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# STERIC ACCELERATION IN THE THERMAL DECARBONYLATION OF HIGHLY COMPRESSED NORBORNEN-7-ONES

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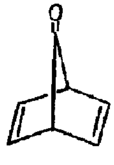
Norbornadien-7-one 1 and its benzo-annellated derivatives are highly reactive molecules, which readily undergo thermal decarbonylation to yield benzene and its benzo-annellated derivatives.[1] Although the factors which contribute to the high reactivity of 1 and its derivatives have not been fully determined, they are apparently largely electronic in nature.[2] Norbornen-7-one 4 and substituted norbornen-7-ones undergo thermal decarbonylation with varying ease. Thus *endo*-tricyclo[3.2.10$^{2,4}$]octen-8-one 2 is moderately reactive, and looses carbon monoxide to give tropilidene at 30-40°,[3,4] while *exo*-tricyclo[3.2.1.0$^{2,4}$]octen-8-one 3,[4,5] norbornen-7-one 4,[5] and dicyclopentadienone 5[6] decarbonylate at measurable rates only at 110 - 150°. The high reactivity of 2 has been ascribed to cyclopropyl participation.[4]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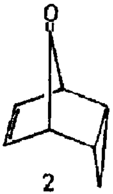
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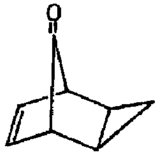
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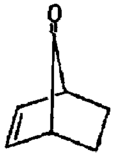
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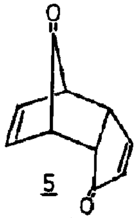
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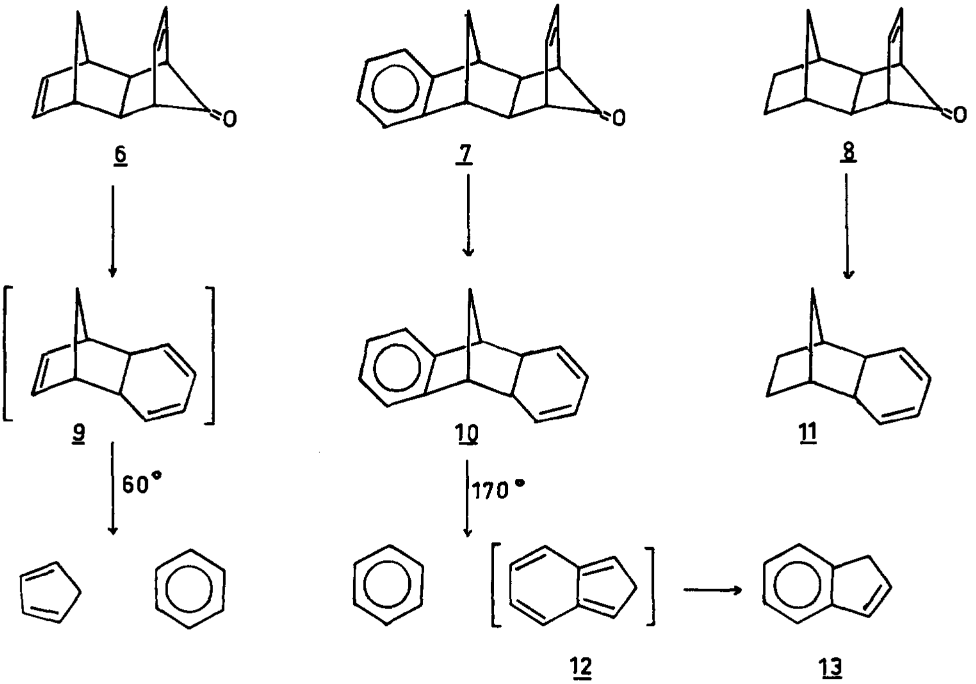
Thus both 1 and 2 owe their reactivity to electronic factors. We now report that ketones[7] 6, 7 and 8 also undergo facile thermal decarbonylation, but that their reactivity is due to steric factors.

The rates of decarbonylation of 6, 7 and 8 were determined spectroscopically by measuring the absorption due to cyclopentadiene and dienes 10[8] and 11, respectively. Good first order kinetics were observed, and the rates and activation parameters are summarized in Table 1. Extrapolation of these rates to 125°C (Table 1) shows that ketones 6, 7 and 8 decarbonylate much more readily than the "normal" norbornen-7-ones 3, 4 and 5. There are clearly no electronic factors which could be invoked to explain the reactivity of 6, 7 and 8. In the accompanying communication,[7] evidence was presented that in these ketones the *syn*-hydrogen atom of the bridging methylene group is compressed against the $\pi$ cloud of the etheno bridge. Such compression would clearly be relieved in the transition state for decarbonylation. The high reactivity of 6, 7 and 8 is thus due to steric acceleration.

The thermal stability of the products of the decarbonylation of 6, 7 and 8 provide some interesting information. Cyclopentadiene and benzene were the only products formed from 6. They presumably arose from a reverse Diels-Alder reaction[9] of the triene 9. When the



decarbonylation of 6 was carried out in a tube in the probe of an NMR spectrometer at 70°, only signals due to 6 and cyclopentadiene and benzene were observed throughout the reaction. Preliminary experiments indicate, however, that triene 9 can be trapped by carrying out the decarbonylation of 6 in the presence of dienophiles.[10]

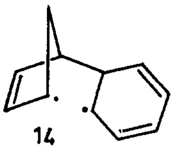
The diene 10, m.p. 64 -64.5° was the only product of the decarbonylation of ketone 6. Diene 10 was much more stable than 9, and had a half-life of *ca.* 2 hours at 170°, and was smoothly converted at and above this temperature to indene (presumably *via* isoindene 12[11]) and benzene. The liquid diene 11, was thermally stable to at least 200°.

The large difference in reactivity between 9 and 10 has a bearing on the question of whether the reverse Diels-Alder reaction proceeds through a 2-centre or 4-centre transition state. In the 2 centre (step-wise) mechanism, the difference in rate of reaction of 9 and 10 should be due to the difference in rate of formation of diradicals 14 and 15. These diradicals differ only in that 14 possesses an allylic radical system where 15 possesses a benzylic radical system. Hence their rates of formation should be very similar,[12] since the allylic carbon-carbon bond dissociation energy in 1-butene (62±2 Kcal.mole$^{-1}$) is very close to the benzylic carbon-carbon bond dissociation energy in ethyl benzene (63.2±1.5 Kcal.mole$^{-1}$)[13]. A step-wise mechanism for both 9 and 10 is therefore ruled out. In a concerted mechanism, 9 can readily undergo continuous electron redistribution along the reaction coordinate to give cyclopentadiene and benzene, two stable products. With 10,

| Compound | Temp., °C | $10^4$ k, Sec$^{-1}$ | $\Delta H^{\ddagger}$ Kcal.mole$^{-1}$ | $\Delta S^{\ddagger}$, e.u. | Rel.rate, 125°C |
|---|---|---|---|---|---|
| 6 [a] | 58.7 | 0.761 | 28.0± 1.0 | 6.7± 2.9 | 4100 |
| | 60.5 | 1.21 | | | |
| | 71.0 | 3.78 | | | |
| | 81.7 | 14.2 | | | |
| | 125.0 | 940 [b] | | | |
| 7 [a] | 60.0 | 0.773 | 27.7± 1.0 | 5.5± 2.9 | 3800 |
| | 70.7 | 3.27 | | | |
| | 82.1 | 11.1 | | | |
| | 125.0 | 870 [b] | | | |
| 8 [a] | 59.6 | 0.276 | 27.9± 1.0 | 4.0± 2.9 | 1400 |
| | 71.0 | 1.28 | | | |
| | 81.3 | 3.74 | | | |
| | 125.0 | 330 [b] | | | |
| 4 | 124.6 | 0.23 [c] | | | 1 |
| 5 | 124.5 | 1.29 [d] | | | 5.6 |
| 3 | 125.0 | 0.0815 [b,c] | | | 0.35 |

a Cyclohexane as solvent; b Calculated from data at other temperatures;
c Diglyme as solvent: S.C. Clarke and B.L. Johnson, unpublished results;
d Dioxane as solvent: reference 6.

Table 1 First order rate constants and activation parameters (at 70.0°C) for the decarbonylation of bridged ketones.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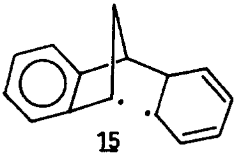
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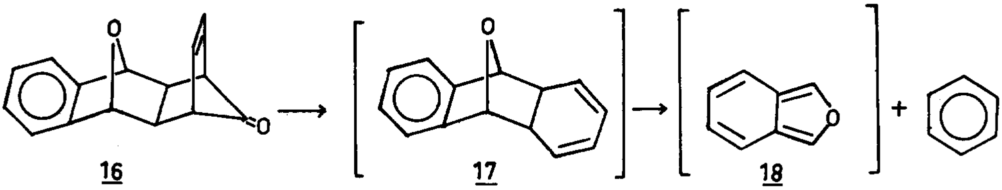
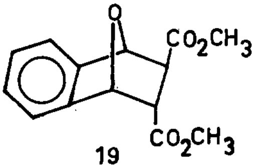
however, a concerted reaction would require disruption of the aromatic character of the benzenoid ring to form the unstable o-quinodimethane system of isoindene, and such a process would be expected to require a higher activation energy. Alternatively, the much lower reactivity of 10 may reflect the higher activation energy required for a step-wise mechanism proceeding via 15. A comparison of the activation parameters for the reverse Diels-Alder reaction of 9 and 10 may provide additional insight into this problem.

Ketone 16, prepared from 1,4-epoxy-1,4-dihydronaphthalene by the addition-dechlorination-hydrolysis procedure[7] was more stable than ketone 7, and decarbonylation did not occur at an appreciable rate below 110°. Unlike diene 10 which was quite stable at this temperature, diene 17 was highly reactive and could not be isolated or trapped. In the presence of dimethyl fumarate, isobenzofuran 18 was trapped in high yield as adduct 19, m.p. 66°, while in the presence of dimethyl maleate, adducts 20, m.p. 105°, and 21 m.p. 146-147°, were formed in a ratio of 2:1.[14]


16 17 18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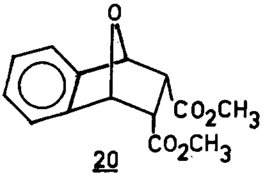
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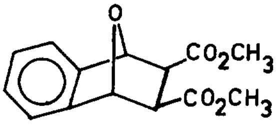
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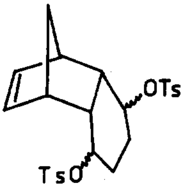
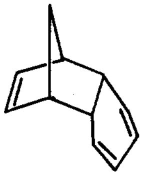
10. Treatment of the *bis*-tosylate (i) with potassium *t*-butoxide in dimethyl sulphoxide at room temperature gave a mixture of olefins which was partly converted to cyclopentadiene and benzene (NMR analysis) on warming to 60°. (T.Dixon and D.Wege, unpublished results). This is strong presumptive evidence for the presence of (ii) in the elimination product, and that (ii) is stable at room temperature. The triene 9 may likewise be capable of existence at or below room temperature.

(i)



(ii)



11. See, *inter alia* K. Alder and M. Fremery, *Tetrahedron*, 14, 190 (1961); J.A. Berson and G.B. Aspelin, *Tetrahedron*, 20, 2697 (1964); W.R. Roth, *Tetrahedron Letters*, 1009 (1964).
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14. For a similar approach to the generation of isobenzofuran see L.F. Fieser and M.J. Haddadin, *Can. J. Chem.*, 43, 1599 (1965).