ON ALLEGED NORBORNADIEN -7-ONES.

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Since we had recently studied (1) the photolysis of certain substituted norbornen-7-ones, we decided to investigate the norbornadien-7-one system I. While there is no a priori reason why this system should not exist, it seems to be a particularly elusive one. Thus the Diels-Alder addition of acetylenes to substituted cyclopentadienones, instead of giving the expected norbornadien -7-ones yields the aromatic products, via decarbonylation (2). Acid hydrolysis of the ketal derivatives of I (3) likewise leads to spontaneous decarbonylation. Although the literature describes several substituted norbornadien -7-ones, our results show that most of these assignments are incorrect.

The synthesis of 2-phenylnorbornadien -7-one II has been reported (4), albeit in very small yield. The substance exhibited I.R. absorption, $\nu_{max.(C=O)}$ 1730 cm^{-1}, melted at 135° (d) and decarbonylated at even higher temperatures yielding diphenyl. These results are in sharp contrast to the thermal lability of substituted norbornadien-7-ones - which decarbonylate spontaneously in the course of attempted synthesis (1c, 2, 11) and to the high C=O absorption of carbonyl bridged six-membered rings which occur at 1780-1800 cm^{-1} (2, 5, 11, 12). Moreover, despite repeated attempts we have been unable to duplicate the reported synthesis. Hence, the assignment of structure II must be questioned.

In another instance, the hemiketal-lactone structure III was assigned to a product obtained (6) by addition of phenylpropiolic acid to phencyclone IV . This assignment obviously violates Bredt's rule. While the compound we isolated displays all the reported (6) properties, its I.R. spectrum exhibits a strong C≡C absorption band at 2225 cm^{-1}. Structure IV is thus ruled out. Consequently, phencyclone IV was treated with a variety of organic acids. Ordinary acids such as acetic or benzoic acid had no effect on it. However, when we used acids of strength similar to that of phenylpropiolic acid (pK 5.9 x 10^{-3}) viz. chloroacetic acid (pK 1.39 x 10^{-3}) and

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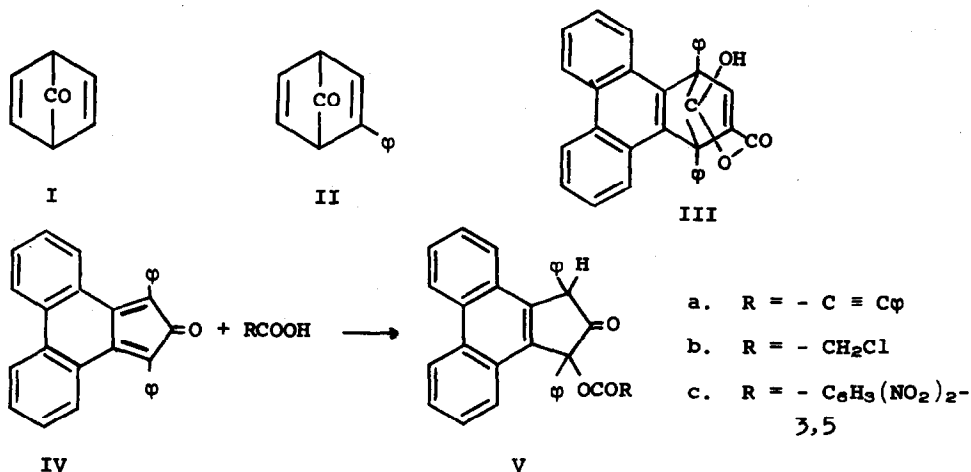
I   II   III

IV   V

a. $R = -C \equiv C\varphi$

b. $R = -CH_2Cl$

c. $R = -C_6H_3(NO_2)_2$-3,5

Table

Properties of adducts V* (7)

Adduct	m.p.,C° yield	$\nu_{max.}$, cm^{-1}	$\lambda_{max.}$, mμ(log ϵ)	τ,(rel.area)
V_a	205 (d) 45%	2225 (C≡C) 1768 (C=O) 1710 (C=O) 0	207 (4.66) 223 (4.49) 250 (4.72) 257 (4.79) 287 (4.36) 290 (4.11) 305 (3.79)	2.8-2.2(23H) 4.42 s(1H)
V_b ‡	212 (d) 9%	3550 (O-H)** 1765 (C=O) 1675 (C=O) 0	209 (4.43) 223 (4.34) 253 (4.52) 278 (4.28) 292 (4.16) 304 (4.05)	2.0-2.9(18H) 4.41 s(1H) 5.88 (2H)
V_c ‡	193-4(d) 98%	1770 (C=O) 1735 (C=O) 0	210 (4.77) 222 (4.72) 250 (4.34) 256 (4.79) 277 (4.06) 292 (3.83) 304 (3.69)	2.1-2.9(21H) 4.40 s(1H)

* Melting points are corrected. I.R. spectra were recorded on a Perkin-Elmer 237 spectrophotometer in CHCl₃. U. V. spectra were recorded on a perkin-Elmer 137 spectrophotometer in ethanol. N.M.R. spectra were taken on a Varian A-60 instrument in CDCl₃ with TMS as internal standard.
‡ Satisfactory elemental analysis was obtained.
**This reproducible small intensity O-H absorption is not very well understood. It could be due to an enolic form of V b.

3,5 dinitrobenzoic acid (pK 1.07×10^{-3}), corresponding 1:1 adducts could be
isolated. Based on their very similar properties (see Table) structure V is
assigned to these adducts (7). Support to this assignment is found in the
instantaneous deep colouring of the solution of V when a drop of sulphuric
acid is added, i.e. the starting materials are reversibly formed in a cat-
alysed equilibrium process. 1,4 additions in substituted cyclopentadienones
are not uncommon (2) for reduction and halogenation processes but - to the
best of our knowledge - are unprecedented for organic acids. The strength
of the acid constitutes a determining factor viz. very strong acids catalyse
the process maintaining a fast exchange system, whereas weak acids do not
react at all. An enhancing driving force in our particular system is prob-
ably the proneness of the phenanthroquinonoid structure III to transform
into the phenanthrene V (8).

The last (9) example is that of 2,3,5,6-dibenzonorbornadiene-7-one VI.
In an early work its formation is assumed and mentioned in a footnote (10)
as a byproduct from the reaction of dilithiumanthracene with dimethylcarbon-
ate, the main product being bis-(9,10-dihydroanthryl) - ketone VII. We have
repeated this reaction and were able to isolate the product in minute quanti-
ties. The substance has a high decomposition point (295-7°), its I.R. spec-
trum displays ν_{CO} 1720 cm^{-1} and its mass spectrum shows fragments of higher
m/e than 206 (the supposed molecular ion of VI). This eliminates VI. Pos-
sible alternative formulations for this as well as for Hafner's (4) compound
would be dimeric structures. The substance possessing structure VI has in
fact recently been reported (11). As expected it exhibits I.R. absorption
$\nu_{max.(C=O)}$1792 cm^{-1} and decarbonylates spontaneously. Very recently a re-
lated compound VIII was described (12) with similar characteristics
($\nu_{max.(C=O)}$ 1766, 1780, 1825 cm^{-1} and $t_{\frac{1}{2}}^{30°} \approx$ 10 min.)

This elusiveness of the norbornadiene-7-one system is worthy of note
and discussion. The gross geometry of the norbornadiene framework appears
not to differ appreciably from that of its saturated analog, norbornane
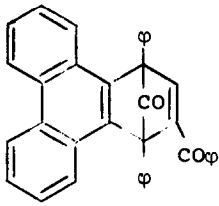

VI   VII   VIII

IX   X   XI
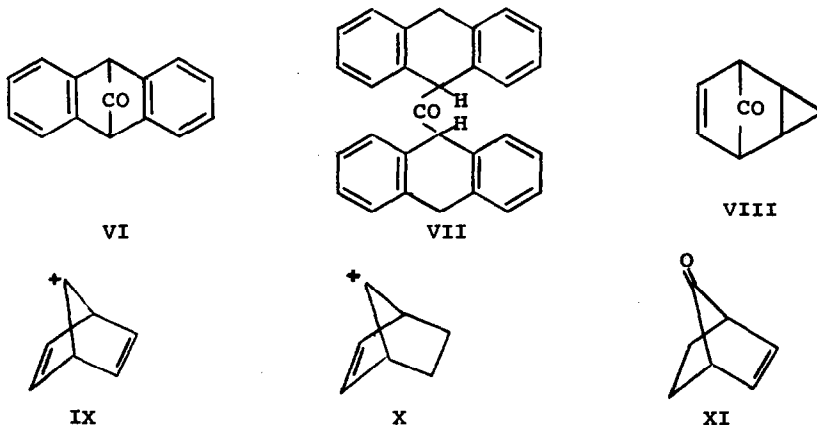
(13a-d). The $C_1-C_7-C_4$ angle, for example has been found to be in both cases
ca. 96-97° (13c,d). Yet 7-norbornanone is a stable, although strained ke-
tone (14) whereas on introduction of one double bond, i.e. in norbornen-7-
ones, these properties change drastically. This is exemplified by chemical
(2,14) and photochemical (1) behavior of the latter, the facile thermal and
light induced decarbonylation being of primary significance. This trend
appears to culminate in the great instability of the norbornadien-7-one
system. The immediate factors one would invoke in an attempt to rationalize
this behavior are strain relief, extra stabilization of excited state inter-
mediates (e.g. diradicals) and the formation of thermodynamically stable
species, viz. CO and conjugated or aromatic molecules. We believe that the
decomposition is, in addition, being triggered by the interaction between
the two juxtaposed - olefinic and carbonylic - Π systems. This interaction
is characterized by a Π-Π* charge transfer transition (cf. (15) and dis-
cussion in (16). The 7-norbornadienyl cation IX has been experimentally
shown to have unsymmetrical structure, with extensive charge delocalization
(16; cf. 17 for a related discussion). Thus, a stabilization of the species
is operating there, by interaction and convergence between the empty C_7-
orbital and the ethylenic Π-orbital. This received theoretical endorsement
from calculations (18) of the potential surface of the 7-norbornadienyl IX
and 7-norbornenyl X cations as a function of bending over of the $C_1-C_7-C_4$
bridge: a minimum is approached by decreasing the angle between the C_1-C_7-
C_4 and $C_1-C_2-C_4$ planes in IX and X.

On the other hand, the interaction of two filled Π orbitals should lead
to a net destabilizing effect of norbornadien-7-one I and - to a lesser ex-
tent - of norbornen-7-one XI. While in the latter the interaction may be
partly circumvented and weakened by bending of the $C_7=O$ bridge towards the
saturated C_5-C_6 bond, it is forcefully imposed in I, where no such choice is
available. An analogous (18) calculation (19) of the potential surface of
norbornen-7-ones, indicates a slight bending away of the CO group from the
perpendicular geometry towards the saturated C_5-C_6 bond. While the latter
result follows the predicted trend, - vide supra -, its full significance
and implication are still to be drawn from further experimental and theoreti-
cal studies on related systems, currently in progress.

References

1. B. Fuchs a) Israel J. Chem. 3, 44p (1965); b) J. Chem. Soc., in press;
    c) unpublished observations.
2. M. A. Ogliaruso, M. G. Romanelli and E. I. Becker, Chem. Rev., 65, 261
    (1965).

3. a) D. M. Lemal, E. P. Gosselink and S. D. McGregor, J. Am. Chem. Soc.,
    88, 582 (1966) and prior publications; b) R. W. Hoffman, H. Häuser,
    Tetrahedron, 21, 89 (1965); c) P. G. Gassman, D. H. Aue and D. S.
    Patton, J. Am. Chem. Soc., 86, 4211 (1964).

4. K. Hafner and K. Goliasch, Chem. Ber., 94, 2909 (1961).

5. C. F. H. Allen, T. Davis, D. W. Stewart and J. A. Van Allan, J. Org.
    Chem., 20, 306 (1955).

6. W. Dilthey, S. Henkels and A. Schaefer, Chem. Ber., 71, 974 (1938).

7. Va was obtained after Dilthey et al. (6); Vb,c were obtained by re-
    fluxing a benzene solution of the reactants for several days followed
    by one to three days at room temperature. The resulting products were
    recrystallized from methylene chloride-pentane. All operations had to
    be conducted with exclusion of light in order to minimize decomposition
    of the products V. The configuration of the latter is not known al-
    though trans-addition would constitute a reasonable assumption.

8. Tetracyclone and acecyclone did not react in similar conditions. Cf.
    also ref. (1b) for a related phenomenon.

9. C. F. H. Allen, A. Bell, A. C. Bell and J. A. Van Allan,
    J. Am. Chem. Soc., 62, 656 (1940) assigned the fol-
    lowing structure to a certain reaction product but
    the authors themselves do not regard the assign-
    ment as definitive and we consider it highly
    improbable.

10. O. Blum-Bergmann, Ann., 484, 26 (1930). We are grateful to Prof. E. D.
    Bergmann, The Hebrew University, Jerusalem, for drawing our attention
    to this source.

11. J. Meinwald and E. G. Miller, Tetrahedron Letters, 253 (1961).

12. S. C. Clark and B. L. Johnson, ibid., 617 (1967).

13. a) G. A. Sim, J. Chem. Soc., 5974 (1965); b) C. F. Wilcox, Jr., S.
    Winstein and W. G. McMillan, J. Am. Chem. Soc., 82, 5450 (1960);
    c) A. C. Macdonald and J. Trotter, Acta Cryst., 18, 243 (1965); ibid.,
    19, 456 (1965); d) C. F. Foote, Tetrahedron Letters, 579 (1963) and
    references cited therein.

14. H. C. Brown and J. Muzzio, J. Am. Chem. Soc., 88, 2811 (1966) and re-
    viewed data therein.

15. H. Labhart and G. Wagnière, Helv. Chim. Acta, 42, 2219 (1959).

16. P. R. Story and M. Saunders, J. Am. Chem. Soc., 84, 4876 (1962);
    cf. ibid., 85, 3630 (1963).

17. E. I. Snyder and B. Franzus, J. Am. Chem. Soc., 86, 1166 (1964).

18. R. Hoffmann, J. Am. Chem. Soc., 86, 1259 (1964).

19. R. Hoffmann, private communication. We express our great appreciation
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