cedure enables calculation of the heterolytic bond dissociation energies (column 3 of Table II) and the heats of formation of alkoxide ions (column 4 of Table II).

The differences between the O–H bond dissociation energies and the electron affinities of the alkoxy radicals (column 5 of Table II) can be calculated using eq 6. Our values for these quantities may be combined with current values for the O–H bond dissociation energies to give electron affinities of the alkoxy radicals (see Table III). Williams and Hamill have measured

Table III. Electron Affinities of Alkoxy Radicals[a]

ROH	$DH°$(RO–H)[b]	EA(RO·) This work	EA(RO·) Williams and Hamill[c]
CH_3OH	102 ± 2	39 ± 2.8	
C_2H_5OH	102 ± 2	41 ± 2.7	39 ± 2
$(CH_3)_2CHOH$	103 ± 2	43 ± 2.7	41 ± 2
$(CH_3)_3COH$	103 ± 2	44 ± 2.6	

[a] All values in kcal/mol. [b] Reference 3. These values were assumed in our calculation of the electron affinities. [c] Reference 6.

EA(RO·) from the differences in the appearance potentials for processes such as

$$ROR + e^- = R^+ + RO^- + e^- \quad (13)$$

$$ROR + e^- = R^+ + RO\cdot + 2e^- \quad (14)$$

Comparison of the pulsed icr data with the appearance potential data in Table III shows surprisingly good agreement considering how different the two methods are. Recent studies indicate that the electron affinities of alkoxy radicals can be measured accurately by electron photodetachment experiments.[18] It may be possible to combine these values with our measurements of $DH°$(RO–H) − EA(RO·) to obtain more accurate values for the O–H bond dissociation energies.

Ionic equilibria studied by pulsed icr provide an independent means for calculating heterolytic bond dissociation energies and heats of formation of anions. Further studies of this type are in progress for species of known electron affinities.

Acknowledgments. We are grateful for support from the National Science Foundation (GP-38170X), the Research Corporation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(19) Alfred P. Sloan Fellow, 1973–1975.

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The Thermal Conversion of Triquinacene to Azulene

Sir:

We have found triquinacene (**1**)[1] remarkably resistant to thermal change. The hydrocarbon survives passage through a quartz flow system[2] heated to 500° and remains incompletely consumed even at 900°. Such a degree of thermal stability exceeds that of all other known $(CH)_{10}$ compounds,[3] which now number greater than 20, and signifies that triquinacene must lie in an exceptionally deep well on the $(CH)_{10}$ energy surface.

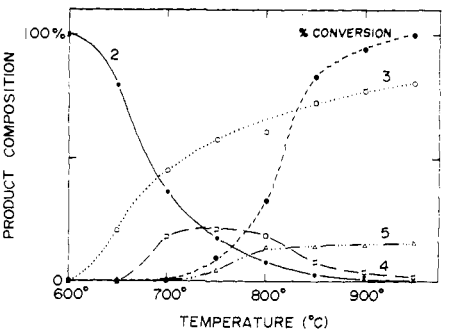


Figure 1. Temperature dependence of the triquinacene pyrolysis.[2] Product compositions were determined by quantitative glc, with appropriate detector response corrections; a good material balance was observed.

At 600° triquinacene undergoes a clean transformation to azulene (**2**, low conversion).[4] This blue hydrocarbon has not previously been reported among the pyrolysis products of any $(CH)_{10}$ isomer[3] and requires the loss of two hydrogen atoms from **1**, possibly as molecular hydrogen. The thermal conversion of triquinacene to azulene thus represents the lowest energy unimolecular reaction available to **1**.

At 650° naphthalene (**3**) accompanies the azulene. Under these conditions azulene rearranges partially to naphthalene,[5] and this isomerization could reasonably account for the formation of **3**.

At 700° a third product appears which does not come from either azulene or naphthalene but must be derived from triquinacene by a competing pathway. This compound, identified as 1,2-dihydronaphthalene (**4**), appears only at temperatures of 700° and above and must therefore be separated from **1** by an energy barrier higher than that between triquinacene and azulene.

At 750° indene (**5**) is found together with **2**, **3**, **4**, and unchanged **1** in the pyrolysate. No additional products were detected in greater than 5% yield below 950°, at which temperature triquinacene no longer survives.[6] Indene and naphthalene constitute the products of independent 1,2-dihydronaphthalene pyrolysis under these conditions. The formation of indene requires a loss of CH_2, the fate of which remains undetermined.[7] Scheme I and Figure 1 summarize these thermal transformations and their temperature dependence.

Progressively lengthening the contact time at 735°

(1) (a) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, **86**, 3162 (1964); (b) I. T. Jacobson, *Acta Chem. Scand.*, **21**, 2235 (1967); (c) H. Prinzbach and D. Stusche, *Helv. Chim. Acta*, **54**, 755 (1971); (d) A. de Meijere, D. Kaufmann, and O. Schallner, *Angew. Chem., Int. Ed. Engl.*, **10**, 417 (1971); (e) C. Mercier, P. Soucy, W. Rosen, and P. Deslongchamps, *Syn. Commun.*, **3**, 161 (1973); (f) M. J. Wyvratt and L. A. Paquette, *Tetrahedron Lett.*, in press.

(2) All pyrolyses were conducted in a quartz tube packed with quartz chips at atmospheric pressure using a slow stream of N_2 as carrier gas. The contact time in the hot zone was adjusted to *ca.* 0.5 sec unless otherwise indicated.

(3) L. T. Scott and M. Jones, Jr., *Chem. Rev.*, 72, 181 (1972); E. E. van Tamelen, *Accounts Chem. Res.*, **5**, 186 (1972); S. Masamune and N. Darby, *ibid.*, **5**, 272 (1972).

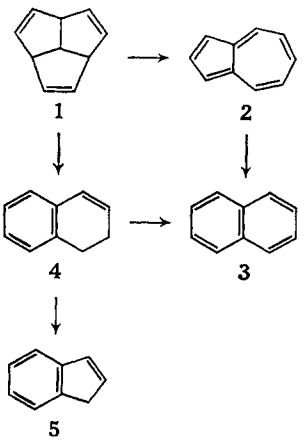
(4) All pyrolysis products were identified by comparison of their glc behavior, mass spectra, and electronic spectra with those of authentic samples.

(5) This rearrangement was first reported by E. Heilbronner, P. A. Plattner, and K. Wieland, *Experientia*, **3**, 70 (1947); E. Heilbronner and K. Wieland, *Helv. Chim. Acta*, **30**, 947 (1947).

(6) Above 850° a minor product is produced (*ca.* 3% yield) which has the same glc retention time as styrene.

(7) In the glc we see no significant peaks for C_{11} hydrocarbons.

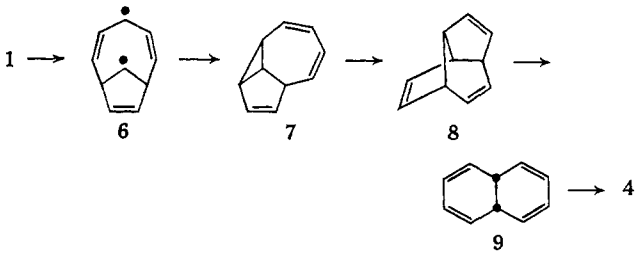
Scheme I



yields increasing amounts of both naphthalene and indene at the expense of **1**, **2**, and **4**. In the limit (735°, 20 sec, 100% conversion) the ratio of **3** to **5** reaches 7:1.

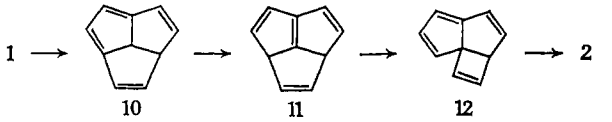
Carbon–carbon bond rupture to produce **6** represents one of the more plausible molecular changes which triquinacene might suffer at elevated temperatures. This diradical could collapse to "isobullvalene" (**7**),[8] a $(CH)_{10}$ isomer which has been reported[8] to rearrange quantitatively at room temperature to "lumibullvalene" (**8**).[9] Above 280° the latter compound is known[9] to isomerize further to *cis*-9,10-dihydronaphthalene (**9**). We have found that **9** fails to survive under our pyrolysis conditions (700°, 0.5 sec), giving **3**, **4**, and **5** as the principal products.[10] Thus the reaction pathway outlined in Scheme II could readily account for the formation of **4** from triquinacene; since **7**, **8**, and **9** all isomerize faster than **1** itself, they should not be expected among the pyrolysis products.

Scheme II



The mechanistic details for the lower energy thermal conversion of triquinacene to azulene, on the other hand, appear less obvious. In particular most known $(CH)_{10}$ hydrocarbons, including **7**, must be excluded as possible reaction intermediates, for none yields azulene on heating;[3] in fact most rearrange ultimately to **9**, another thermal sink on the $(CH)_{10}$ energy surface.[3] Concerted loss of molecular hydrogen from triquinacene[11] to give **10** would remove the molecule from the $(CH)_{10}$ energy surface and thereby preclude isomerization to **9**. We wish to suggest that **10** could suffer sequential [1,5]-sigmatropic shifts of hydrogen and carbon, respectively, to produce **12**, which should open to azulene above 600° (Scheme III). This mechanistic hypothesis predicts an exclusive loss of allylic hydrogens from triquinacene, and labeling studies designed to test this proposition have been initiated in our laboratory.

Scheme III



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Synthesis of Coformycin

Sir:

Coformycin (**1**) is a unique nucleoside, having a moiety of 3,6,7,8-tetrahydroimidazo[4,5-*d*][1,3]diazepin-8(*R*)-ol as the base moiety, and has an interesting biological property.[1] We now wish to report the total synthesis of coformycin starting from a purine ribonucleoside (Scheme I).

9-β-D-Ribofuranosylpurine (**2**) was taken as the starting material, since it is a naturally occurring nucleoside antibiotic called nebularine[2] and was already synthesized,[3] and even coformycin might be biologically formed by ring expansion from such a purine riboside. Treatment of **2** with acetic anhydride in pyridine at 5° for 2 days afforded 9-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)purine (**3**) in 98% yield [M^+ 378, $[\alpha]^{26}D$ −10.8 (*c* 1.5, CH_3OH)].[4] The introduction of a C_1-unit, which can be used for the ring expansion of purine moiety, was achieved by the application of the method of Linschitz and Connolly.[5] Thus, the photoaddition of methanol to **3** was carried out under argone atmosphere and irradiation (10-W low-pressure mercury lamp) at 5° for 3.5 hr, affording 9-(2,3,5-tri-*O*-acetyl-β-D-ribofuranosyl)-6-hydroxymethyl-1,6-dihydropurine (**4**) in 96% yield [M^+ 410, mp 84–86°, uv_{max} (CH_3OH)

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(5) H. Linschitz and J. S. Connolly, *J. Amer. Chem. Soc.*, **90**, 2980 (1968).