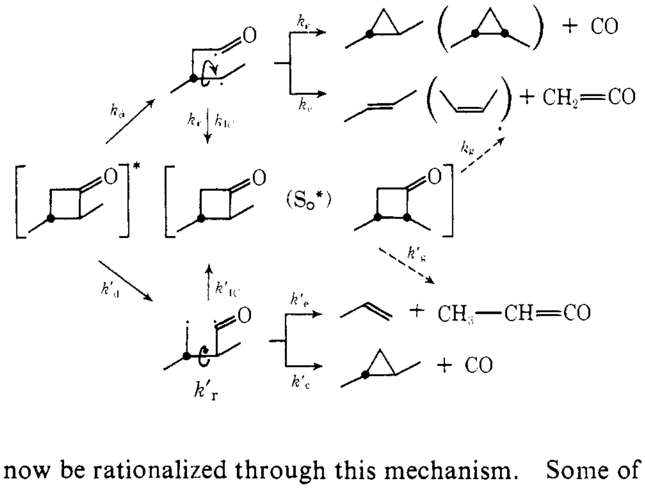


Obviously the most intriguing results are the trans/cis ratios of the DMCP yield obtained in (4) compared to that obtained in (2); it is surprising that DMCP is formed preferentially with inversion of the stereochemistry of the parent DMCB, as shown more clearly in the direct photolysis of *trans*-2,4-DMCB than in the case of *cis*-2,4-DMCB. By no means is the stereoinversion complete. Interestingly enough, an analogous case of stereoinversion has been found in the pyrolysis and the photolysis of *cis*- and *trans*-3,5-dimethyl-1-pyrazoline.[3,4] A significant portion of the decarbonylation process must be steered by a *conrotatory* C_3-ring closure–decarbonylation, if a concerted mechanism permitted by the orbital symmetry rules[5] operates.

We now have firm estimates on the lifetime of 2,4-DMCB (S_0*) in its vibrationally "hot," ground electronic state with an excess internal energy of 88 kcal/mol, through the pressure dependence of decomposition–stabilization, and the lieftimes of 2,4-DMCB (S_0*) and cyclobutanone (S_0*) should be compared in light of the RRKM theory of unimolecular decomposition rates. We estimate the unimolecular lifetime of the photoactivated 2,4-DMCB (S_0*) to be $\sim 1 \times 10^{-7}$ sec with respect to the *concerted*[2] ring-fission process a and b, since the observed value of $P_{1/2}$ is 0.9 Torr of 2,4-DMCB, while we estimate the lifetime of the photoactivated CB (S_0*) at 325.0 nm to be $\sim 3 \times 10^{-10}$ sec with respect to the ring-fission process, from our early photoactivation study of cyclobutanone.[6] Therefore, the substitution of two methyl groups lengthens the unimolecular lifetime by a factor of ~300, while it is expected to lengthen the lifetime by two orders of magnitude when an approximate application of the RRKM rate theory is carried out.[6] Thus, the agreement between experiment and theory with regard to the lifetimes of the internally converted intermediates (S_0*) produced here is reasonably satisfactory.

Our observation of a pressure-unquenchable pathway for propylene formation in the photolysis of the 2,4-DMCB isomers must be compared to similar studies on the 2,3-DMCB isomers. For the latter compounds, the pressure-quenchable as well as pressure-unquenchable 2-butene yields and the 1,2-DMCP yields in the direct photolysis (325.0 nm) of *cis*- and *trans*-2,3-DMCB show only partial stereospecific retention.[7] These experiments provide a basis for postulating a "nascent" diradical intermediate, and a mechanistic scheme for the disappearance of the electronically excited DMCB, exemplified for *trans*-2,3-DMCB, is shown as Scheme II. All of the known experimental observations can now be rationalized through this mechanism. Some of the less obvious facts are: (1) the CH_3 substitution in the C_2 (or C_4) position makes $k_d \gg k_d'$ as expected in a radical generating mechanism, while in contrast it makes $k_g < k_g'$ in pyrolysis and in the decomposition of the internally converted state;[2] (2) $k_{IC} > k_r \approx k_e > k_c$ on 325.0-nm excitation; (3) the intermediacy of the acyl-alkyl diradical provides a "*chemical isomerization*" route for the intriguing $S_1 \rightsquigarrow S_0$ internal-conversion process.[6,8] Our gas-phase photolyses[2] indicate

Scheme II



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[4] See an interesting discussion by R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

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[6] N. E. Lee and E. K. C. Lee, *J. Chem. Phys.*, **50**, 2094 (1969).

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that the diradical lifetimes are extremely short, since the diradical components are unquenched by up to 200 Torr of added oxygen. Liquid-phase DMCB photolyses support such a short lifetime.

A more quantitative and extensive investigation of this interesting diradical system is underway in order to study the energetics, rates, and mechanism.

Acknowledgment. Helpful discussions on the orbital symmetry conservation with Professors Marjorie C. Caserio and H. W. Moore are appreciated.

* Address correspondence to this author.

Howard A. J. Carless, Edward K. C. Lee*
Department of Chemistry, University of California
Irvine, California 92664

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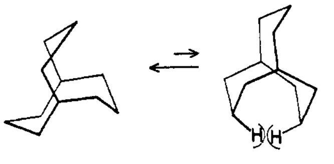
Synthesis and Characterization of Bicyclo[3.3.3]undecane and 1-Azabicyclo[3.3.3]undecane

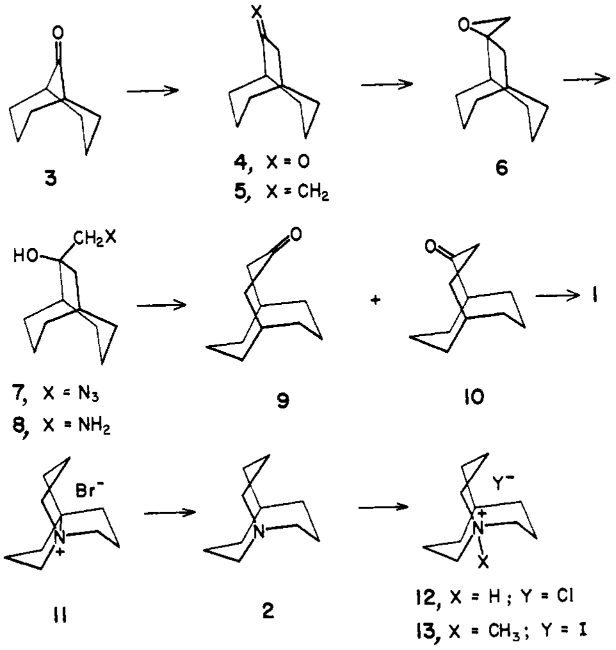
Sir:

We wish to report the synthesis of two prototype compounds consisting of three eight-membered rings, namely, bicyclo[3.3.3]undecane (**1**) and 1-azabicyclo-[3.3.3]undecane (**2**). Compounds possessing this bridged ring system are of particular interest with regard to their possible conformations and their chemical reactivity in comparison with other multicyclic systems including adamantane.

Interest also stems from the conformational relationship to eight-membered rings[1] in the carbocyclic series,[2] when one or more ring atoms are replaced by heteroatoms,[3] and when the eight-membered ring has been constrained by a charge interaction,[4] or by a hydrocarbon bridge of one[5] or two[6] atoms. For unconstrained eight-membered rings, nmr[2e] and X-ray crystallographic[7] evidence has shown the boat–chair (BC), or twist forms thereof, to be the favored conformation. This is also the case for the charge-constrained system 5-methyl-1-thia-5-azacycloocten-1-oxide perchlorate.[4] For the bicyclo[3.3.1]nonane[8] and bicyclo[3.3.2]decane[6,9] systems, accumulated evidence suggests the boat–boat (BB) conformation for the eight-membered ring. Molecular models (Dreiding) of the BB conformation of the eight-membered ring indicate that the transannular H–H distance diminishes in going from the bicyclo[3.3.1]nonane to the bicyclo[3.3.2]decane system, and finally in the bicyclo[3.3.3]undecane system the transannular hydrogens are in contact when one of the eight-membered rings is in the boat–boat conformation (**1b**). On this basis we predict that in the bicyclo[3.3.3]undecane system the all-boat–chair conformation (**1a**) should be favored over the crown–BC–BB conformation (**1b**). Calculations based on the strain energy of the boat–chair, crown, and boat–boat conformations of cyclooctanes[2a] suggest that the all-BC form (**1a**) should be *at least* 6 kcal more stable than alternative conformations.[10]



1a BC–BC–BC **1b** Crown–BC–BB



The synthesis of bicyclo[3.3.3]undecane (**1**) was accomplished by lengthening the short bridge of a bicyclo-[3.3.1]nonane compound. Ring expansion of bicyclo-[3.3.1]nonan-9-one (**3**)[11] with methanolic diazomethane[12] afforded bicyclo[3.3.2]decan-9-one (**4**):[13] mp 177–179°; sublimed 60° (10 mm); 75% yield; ir ($CHCl_3$) 1690 cm^{-1}; nmr ($CDCl_3$) δ 2.85 (m, 1, CHCO), 2.50 (d, 2, $J = 6$ Hz, CH_2CO). This compound failed to react further with diazomethane under the same conditions, and numerous routes to the amino alcohol **8**

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