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# *Communications to the Editor*

## Photolysis of Two Tricyclic Nonenediones. Direct Observation of Norcaradiene

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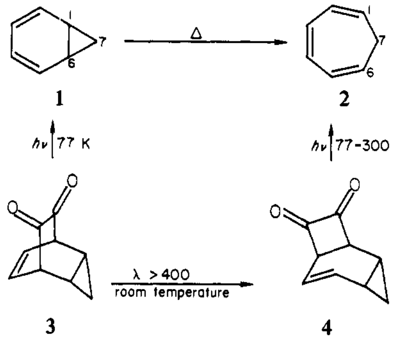
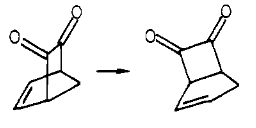
The norcaradiene (**1**)–cycloheptatriene (**2**) equilibrium has been of interest for almost a century,[1] dating back to Buchner's work on the products formed by decomposition of diazoacetic ester in benzene and later to the isolation of products containing a cyclopropane ring from Diels–Alder reactions of **2**. Both theoretical[2] and experimental[3] treatments of this equilibrium have continued to appear in the literature to the present day. While the cycloheptatriene form is normally appreciably more stable, structural modifications such as suitable bridging, fusion of additional rings, or substitution can reverse the usual order of stability. Thus, for example, the 7,7-dicyano derivative[4] is observed only as the norcaradiene isomer, while both isomers have been detected by variable-temperature NMR spectroscopy in a few other 7-substituted cases.[5] Although its existence is well accepted, norcaradiene itself has not been detected previously. We now wish to report direct observation of this elusive species and determination of the kinetics of the isomerization $\mathbf{1} \rightarrow \mathbf{2}$.

Room temperature irradiation (404 or 436 nm) of solutions of tricyclo[3.2.2.0$^{2,4}$]non-6-ene-8,9-dione[6] [**3**: $\lambda_{max}$ (cyclohexane) 446 nm (83); $\nu_{max}$ 1740 cm$^{-1}$] resulted in the anticipated isomerization[7,8] to tricyclo[5.2.0.0.$^{4,6}$]-non-2-ene-8,9-dione [**4**: $\lambda_{max}$ (cyclohexane) 515 nm (155); $\nu_{max}$ 1770, 1795 cm$^{-1}$], as illustrated in Figure 1. In addition to the isosbestic points at 382 and 465 nm shown in Figure 1, additional isosbestic points were observed at 235 and 255 nm;[9] the quantum yield at 436 nm was 0.47. Photobisdecarbonylation[7] of **4** (436–546 nm) at room temperature afforded **2** in quantitative chemical yield with a quantum yield (515 nm) of 0.30.

It was hoped that low-temperature irradiation of **4** would proceed with loss of two molecules of carbon monoxide while preserving the bicyclo[4.1.0] skeleton, thus leading to the formation of **1**. However, irradiation of **4** at 77 K in hydrocarbon glass at wavelengths ranging from 254 to 436 nm ($\phi_{436}{}^{77} = 0.1$) afforded **2** directly, with the same isosbestic behavior observed in room temperature experiments. There was no evidence for the formation of any thermally unstable intermediate.





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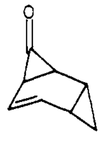

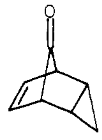

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Earlier work[10] had shown that the quantum yield for isomerization of a related diketone, bicyclo[2.2.1]heptenedione (**5**), at 436 nm to bicyclo[3.2.0]heptenedione (**6**) exhibited a marked temperature dependence. Similar behavior was observed with **3** in 2-methyltetrahydrofuran[11] (2-MTHF) at 436 nm, the quantum yield decreasing to 0.01 of the room temperature value at 170 K. However, at 404 nm the temperature dependence was less dramatic (the quantum yield at this wavelength at 77 K was only one-tenth the room temperature value), suggesting that low temperature, short wavelength irradiation of **3** might provide a route to **1**.

The spectroscopic results obtained upon irradiation[12] of **3** at 77 K in hydrocarbon glass with light of wavelength 240–400 nm are shown in Figure 2. The maximum of **3** at 250 nm disappeared upon irradiation and a new maximum of approximately equal intensity appeared at 265 nm ($\epsilon \sim 2500$); this spectrum remained unchanged upon further irradiation or continued standing in the dark at 77 K. When the glass was warmed briefly to about 110 K and then recooled, the spectrum of **2** was observed ($\lambda_{max}$ 261 nm) with an intensity corresponding to quantitative conversion.[13] In a similar experiment at 77 K in 2-MTHF glass[11] in an apparatus suitable for measuring infrared spectra, the carbonyl maximum of **3** at 1740 cm$^{-1}$ disappeared as the irradiation progressed with concomitant appearance of the absorption maximum of carbon monoxide at 2140 cm$^{-1}$; no new carbonyl ab-

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(4) Ciganek, E. *J. Am. Chem. Soc.* **1967**, *89*, 1454.

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(8) The quantum yield for this reaction, under anhydrous conditions, was independent of solvent (cyclohexane, benzene, methylene chloride, 2-MTHF), presence or absence of oxygen, or presence of added (1 × 10$^{-3}$ M) anthracene.

(9) The deviation from isosbestic behavior (Figure 1) at late stages of the reaction is due to light absorption by the product leading to formation of **2**.

(10) Rubin, M. B.; Weiner, M.; Katraro, R.; Speiser, S. *J. Photochem.* **1979**, *11*, 287.

(11) This change is solvent was necessitated by the low solubility of **3** in hydrocarbon solvents at low temperature.

(12) A specially constructed Dewar vessel which fits into the sampel compartment of a Cary 15 spectrometer was used. Solutions (3 mL) of **3**, 2–5 × 10$^{-4}$ M in 1:1:1 methylcyclohexane–isohexane–isopentane, in 10- × 10 mm quartz cells were cooled with liquid nitrogen and irradiated through a Corning 7-54 filter (10% transmission at 240 and 400 nm) with light from a 200-W high-pressure mercury lamp (Osram HBO 200) for 40–50 min to achieve complete conversion.

(13) After completion of low-temperature measurements, the solutions were allowed to warm to room temperature and the concentration of **2** determined from the UV spectrum. Conversions were about 80% in agreement with the fact that the unmasked area of the cell was 81% of the total area of the filled portion of the cell.

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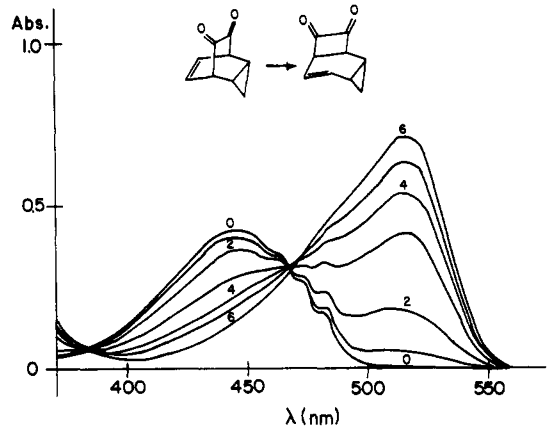

Figure 1. Progress of 404-nm irradiation of $3.4 \times 10^{-3}$ M **3** in air-saturated cyclohexane at room temperature.

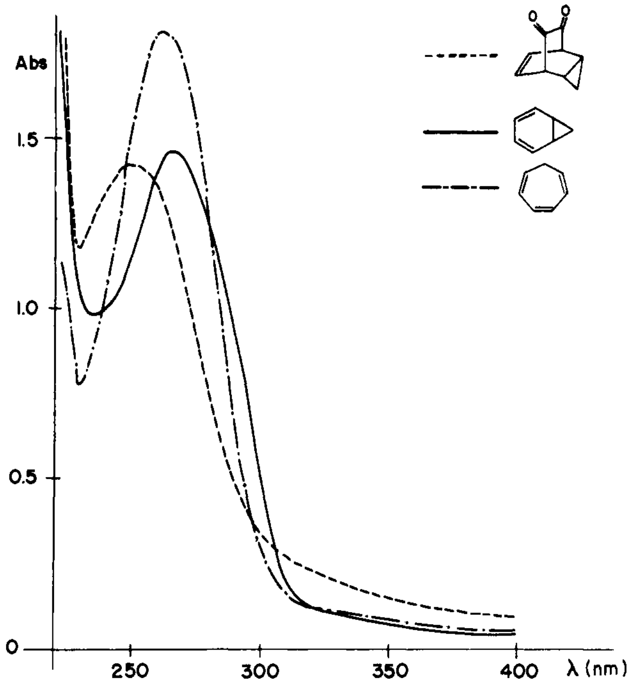

Figure 2. Ultraviolet spectra in 1:1:1 methylcyclohexane–isohexane–isopentane at 77 K: (---) $3.94 \times 10^{-4}$ M **3**; (—) after 50 min of irradiation at 240–400 nm; (-···) after warming to 110 K and recooling.

sorption was observed. We therefore attribute the norcaradiene structure to the thermally unstable product of low-temperature photolysis of **3**. The ultraviolet spectrum is consistent with this assignment,[14] and the infrared spectrum rules out any thermally labile ketone such as the cyclopropanone **7** as a precursor for **2**.[15] The contrast in the photochemical behavior of **3** and **4** at low temperature is a matter of continuing interest.

Differences in the ultraviolet spectra of **1** and **2** (cf. Figure 2) were sufficiently great to allow measurement of the kinetics of the isomerization **1** → **2** by monitoring the increase in optical density at 261 nm. Good first-order behavior was observed at 93, 98, and 103 K; the results fit the Arrhenius expression

$$k_{1\rightarrow 2} = (6.0 \pm 0.3) \times 10^{11} e^{(-6500\pm 1000)/RT}$$

The value of the preexponential term gives $\Delta S^{\ddagger}{}_{100} = -2.5$ eu and $\Delta G^{\ddagger}{}_{100} = 6100$ cal/mol. The calculated rate constant for **1** → **2** at 25 °C is $1 \times 10^7$ s$^{-1}$. The corresponding values at 25 °C are $\Delta S^{\ddagger} = -4.5$ eu and $\Delta G^{\ddagger} = 7.2$ kcal/mol which are quite similar to those determined[5c] by variable-temperature NMR ($E_a = 7$ kcal/mol, $\Delta S^{\ddagger} = -4$ eu) for the isomerization of 7,7-bis(methoxycarbonyl) norcaradiene to the cycloheptatriene isomer, even though the relative stabilities of the two isomers are very different in these two cases.

It has been suggested[16] that the equilibrium concentration of **1** in **2** at 20 °C is 0.1%. Using the equilibrium constant based on this proposal, the free energy difference between **1** and **2** at 25 °C is of the order of −4 kcal/mol and $\Delta G^{\ddagger}{}_{2\rightarrow 1} \simeq 11$ kcal/mol. Assuming that the entropy of activation for **2** → **1** is close to zero, the approximate Arrhenius expression becomes

$$k_{2\rightarrow 1} \simeq 6 \times 10^{12} e^{-12000/RT}$$

Application of the low-temperature photochemical method described above to synthesis of substituted norcaradienes is being investigated. We note that the analogous monoketone, tricyclo[3.2.1.0$^{2,4}$]oct-6-en-8-one[17] (**8**), afforded **2** quantitatively under the same conditions used for successful conversion of **3** to **1**.

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[14] (14) For example, 7,7-dicyanonorcaradiene[4] has $\lambda_{max}$ (cyclohexane) 271 nm (2900).

[15] (15) The NMR spectrum would constitute an ideal proof of structure for **1**. Unfortunately, the required temperature is so low ($t_{1/2}{}^{-170} = 63$ s) that this was not feasible.

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# Tertiary Phosphine Derivatives of the f-Block Metals. Preparation of $X_4M(Me_2PCH_2CH_2PMe_2)_2$, where X Is Halide, Methyl, or Phenoxo and M Is Thorium or Uranium. Crystal Structure of Tetra(phenoxo)bis[bis(1,2-dimethylphosphino)ethane]uranium(IV)

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Though a number of tertiary phosphine complexes of uranium halides have been claimed,[1] most of the claims have been shown to be false.[2] In this communication we describe the synthesis of some authentic bis(1,2-dimethylphosphino)ethane (dmpe) complexes of uranium(IV) and thorium(IV) halides of the type $X_4M(dmpe)_2$ and their conversion to the tetramethyl and tetraphenoxo derivatives. The crystal structure of the phenoxo derivative, $(PhO)_4U(dmpe)_2$, is described.

Uranium tetrachloride dissolves in a mixture of dichloromethane and a threefold molar excess of bis(1,2-dimethylphosphino)ethane (dmpe) at room temperature to give a blue green solution from

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