

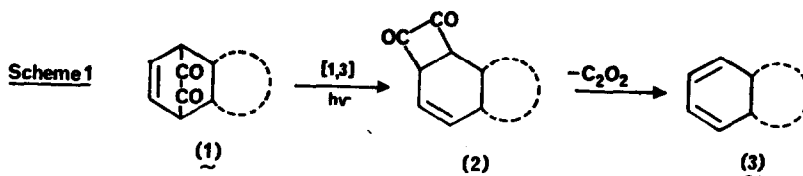
PHOTO-BISDECARBONYLATION¹. AN ENTRY INTO
THE HIGHLY REACTIVE ISOBENZOSYSTEM: ISOINDENE

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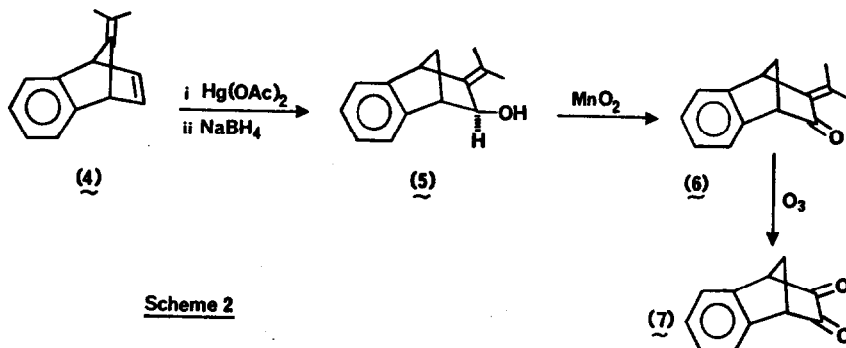
Rubin, Weiner and Scharf have recently reported² that alicyclic bridged α -diketones (1) do not lose C_2O_2 (or 2 x CO) directly upon irradiation at long wavelength (404, 436 nm), but undergo preliminary rearrangement to a cyclobutanedione (2), and this serves as the immediate precursor to the diene end-product (3) - Scheme 1.



In view of this finding it is of interest to compare the behavior of a system where the original β,γ -olefin is locked into an aromatic system. In the event significant change does occur in the reaction pathway at longer wavelength (>300 nm), but short wavelength irradiation (254 nm) leads to efficient bisdecarbonylation. Thus this method has served as an entry into the isobenzo-series, illustrated herein by the generation of the highly reactive isoindene molecule (10) from α -diketone (7).

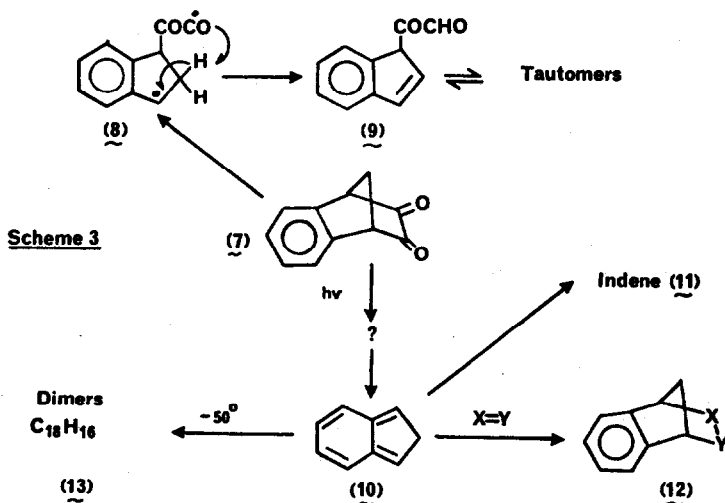
The benzonorbornenedione (7) was prepared via the sequence (4) \rightarrow (7)³. A significant step in this reaction is the regiospecific mercuration $[Hg(OAc)_2/NaBH_4]$ ⁵ of the $\Delta^{2,3}$ olefin of the benzo-bicyclo [2.2.1] hepta-2,5-diene (4) which leads directly to the rearranged *exo*-enol (5). This reaction may well constitute the clearest example of the carbonium ion-type addition involving the Hg(II) reagent^{6,7}, and contrasts with the simple norbornenes which do not rearrange under these conditions⁵. The oxidation step (5) to (6) can be achieved under Oppenauer conditions⁸, although we prefer activated manganese dioxide in benzene solution to generate the ketone (6). Other oxidizing agents cause deep-seated molecular reorganization⁹.

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In contrast with other α -diketones^{1,2}, long wavelength light (>300 nm; benzene or acetone, 0°C) did not effect smooth rearrangement to a product suitable for C_2O_2 elimination, but yielded the ketoaldehyde (9)¹⁰ as the major product (85%) together with indene (15%). The first step in this reaction is considered to involve Norrish Type I α -cleavage to yield the diradical (8) which forms the ketoaldehyde (9) by hydrogen migration (arrows Scheme 3). A similar diradical could well be involved in the rearrangement of (1) to (2), since the finer mechanistic details of the rearrangement remain to be determined². With the present example, formation of a compound related to (2) would involve dislocation of the aromatic ring and the alternative hydrogen migration step predominates.

Irradiation of the α -diketone (7) with shorter wavelength u.v. light (250 nm) in acetone solution at 0° , reduced α -cleavage to a minor role and raised the yield of indene to 70%. The ketoaldehyde (9) was shown not to be a source of indene under these conditions. Similar irradiations of (7) carried out in the presence of dienophile, resulted in the formation of [$\pi_8^8 + \pi_2^2$] adducts of isoindene, together with the ketoaldehyde (9).



Thus N-methyl maleimide gave stereospecifically the endo-adduct of type (12), m.p. 158° (p.m.r. in CDCl_3 : δ 1.91, 2.11, dd $J=8\text{Hz}$, methylene; δ 2.28, s, N-methyl; δ 3.49, 3.81, m, methine protons, AA'XX' pattern typical of endo-adducts; δ 7.19, m, aromatics), while dimethyl azodicarboxylate yielded a related adduct, an oil (p.m.r. in CDCl_3 : δ 2.10, br, methylene, δ 3.80, brs, methine, δ 7.2-7.6, m, aromatics; the line broadening is due to the dynamic character of the N-substituents of such adducts).

The above results are best explained by the intermediacy of isoindene¹¹ in the short wavelength photodecarbonylation reaction, which forms indene by a thermal 1,5-hydrogen shift in the absence of trapping agents and adducts in their presence.

Model experiments with 1,1,3-trideuteroindene ruled out indene to isoindene isomerisation as an alternative explanation. Thus no adducts were formed when this reagent was irradiated in the presence of N-methyl maleimide, and no deuterium incorporation was observed in the adducts formed when the diketone (7) was decomposed in the presence of both the trapping agent and the indene- d_3 .

While no direct evidence for isoindene could be observed (Pmr monitor) in low temperature (-50°) irradiations of the diketone (7); no indene was present either.

Work up of the complex mixture yielded two products ($\text{C}_{18}\text{H}_{16}$, m/e 232), which were isolated by P.L.C. Incorporation of indene- d_3 in the low temperature experiment did not alter the course of the reaction and no deuterium was incorporated in the dimeric fraction. This suggests that 1,5-sigmatropic migration has been frozen at this temperature, thus allowing intermolecular dimerisation (photochemical or thermal) of the isoindene nucleus, rather than trapping of isoindene by partially isomerized indene¹².

Experiments designed to utilize precursor (7) as a source of isoindene in matrix isolation studies are currently in progress, and will be reported, together with the structures of the above-mentioned dimers, in due course.

Acknowledgement: We thank the Australian Research Grants Committee for Financial Support.

References and Footnotes

1. Considered as photo-bisdecarbonylation III. Part I E.E. Nunn, W.S. Wilson and R.N. Warrenner, Tetrahedron Letters, 1972, 1975. Part II R.N. Warrenner, E.E. Nunn and M.N. Paddon-Row, Tetrahedron Letters, 1976, 2355.
2. M.R. Rubin, M. Weiner and H-D. Scharf, J. Amer. Chem. Soc., 1976, 98, 5699, and references therein.
3. This route is superior to SeO_2 oxidation which proceeds in poor yield⁴.
4. H. Tanida, Y. Hata, S. Ikegami and H. Ishitobi, J. Amer. Chem. Soc., 1967, 89, 2928.
5. H.C. Brown, J. Kawakami and K.T. Lui, J. Amer. Chem. Soc., 1973, 95, 2209.
6. S.J. Cristol, J.S. Perry, Jr. and R.S. Beckley, J. Org. Chem., 1976, 41, 1912.
7. It should be noted that solvolysis⁸ of the tosylate of the endo-2-ol related to 2,3-dihydro (4) yields a mixture of the exo- and endo-3-ols related to (5).
8. J. Ipaktschi, M.N. Iqbal and D. Lenoir, Chem. Ber., 1974, 107, 1126.
9. R.N. Warrenner, R.A. Russell, M.N. Paddon-Row and T.S. Lee, unpublished results.
10. This compound is present in solution as a mixture of tautomers containing the benzofulvene nucleus.
11. Whether this is formed directly from diketone (7), or a rearranged isomer of type (2), has not been determined.
12. Recent routes to substituted isoindenes and their isomerisation to indenes are reported in the following articles: a) W.R. Dolbier, L. McCullagh, D. Rolison and K.E. Anapolle, J. Amer. Chem. Soc., 1975, 97, 934. b) D.J. Field, D.W. Jones and G. Kneen, J.C.S. Chem. Commun., 1975, 754. c) J.J. McCullough and A.J. Yarwood, J.C.S. Chem. Commun., 1975, 485 and references cited therein.