

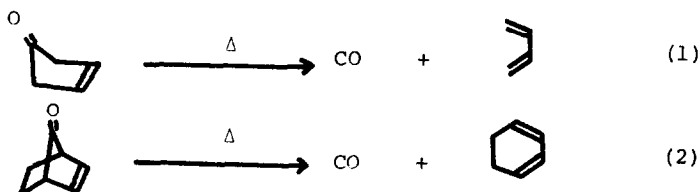
THE THERMAL DECARBONYLATION OF CERTAIN
SUBSTITUTED NORBORNEN-7-ONES

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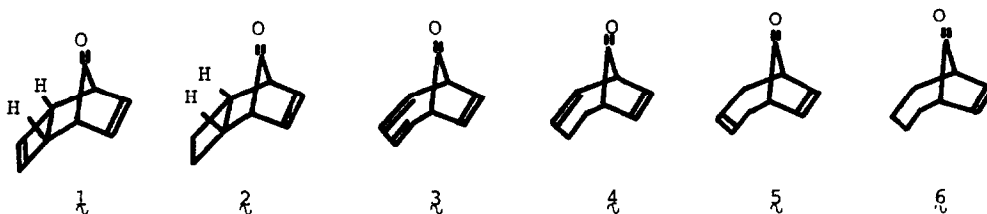
The thermal decarbonylation of the 3-cyclopentenone system to the butadiene system has been discussed theoretically (eq. 1).¹ Furthermore, the surprising ease of the thermal decarbonylation of the norbornen-7-one system producing cyclohexadiene is also well documented (eq. 2).² Recently, we successfully



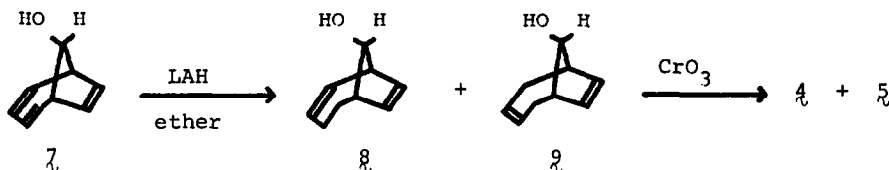
synthesized several norbornen-7-one derivatives, e.g., endo-tricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (λ), endo-tricyclo[4.2.1.0^{2,5}]nona-7-en-9-one (μ), bicyclo[4.2.1]nona-2,4,7-trien-9-one (ν), bicyclo[4.2.1]nona-2,7-dien-9-one (ξ), bicyclo[4.2.1]nona-3,7-dien-9-one (η), and bicyclo[4.2.1]nona-7-en-9-one (θ). We now report that λ and μ are quite reactive, and lose carbon monoxide to give cyclooctatetraene and 1,3,5-cyclooctatriene, respectively, at 100°, while ν , ξ , η and θ decarbonylate at measurable rates to give cyclooctatetraene, 1,3,5-cyclooctatriene, 1,3,6-cyclooctatriene and 1,3-cyclooctadiene, respectively, at only ca. 300°.

The series of compounds λ , μ and ν were synthesized by previously reported methods.³ The unknown ketones ξ , η and θ ⁴ were prepared from syn-9-hydroxy-bicyclo[4.2.1]nona-2,4,7-triene (ζ).^{3b} LAH reduction of ζ gave a 4:6 mixture

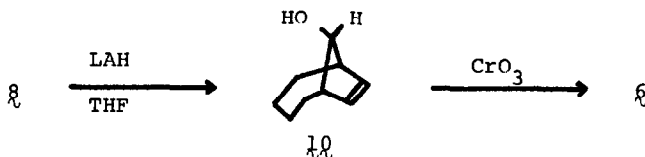
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of syn-9-hydroxybicyclo[4.2.1]nona-2,7-diene (**8**), mp 80.0~80.5°, and syn-9-hydroxybicyclo[4.2.1]nona-3,7-diene (**9**), mp 51.0~51.5°. Chromic acid oxidation



of a mixture of **8** and **9**, followed by glpc separation, gave pure **4** and **5** as waxy solids. Prolonged reaction of **8** with LAH in THF gave syn-9-hydroxybicyclo[4.2.1]nona-7-ene (**10**), mp 115~117°, which was oxidized with CrO₃ to give **6**.



The rates of the thermal decarbonylation of **1** ~ **6** were determined by nmr spectroscopy.⁵ The first-order rate constants for the decarbonylation of the norbornen-7-one system are given in Table I. The relative rates are in the sequence, **2** > **1** > norbornen-7-one > **6** > **5** > **4** > **3**.

It is noteworthy that the rates for **1** and **2** are markedly faster than those for the ketones, **3**, **4**, **5** and **6**.⁶ The retarding effects of **3** ~ **6** are explicable in terms of the geometry of these compounds.⁷ The decarbonylation is caused by the interaction between the CO group and the two-carbon bridge (C₇-C₈ olefinic π system), and this is enhanced by decreasing the angle between the C₁-C₉-C₆ and C₁-C₇-C₆ planes. However, as pointed out by Mukai,^{8a} the molecular models for **3** ~ **6** indicate a bending away of the CO group from the perpendicular geometry towards the four-carbon bridge (C₂-C₃-C₄-C₅ unit).⁹ Thus, the reactivity of **3**

is similar to that of 3,5-cycloheptadienone rather than 3-cyclopentenone system. Photochemical decarbonylation of 3,5-cycloheptadienone giving 1,3,5-hexatriene is a well-known reaction,^{8b,d} and actually, it is recently reported^{8a} that \mathfrak{z} undergoes photochemical decarbonylation with ease.

The UV spectrum of \mathfrak{z} also supports the existence of substantial interaction of the triene system with the carbonyl group (Table II). The absorption at 265 and 280 m μ (ϵ 2800, 2700) is 10^2 times stronger than that of norbornen-7-one. The geometric relation of the carbonyl to the diene is expected to be similar to that of 3,5-cycloheptadienone. Meinwald¹⁰ concluded that there is some sort of transannular interaction between the diene system and the carbonyl group.

The geometry of those ketones can be chemically confirmed by the reaction with NaBH₄ in methanol. Hydride attack should occur predominantly from the less hindered side of the carbonyl group to give the corresponding alcohol. While the reaction of \mathfrak{t} or \mathfrak{r} with NaBH₄ in methanol at room temperature gave a 1:1 mixture of the corresponding syn and anti-alcohol, the reaction of \mathfrak{z} produced only syn-alcohol. Similarly, the reaction of $\mathfrak{4}$, $\mathfrak{5}$ or $\mathfrak{6}$ with NaBH₄ gave predominantly the syn-alcohols (Table III).

Table I. Decarbonylation Rate Data for Norbornen-7-one System at 100° in C₆D₆

| Compound | 10 ⁶ k sec ⁻¹ | Rel. Rate |
|-----------------|-------------------------------------|------------------------|
| \mathfrak{t} | 350* | 2.3 x 10 ² |
| \mathfrak{r} | 450 | 3.0 x 10 ² |
| \mathfrak{z} | 0.003** | 2.0 x 10 ⁻³ |
| $\mathfrak{4}$ | 0.040** | 2.6 x 10 ⁻² |
| $\mathfrak{5}$ | 0.094** | 6.3 x 10 ⁻² |
| $\mathfrak{6}$ | 0.125** | 8.3 x 10 ⁻² |
| norbornen-7-one | 1.5 | 1.0 |

* A. Diaz reports^{8e} 282 x 10⁻⁶ sec⁻¹. ** Calculated from data at higher temp.

Table II. UV Spectra

| Compound | λ_{\max} , m μ (log ϵ) |
|---------------------------------|--|
| \mathfrak{z} | 319 (2.76), 280 (3.45), 265 (3.45), 215 (3.55) |
| 3,5-cycloheptadienone | 290 (2.75), 214 (3.75) ¹⁰ |
| norbornen-7-one | 272 (1.60) ¹² |
| bicyclo[4.2.1]nona-2,4,7-triene | 256 ¹¹ |
| 1,3-cycloheptadiene | 248 (3.87) ¹⁰ |

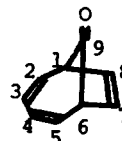


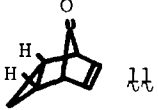
Table III. NaBH_4 Reduction of Norbornen-7-one System in MeOH at R.T.

| Compound | <u>syn</u> -alcohol (%) [*] | <u>anti</u> -alcohol (%) [*] |
|----------|--------------------------------------|---------------------------------------|
| 1 | 50 | 50 |
| 2 | 50 | 50 |
| 3 | 100 | 0 |
| 4 | 90 | 10 |
| 5 | 70 | 30 |
| 6 | 80 | 20 |

* The syn and anti-alcohol were analyzed by glpc, using a carbowax column.

In conclusion, the low reactivities of 3 ~ 6 can be ascribed to the geometry of these systems, but the difference in the rates of 4, 5 and 6 is rather small and difficult to explain so far. More quantitative approaches to this problem will be reported in the near future.

References and Footnotes

- (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, N.Y. 1970; (b) J. E. Baldwin, *Canad. J. Chem.*, **44**, 2051 (1965).
- (a) C. F. H. Allen, *Chem. Rev.*, **37**, 209 (1945); **62**, 653 (1962); (b) S. Yankelovich and B. Fuchs, *Tetrahedron Lett.*, 4945 (1967); (c) R. McCulloh, A. R. Rye, and D. Wege, *ibid.*, 5231 (1969); (d) B. Halton, et al, *J. Am. Chem. Soc.*, **89**, 5964.
- (a) M. Sakai, A. Diaz, and S. Winstein, *ibid.*, **92**, 4454 (1970); (b) M. Sakai, R. F. Childs, and S. Winstein, *J. Org. Chem.*, **37**, 2517 (1972); (c) T. A. Antkowiak, et al, *J. Am. Chem. Soc.*, **94**, 5366 (1972); (d) M. Sakai, unpublished work.
- All new compounds gave correct elemental analyses and spectral data consistent with the assigned structure.
- Solutions of the ketones in C_6D_6 containing a small percentage of TMS were sealed in nmr tubes and heated for appropriate periods.
- Ketones 1 and 2 decarbonylate more readily than the standard norbornen-7-one. It is probable that in 2 the syn-hydrogen of the cyclobutane is compressed against the π -cloud of the two-carbon bridge. Compression would be relieved in the transition state for decarbonylation.
- The high reactivity of 1 has been ascribed to cyclopropyl participation.^{2d}

- (a) K. Kurabayashi and T. Mukai, *Tetrahedron Lett.*, 1049 (1972); (b) O. L. Chapman et al, *J. Org. Chem.*, **26**, 4185 (1961); (c) O. L. Chapman, et al, *J. Am. Chem. Soc.*, **84**, 1220 (1962); (d) D. I. Schuster, et al, *ibid.*, **90**, 1300 (1968); (e) A. Diaz, unpublished work.
- The angles between the $\text{C}_1\text{-C}_9\text{-C}_6$ and $\text{C}_1\text{-C}_7\text{-C}_6$ planes for 1 and 2, and 3 ~ 6 are ca. 120° and 160° , respectively.
- J. Meinwald, et al, *ibid.*, **77**, 4401 (1955).
- T. S. Cantrell and H. Shechter, *ibid.*, **89**, 5868 (1967).
- R. K. Bly and R. S. Bly, *J. Org. Chem.*, **28**, 3165 (1963).