of **6a** afforded 1-(5-amino-5-deoxy-β-D-allofuranosyluronic acid)uracil (**7a**) with mp 238–243° dec from ethanol ($[\alpha]^{23}D$ 17.6° (*c* 0.49, H_2O); nmr (TFA) 5.72 (d, 1, $J_{1',2'}$ = 0.5 Hz, $C_{1'}H$), 6.17 ppm (d, 1, $J_{5,6}$ = 8 Hz, C_5H)) in agreement with the properties of "uracil polyoxin C" described by Isono, *et al.*[2]

In a similar series of reactions the β-D-alluronamide derivative **3b** was converted in 94% yield into the 5-*O*-mesyl derivative **4b** ($[\alpha]^{23}D$ −11.7° (*c* 0.46, MeOH); nmr (acetone-d_6) 6.05 ppm (d, 1, $J_{1',2'}$ = 3 Hz, $C_{1'}$ H)) and thence to the 5-azido-α-L-taluronamide **5b** (75%) ($[\alpha]^{23}D$, 25.2° (*c* 0.1, MeOH); nmr (acetone-d_6) 5.94 (d, 1, $J_{1',2'}$ = 0.5 Hz, $C_{1'}$ H), 7.84 ppm (d, 1, $J_{5,6}$ = 8 Hz, C_6H)), both of which were isolated as analytically pure foams by chromatography on silicic acid. Acidic hydrolysis of **5b** with Dowex-50 (H^+) as above gave the 5-azido-α-L-taluronic acid **6b** (38% with mp 200–202°) and subsequent reduction gave 1-(5-amino-5-deoxy-α-L-talofuranosyluronic acid)uracil (**7b**) with mp 215–217° dec from ethanol: $[\alpha]^{23}D$ 9.9° (*c* 0.45, H_2O); nmr (TFA) 5.67 (d, 1, $J_{1',2'}$ = 1 Hz, $C_{1'}H$), 6.15 ppm (d, 1, $J_{5,6}$ = 8 Hz, C_5H). The amino acids **7a** and **7b** could not be separated by paper chromatography in several solvents. They can, however, be distinguished by their nmr spectra which are very similar but show distinctly different signals for their $C_{1'}$ and C_5 protons either alone or as mixtures.

Deamination of α-amino acids is recognized to occur with retention of configuration[11] and treatment of **7a** and **7b** with nitrous acid gave a pair of chromatographically distinguishable α-hydroxy acids. The acid arising from **7a** was shown to correspond to that obtained by acidic hydrolysis of the amide and acetal functions of **3b**. Similarly, a common product resulted from deamination of **7b** or hydrolysis of **3a**, these results being consistent with the expected inversion of configuration during formation of the azido amides **5a** and **5b** and confirming the stereochemical assignments of the amino acids.

Other routes to both sugar and heterocyclic base analogs of polyoxin nucleosides have been concomitantly developed and will be reported shortly.

(11) P. Brewster, F. Hiron, E. D. Hughes, C. K. Ingold, and P. A. D. S. Rao, *Nature (London)*, **166**, 179 (1950).

(12) Syntex Postdoctoral Fellow, 1968–1970.

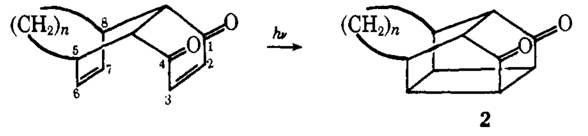
N. P. Damodaran,[12] G. H. Jones, J. G. Moffatt*
Contribution No. 88
Institute of Molecular Biology, Syntex Research
Palo Alto, California 94304

Received April 10, 1971

Solution Photochemistry. VI. Novel Photorearrangement of the Butadiene–Benzoquinone Diels–Alder Adduct[1,2]

Sir:

The photochemical cyclobutane ring-forming reaction between two remote double bonds in the same molecule has traditionally provided organic chemists with a method for the synthesis of highly strained and unusual polycyclic ring systems.[3] For example, the Diels–Alder adducts of *p*-benzoquinone with cyclobutadiene, cyclopentadiene, and cyclohexadiene (**1**, *n* = 0, 1, and 2, respectively) undergo smooth photochemical closure to the corresponding cage compounds **2**.[4]

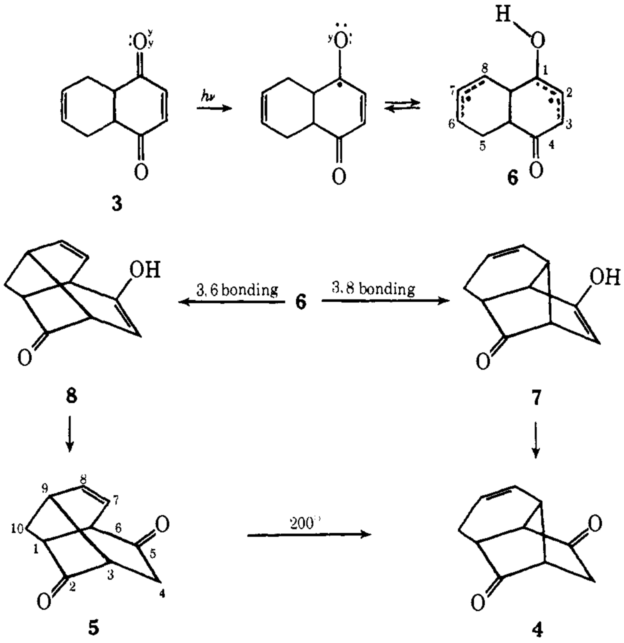


1, *n* = 0,1,2

2

Remarkably, the presence of a bridge or a bond between carbon atoms 5 and 8 seems to be a prerequisite for the success of this reaction; photolysis of the nonbridged butadiene–benzoquinone Diels–Alder adduct **3** (*cf.* Scheme I) has been reported[4a] to lead only to tar and ill-defined products postulated to arise from intermolecular α,β-unsaturated double bond dimerization.

Scheme I



Interest in this dichotomy has led us to a reinvestigation of the photochemistry of the butadiene–benzoquinone Diels–Alder adduct **3**. We report here that irradiation of this material under carefully controlled conditions does not lead to cage product formation but gives instead two novel tricyclic ene-diones in low but nevertheless useful yields; the first of these, **4**, represents a facile entry into the copaborneol,[5a] copacamphene,[5a] and sativene[5b] ring systems while the other, **5**, possesses a previously unknown carbon skeleton.

Conventional irradiation of **3**[6] (*i.e.*, 450-W Hanovia lamp, Pyrex filter, immersion well apparatus) at varying concentrations in a variety of solvents led, in agreement with literature reports,[4a] to amorphous, uncharacterizable material. However, selective n → π^* ex-

---

(1) Part V: J. R. Scheffer and B. A. Boire, *J. Amer. Chem. Soc.*, in press.

(2) Support of this research by the National Research Council and the University of British Columbia is gratefully acknowledged.

(3) W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

(4) (a) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964); (b) P. E. Eaton and S. A. Cerefice, *Chem. Commun.*, 1494 (1970).

(5) (a) M. Kolbe-Haugwitz and L. Westfelt, *Acta Chem. Scand.*, **24**, 1623 (1970), and references cited therein; (b) P. de Mayo and R. E. Williams, *J. Amer. Chem. Soc.*, **87**, 3275 (1965).

(6) Synthesized by the method of E. E. van Tamelen, *et al.*, *ibid.*, **91**, 7315 (1969).

citation of **3** (10^{-2} *M* in benzene; λ_{max} 370 nm (ϵ 63))[7] using a Corning 7380 glass filter (transmitting $\lambda >$ 340 nm) and an external 275-W sun lamp gave, in addition to extensive polymer formation, two new photoproducts **4** and **5** in a ratio of 1:7 after 24–48 hr. These products could be isolated in approximately 10% yield by passage of the crude photolysate through a short neutral alumina column (chloroform eluent); final separation of **4** and **5** was achieved by means of preparative vapor-phase chromatography (70% recovery).[8] Photolysis using *tert*-butyl alcohol–benzene (80:20) as solvent under otherwise identical conditions led to a **4**:**5** ratio of 5:1; employment of methanol, hexane, or acetonitrile afforded virtually complete polymer formation.

Photoproducts **4**, mp 67.5–68.5°, and **5**, mp 147–150°, were shown to be isomeric with starting material by means of elemental analysis and mass spectrometry. Their structures were assigned on the basis of spectral data, hydrogenation studies, mechanistic consideration, their thermal interconversion, and finally, in the case of **4**, on a single-crystal X-ray structure determination.

Distinguishing spectral features of **4** which support its structure are the following: a 5.72-μ carbonyl ir stretch,[9] a two-proton vinyl hydrogen multiplet centered at τ 4.15, and a broad uv absorption (MeOH) at 293 nm (ϵ 17, n $\rightarrow \pi^*$). Hydrogenation over palladium on charcoal gave the dihydro derivative:[10] bp 55° (0.05 mm); ir ($CHCl_3$) 5.71 (C=O) μ; uv max (MeOH) 288 nm (ϵ 48, n $\rightarrow \pi^*$).

Crystals of tricyclo[4.4.0.0^{3,7}]dec-8-ene-2,5-dione (**4**) are monoclinic, a = 6.806 (1), b = 15.171 (1), c = 7.667 (1) Å, β = 92.18 (1)°, Z = 4, space group $P2_1/n$. The structure was determined with Cu Kα scintillation counter data by direct methods (symbolic addition procedure programmed by Long[11]), and refined by full-matrix least squares, the final R being 0.046 for 984 observed reflections. Anisotropic thermal factors were used for C and O; H atoms were refined isotropically. Bond lengths are normal, and the associated angles show slight deviations from the expected values[12] which may be related to the bridged structure. Intermolecular contacts correspond to van der Waals interactions. A complete report of the crystallographic analysis will be published separately.[13]

The structure of photoproduct **5** was indicated by infrared (KBr) carbonyl stretching frequencies at 5.68 and 5.80 μ and by uv (MeOH) n $\rightarrow \pi^*$ absorptions at 296 (ϵ 260) and 310 nm (ϵ 230) characteristic of β,γ-unsaturated ketones.[14] The 220-MHz nmr spectrum, while complex, supported structure **5**. The vinyl hydrogens appeared essentially as triplets centered at τ 3.39 and 4.07 with a mutual coupling of 8 Hz. The C_4 methylene protons (τ 6.90 and 7.69) were basically doublets with a geminal coupling of 17 Hz; the large exo–endo chemical-shift difference is similar to that observed for the α-methylene protons of camphor.[15] The C_{10} methylene protons appeared at τ 8.04 and 8.40 with a geminal coupling of 12 Hz; both were essentially doublets with smaller vicinal couplings. The C_6 methine appeared as a clean triplet, J = 7 Hz, at τ 6.66. The remaining methine protons gave complex multiplets centered at τ 6.81, 7.37, and 7.56. Hydrogenation of **5** over palladium on charcoal gave the dihydro derivative:[10] mp 151–152°; ir ($CHCl_3$) 5.70 and 5.81 (C=O) μ; uv max (MeOH) 292 nm (ϵ 55, n $\rightarrow \pi^*$); and no vinyl hydrogens in the nmr.

Sealed tube thermolysis of **5** at 200° gave complete conversion to **4** within 4 hr, further substantiating the former's sutructure. This thermolysis did not occur under the vpc conditions employed[8] in the separation of **4** and **5** nor were **4** and **5** sensitive to the photolysis conditions.

The mechanism we currently favor for the conversion of the butadiene–benzoquinone adduct to **4** and **5** is shown in Scheme I. This involves n $\rightarrow \pi^*$ excitation of **3** followed by β-hydrogen abstraction through a five-membered transition state[16] giving resonance-stabilized diradical **6** which may close to either **7** or **8** followed by ketonization to afford **4** and **5**, respectively. It is tempting to speculate that the failure of adducts **1**, n = 1 and 2, to undergo this rearrangement is due to the bridgehead character of the radical which would necessarily be formed by β-hydrogen abstraction.

Diradical **6** in its ketonized form is a likely intermediate in the thermolysis of **5** to **4** in view of the steric requirements of the concerted process.[17]

Further product and mechanistic studies with a variety of quinone–diene adducts are in progress.

---

[7] The n $\rightarrow \pi^*$ nature of this absorption was verified by its progressive blue shift in solvents of increasing polarity: hexane, 370 nm; ether, 367 nm; ethyl acetate, 365 nm; acetone, 364 nm; acetonitrile, 362 nm; methanol, 358 nm.

[8] Vapor-phase chromatography isolation was achieved using a 5 ft × 1/4 in. stainless steel column packed with 20% DEGS on 60–80 Chromosorb W at a temperature of 170° and a helium flow rate of 140 ml/min.

[9] This value is in accord with the 5.72-μ carbonyl band observed for 2-norbornanone. See Sadtler Standard Infrared Spectra Catalog 20, No. 20280, Sadtler Research Laboratories, Inc., Philadelphia, Pa., 1962.

[10] All new compounds gave satisfactory elemental analyses.

[11] R. E. Long, Ph.D. Thesis, University of California at Los Angeles, 1965.

[12] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965).

[13] J. Trotter and C. S. Gibbons, manuscript in preparation.

[14] H. Labhart and G. Wagniere, *Helv. Chim. Acta*, 42, 2219 (1959).

[15] P. V. Demarco, D. Doddrell, and E. Wenkert, *Chem. Commun.*, 1418 (1969).

[16] Intramolecular hydrogen abstractions of this type through cyclic five-membered transition states, although rare, have been previously observed; see A. Padwa and W. Eisenhardt, *J. Amer. Chem. Soc.*, 93, 1400 (1971).

[17] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969); J. A. Berson, *Accounts Chem. Res.*, 1, 152 (1968).

[18] National Research Council Predoctoral Fellow, 1968–present.

John R. Scheffer,* James Trotter, Rockford A. Wostradowski[18]
Cyril S. Gibbons, Kuldip S. Bhandari
Department of Chemistry, University of British Columbia
Vancouver 8, Canada

Received April 22, 1971

Photochemical Isomerization of 4-Isopentyl-4-methylcyclopentenone

Sir:

We wish to describe briefly the photochemical isomerization of 4-isopentyl-4-methylcyclopentenone (**1**) and to point out that the transformations observed can be best explained by assuming intramolecular abstraction of hydrogen by the β-carbon atom of the α,β-unsaturated ketone system.

Cyclopentenone **1** was prepared from known[1] diethyl

---

[1] G. L. Handley, E. R. Nelson, and T. C. Somers, *Aust. J. Chem.*, 13, 129 (1960).