Experimental Section

Materials.—Bromotrichloromethane, benzocyclohexene, benzocyclopentene, and *tert*-butylbenzene were obtained from commercial sources. Benzocyclobutene was kindly donated by Professor Phillip Radlick. Benzocycloheptene was prepared from the Wolff–Kishner reduction of 1-benzosuberone. All materials were purified before use. Purities greater than 99% were determined by glc.

Product Studies.—A mixture of 4.232 g (32.186 mmol) of benzocyclohexene and 36.60 g (184.64 mmol) of bromotrichloromethane were treated under nitrogen for 18 hr at 70° with irradiation by our standard source. After reaction and removal of excess bromotrichloromethane, the reaction mixture was analyzed by gas–liquid chromatography on a 5% SE-30 column. It was shown that about 40% of the tetralin had reacted and one product with a slightly longer retention time than tetralin was formed. The compounds were collected as they eluted from the glc column. An nmr spectrum identified the product as 1,2-dihydronaphthalene. This was formed by probable dehydrohalogenation of the initially formed bromide. The unreacted starting material amounted to 19.311 mmol (2.51 g) and the product to 1.49 g (11.620 mmol). The material balance thus found is 96.1%. Although no attempt was made to isolate the initial bromide, its presence could be readily detected in the reaction mixture by nmr spectroscopy. No elimination product could be detected in the reaction mixture before passage through the SE-30 column.

Kinetic Studies.—Solutions of fluorene, a cycloalkene, bromotrichloromethane, and *tert*-butylbenzene were prepared in the approximate molar ratio of 2:4:20:1. Approximately 0.75 ml of the solution was placed in each of the several ampoules. The ampoules were cooled to Dry Ice–isopropyl alcohol temperature until the solutions solidified. The ampoules were evacuated at 0.5–1.0 mm and flushed with nitrogen several times with three intermediate thawings. The ampoules were sealed under vacuum and one was reserved for the analysis of the unreacted starting materials. The remainder were placed horizontally just below the surface of a mineral oil constant-temperature bath maintained at 70.0 ± 0.5°. The solution was irradiated with ultraviolet light provided by a Sylvania 275-W sun lamp placed 20 cm above the surface of the oil. Reaction times varied from 20 to 40 hr, by which time 30–70% of the total hydrocarbons had reacted. The ampoules were then cooled and opened. Analysis of the mixtures, both before and after the reaction, was carried out *via* nmr spectroscopy. All determinations were run in replicate.

Registry No.—Trichloromethyl radical, 3170-80-7.

Acknowledgments.—We wish to thank the Computer Center of Oregon State University for supplying the requisite funds for these calculations. Deepest gratitude is also expressed to Professor Phillip Radlick of the University of California, Riverside, who generously supplied us with a sample of benzocyclobutene.

Communications

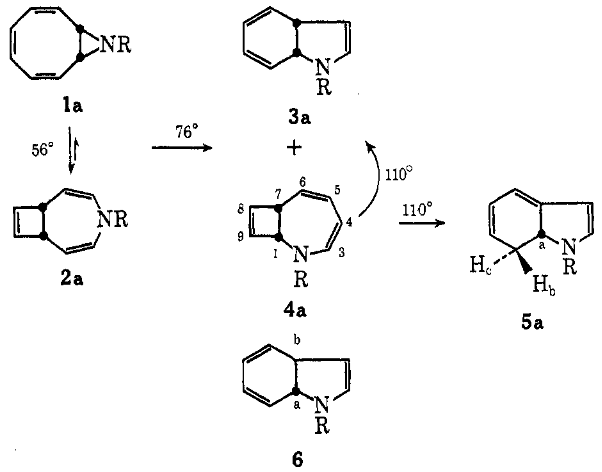
See Editorial, *J. Org. Chem.*, **38**, No. 19, 4A (1972)

Thermal Reorganization of Select Azabicyclo[*m.n.*0] nonatrienes. Generation of a *cis,cis,trans,cis*-Azonine

Summary: Mild thermal exploration of the C_8H_8NAc energy surface resulted in the discovery of a variety of mechanistically revealing transformations and the detection of a *cis,cis,trans,cis*-azonine.

Sir: Recently, we described the thermal behavior of various *N*-methoxycarbonylazabicyclo[*m.n.*0]nonatrienes.[1] We now report on the thermolysis of the acetamide analogs in terms of (i) product distribution and (ii) cycloadditive trapping.

SCHEME I



a, R = Ac

b, R = COOEt

When warmed to 56° in deaerated (N_2) benzene, **2a**[2] produces a two-component equilibrium consisting (nmr) of ~95% **2a** and 5% **1a** (Scheme I). In turn, when exposed to a higher temperature (76°) this pair undergoes rapid ($t_{1/2}$ ~80 min) and irreversible thermolysis to **3a** and **4a** in the ratio of 1.2:1, respectively (nmr). The thermolysate was separated into its individual components by chromatography at −15° and **3a** was characterized on direct comparison (nmr, ir) with an authentic sample[3] while **4a** was formulated on the basis of its spectra: ν_{CO}^{neat} 1675 cm^{-1}; *m/e* 161 (P^+, 13%); $\lambda_{max}^{C_6H_{14}}$ 282 nm (ϵ 4300), 214 (6000); nmr (100 MHz, benzene-d_6, ~60°) τ 3.92 (1 H, dd, J = 2.6, 1.0 Hz, H_8 or H_9), 4.02 (1 H, d, J = 8.5 Hz, H_3), 4.1 (1 H, br d, $J \sim$ 5 Hz, H_1), 4.30 (1 H, dd, J = 11.5, 6.0 Hz, H_6), 4.48 (1 H, dd, J = 2.6, 0.7 Hz, H_8 or H_9), 4.51 (1 H, dd, J = 11.5, 5.7 Hz, H_5), 4.89 (1 H, dd, J = 8.5, 5.7 Hz, H_4), 6.58 (1 H, dd, J = 6.0, 4.8 Hz, H_7), 8.28 (3 H, s, methyl).[4] While isomers **3a** and **4a** do not intercon-

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(1) A. G. Anastassiou, R. L. Elliott, and A. Lichtenfeld, *Tetrahedron Lett.*, 4569 (1972).

(2) A. G. Anastassiou, S. W. Eachus, R. L. Elliott, and E. Yakali, *J. Chem. Soc., Chem. Commun.*, 531 (1972).

(3) A. G. Anastassiou, S. W. Eachus, R. P. Cellura and J. H. Gebrian, *Chem. Commun.*, 1133 (1970).

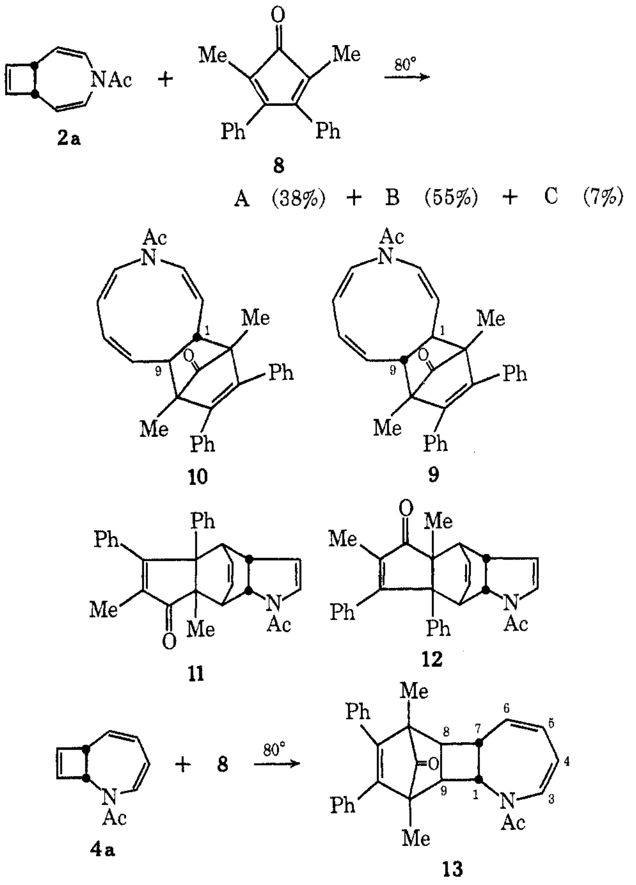
(4) Spectral analysis required extensive decoupling procedures.

vert under the reaction conditions they do differ in their sensitivity to more demanding thermal treatment. Thus, whereas **3a** remains unaffected on brief (~9 min) passage through a vpc column at 150°, **4a** readily thermolyzes at 110° to yield a mixture consisting (nmr) of ~35% **3a** and 65% **5a**.[5] Compounds **3a** (nmr) and **5a** [$\nu_{\mathrm{CO}}^{\mathrm{neat}}$ 1665 cm^{-1}; m/e 161 (P$^+$, 34%); $\lambda_{\mathrm{max}}^{\mathrm{C_6H_{14}}}$ 228 nm (ϵ 12,500), 345 (9500);[6] nmr (100 MHz, benzene-d_6, 10°) τ 3.96 (1 H, d, J = 4 Hz), 3.9–4.1 (1 H, m), 4.3–4.6 (2 H, m), 4.67 (1 H, d, J = 4.0 Hz), 5.54 (1 H, dd, J = 20.5 Hz, 8.5 Hz, H_a), 6.51 (1 H, qd, J = 17.0, 8.5, 6.0 Hz, H_b), 7.93 (1 H, dd, J = 20.5, 17.0 Hz, H_c), 8.49 (3 H, s, methyl)] were obtained pure on chromatography of the thermolysate at about −15°. The presence of a [4.3.0] skeleton in **5a** was securely established on catalytic hydrogenation (Rh/C) of this substance to *N*-acetyl-*cis*-8,9-octahydroindole (ir).[7,8]

Analysis of Scheme I by the method of orbital symmetry establishes the cis-fused dihydroindole (**3a**) as the sole "disallowed" valence tautomer.

To search for intermediates in Scheme I, **2a** was exposed to an equimolar quantity of 2,5-dimethyl-3,4-diphenyl-cyclopenta-2,4-dienone (**8**)[11] in boiling benzene for 24 hr. The product mixture consisted almost exclusively (~93% by nmr) of two 1:1 adducts[12] (Scheme II): A [~38%, white powder, mp 141–142°, $\nu_{\mathrm{(ketonic\ CO)}}^{\mathrm{KBr}}$ 1775 cm^{-1}, m/e 421 (P$^+$, 9%), J_{19} = 4.5 Hz[13]] and B [~55%, white crystals, mp 187.5–188.5°, $\nu_{\mathrm{(ketonic\ CO)}}^{\mathrm{KBr}}$ 1775 cm^{-1}, m/e 421 (P$^+$, 7%), J_{19} = 4.5 Hz[13]]. Of these, B was unambiguously characterized as **10** on the basis of single-crystal X-ray diffraction analysis (Figure 1).[14] Moreover, this information and the close spectral similarity of the two adducts, necessitates the formulation of A as **9**, *i.e.*, the diastereomer of **10**.

SCHEME II



Finally, the minor product (~7%) of cycloaddition between **2a** and **8** was isolated by column chromatography and was shown to be **11** (or **12**) by direct spectral (nmr, ir) comparison with a synthetic sample (mp 254.5–255.5°) prepared on treatment of **3a** with **8** in boiling benzene.

The structural features of **9** and **10** require that these substances form through symmetry controlled [$_{\pi}2_s$ + $_{\pi}4_s$] cycloaddition of **8** onto *N*-acetylazonine incorporating a remote trans double bond, *i.e.*, one not directly linked to nitrogen. Since both possible rotamers of such an azonine, *i.e.*, the cis,cis,trans,cis and cis,-trans,cis,cis variants shown in **14** and **15**, respectively,[15] can in principle react with **8** to produce **9** and **10**, and, since rotamer **15** is formally relatable to **4a** (a major thermal product of **2a** at 76°) through symmetry-allowed conrotation of the cross-link, it was necessary to assess the thermal response of **4a** in the presence of **8**. Prolonged exposure (~48 hr) of **4a** to an equimolar proportion of **8** in boiling benzene produced a mixture containing (nmr) only minor quantities of **9** and (possibly) **10**. Column chromatography of this product mixture led to the isolation of **13** [$\nu_{\mathrm{(ketonic\ CO)}}^{\mathrm{KBr}}$ 1770 cm^{-1}; m/e 421 (P$^+$, 5%); nmr (100 MHz, CDCl$_3$, 90°) τ 2.8–3.2 (10 H, m), 3.59 (1 H, d, J_{34} = 8.5 Hz, H_3), 3.89 (1 H, dd, J_{65} = 11.5, J_{67} = 7.0 Hz, H_6), 4.22 (1 H, dd, J_{56} = 11.5 Hz, J_{54} = 6.0 Hz, H_5), 4.45 (1 H, dd, J_{43} = 8.5 Hz, J_{45} = 6.0 Hz, H_4), 4.75 (1 H, dd, J_{17} =

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(5) While reasonably inert at 110°, **5** rapidly isomerizes to two pyrrole-containing substances (nmr, uv, ir, mass spectra) when exposed to 150°.

(6) Band intensities are necessarily approximate owing to serious difficulties encountered in handling this substance which readily resinifies when neat.

(7) Significantly, catalytic hydrogenation of a hydrocarbon analog of **5** also leads to a cis-fused perhydro skeleton: S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969).

(8) Interestingly, the thermal behavior of the **1a–2a** equilibrium pair, summarized in Scheme I, differs from that of its methoxycarbonyl analog which, as we noted recently,[1] reorganizes chiefly to a trans-fused dihydroindole when heated at 76°. Fully as anticipated and in obvious contradiction of a recent claim by Masamune, *et al.*,[9] we find urethane **2b** also to yield a trans-fused dihydroindole (**6b**) as the major product (~68% of thermolysate based on the combined amount of **5b** and **6b** isolated) of reorganization at 76°. An earlier report by Masamune, *et al.*,[10] to the effect that thermolysis of **1b** leads to **2b**, is also incomplete. In brief, we discovered that thermal treatment of a deaerated benzene solution of **1b** at 56° leads rapidly ($t_{1/2}$ ~ 75 min) to a product mixture consisting (chromatography at −15°) of ~71% **2b** (nmr), 23% **6b** [$\nu_{\mathrm{CO}}^{\mathrm{neat}}$ 1720 cm^{-1}; m/e 191 (P$^+$, 38%); $\lambda_{\mathrm{max}}^{\mathrm{C_6H_{14}}}$ 229 (ϵ 15,500);[6] nmr (60 MHz, benzene-d_6) τ 2.8 (1 H, br d, J ~ 10 Hz), 3.28 (1 H, dd, J = 4.5, 3.0 Hz), 3.7–4.3 (3 H, m), 5.05 (1 H, dd, J = 4.5, 1.5 Hz), 6.05 (2 H, q), 6.07 (1 H, d, J_{ab} = 24 Hz), 6.78 (1 H, d, J_{ab} = 24 Hz), 9.05 (3 H, t)] and 6% **3c** (nmr, ir). In contrast, prolonged exposure (~8 hr) of **2b** at 56° does not effect rearrangement to **6b** but merely generates a mixture of ~95% **2b** and 5% **1b** (nmr). It follows that *the [6.1.0] skeleton,* **1b**, *rather than its [5.2.0] counterpart* **2b**, *is the major source of* **6b** *at* **56°**.

(9) S. Masamune and N. Darby, *Accounts Chem. Res.*, **5**, 272 (1972).

(10) S. Masamune and N. T. Castellucci, *Angew. Chem.* **76**, 569 (1964).

(11) C. F. H. Allen and J. A. Van Allan, *J. Amer. Chem. Soc.*, **64**, 1260 (1942); **72**, 5165 (1950).

(12) The adducts are stable to prolonged heating at the reaction temperature.

(13) The determination of this value necessitated triple irradiation with a frequency extending over the entire 6 H olefinic region.

(14) The X-ray analysis will be fully detailed in our complete account of the work. Full-matrix least-squares refinement with anisotropic temperature factors for all nonhydrogen atoms converted to the present minimum of 0.12 for the conventional discrepancy index. All bond distances and angles agree well with generally accepted values and there are no abnormally short intermolecular contacts.

(15) The convention adopted here for the sequential differentiation between rotamers **14** and **15** places the NAc function (CH$_2$ function for the hydrocarbon counterparts) at the origin and the system is then labeled along such a direction as is necessary for encountering the trans double bond from the side of its "outer" proton.

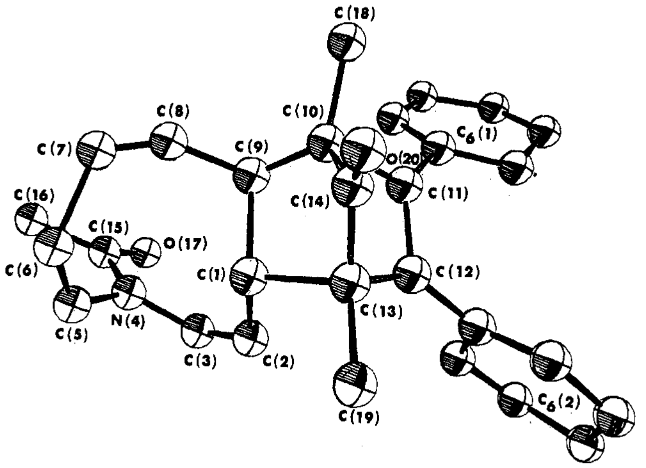
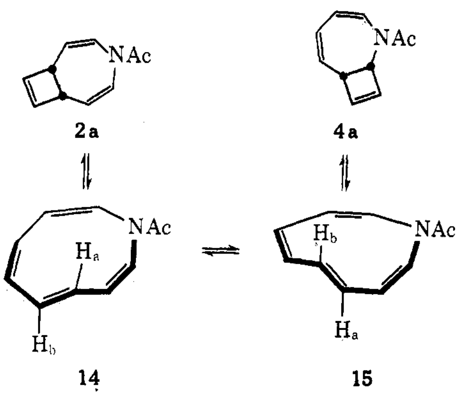


Figure 1.—A structural view of 10 as determined by X-ray analysis depicting conformation.

5.0 Hz, J_{19} = 10.0 Hz, H_1), 7.25 (2 H, m, $H_7 + H_9$), 7.60 (1 H, dd, J_{87} = 10.0 Hz, J_{89} = 4.5 Hz, H_8), 7.90 (3 H, s), 8.79 (3 H, s), 8.82 (3 H, s)],[4] *i.e.*, the product of symmetry-controlled $[_\pi 2_s + _\pi 4_s]$ cycloaddition of **8** onto the cyclobutene double bond of **4a** as a major constituent. It follows that the mono-*trans*-azonine responsible for the formation of cycloadducts **9** and **10** in the trapping of thermally activated **2a** with **8** is derived directly from **2a**, *i.e.*, without prior isomerization of this substance to **4a**. The question of whether the initially generated *trans*-azonine is trapped prior to its rotational conversion to **15** cannot be answered at present. Nonetheless, the absence of **13** among the cycloadducts of thermally activated **1a** could be interpreted to mean that any participation of **15** in the formation of **9** and/or **10** is minor.

The thermal rearrangement of **2a** can be dissected into symmetry-allowed (k_a) and forbidden (k_f) components; it is instructive to contrast the thermal reactions of **2a** in the presence and absence of **8** in terms of the ratio of k_a/k_f. Comparison of past[1] and present findings reveals that this ratio increases from (**4a**)/(**3a**) $\sim$ 0.8 in the absence of trapping agent to (**9** + **10**)/(**11** or **12**) $\sim$ 13 in the presence of **8**. Clearly then, the use of isomer product ratios grossly underestimates the control imposed on the various steps by orbital symmetry. Undoubtedly, this misrepresentation is chiefly due to the reversibility of various symmetry-allowed steps that generate fleeting intermediates, *e.g.*, Scheme III, providing for eventual drain through less accessible but irreversible symmetry-disallowed channels. This rationale also accounts for the thermolytic behavior of the carbocyclic members of the family. It is readily seen for example that the k_a/k_f ratio associated with the thermal response of *cis*-bicyclo[6.1.0]nona-2,4,6-triene at 80° increases in magnitude from $\sim$0.1 in the absence of trapping agent[16] to $\sim$3 in the presence of **8**.[17]

SCHEME III



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[16] E. Vogel, *Angew. Chem.*, **73**, 548 (1961); **74**, 829 (1962).

[17] A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971).

[18] NDEA Graduate Fellow, 1971–1974.

[19] Camille and Henry Dreyfus Foundation Teacher–Scholar Grant Awards, 1972–1977.

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RECEIVED FEBRUARY 9, 1973

Selective Demethylation of Quaternary Salts with Lithium *n*-Propylpercaptide in Hexamethylphosphoramide[1]

Summary: Lithium *n*-propylmercaptide in hexamethylphosphoramide provides a mild, rapid, and convenient system for dealkylation of quaternary ammonium salts in excellent yield with high propensity for methyl group removal.

Sir: The perennial problem of dealkylating quaternary ammonium salts has received considerable attention and led to the development of several reagent systems for effecting such transformations. The most successful of these include alkyl displacement using lithium aluminum hydride,[2a] sodium in ammonia,[2b] ethanolamine,[2c] thiophenoxide anion,[2d] lithium iodide,[2e] or acetate anion.[2f]

The recent disclosure of the exceptional nucleophilic displacement ability of lithium *n*-propylmercaptide in hexamethylphosphoramide (HMPA)[3] prompts this report of the utility of this reagent system as an effective, mild, and rapid method for dealkylation of aromatic and aliphatic quaternary ammonium salts with superior selectivity for displacement of methyl

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(1) Presented in part of the 7th Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1972.

(2) (a) A. C. Cope, E. Ciganek, L. J. Fleckenstein, and M. Meisinger, *J. Amer. Chem. Soc.*, **82**, 4651 (1962); (b) E. Grovenstein, Jr., S. Chandra, C. Collum, and W. Davis, Jr., *ibid.*, **88**, 1275 (1966); (c) S. Hunig and W. Baron, *Chem. Ber.*, **90**, 395 (1957); (d) M. Shamma, N. C. Deno, and J. F. Remar, *Tetrahedron Lett.*, 1375 (1966); (e) H. O. House, H. Muller, C. Pitt, and P. Wickham, *J. Org. Chem.*, **28**, 2407 (1963); (f) N. D. V. Wilson and J. A. Joule, *Tetrahedron*, **24**, 5493 (1968). In addition, 1,4-diazabicyclo-[2.2.2]octane in DMF or HMPA has recently been shown to effectively dealkylate quaternary salts; see T. L. Ho, *Synthesis*, 702 (1972).

(3) P. A. Bartlet and W. S. Johnson, *Tetrahedron Lett.*, 4659 (1970).