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2,4-DI-TERT-BUTYL- AND 2,3,4,5-TETRACHLORONORCARADIENE

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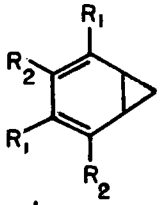
Abstract - The title norcaradienes have been synthesized by low temperature photolysis and the activation parameters for their isomerization to cycloheptatrienes determined.

We have recently reported[1] the synthesis of norcaradiene (**1a**) by low temperature photolysis of the unsaturated diketone **2a** and now wish to describe the preparation of the title compounds (**1b**, **1c**) and their isomerization to the stable cycloheptatrienes **4**. The general approach, low temperature photolysis, was the same as in the earlier work but the immediate precursors were not. In the synthesis of **1a**, the room temperature photoisomerization product of **2a**, cyclobutanedione **3a**, was photolyzed directly to **4a** under all conditions of temperature and wavelength including those which successfully led to formation of **1a** from **2a**. In the present work, the analogous cyclobutanediones **3b** and **3c** proved to serve as precursors to norcaradienes while **2b,c** did not.

Room temperature irradiations of 1,6-di-t-butyltricyclo[3.2.2.0^{2,4}]non-6-ene-8,9-dione[2], λ_{max} (cyclohexane) 447 nm (112) and the 1,6,7,8-tetrachlorodione[3] **2c** (λ_{max} (cyclohexane) 431 nm (124)) at 404 nm resulted in remarkably clean isomerization[4] to the corresponding cyclobutanediones **3b** (λ_{max} 330 (1000), 530 nm (320)) and **3c** (λ_{max} 332 (1500), 517 nm (300)), as illustrated for **2b→3b** in Fig. 1. In addition to the isosbestic points at 394 and 471 nm appearing in the Figure, additional isosbestic points were observed at shorter wavelengths. Quantum yields at 436 nm were 0.21 for disappearance of 2b and formation of **3b**; and 0.66 for the tetrachloro compound.

Irradiation of **3b** in 1:1:1 methylcyclohexane-isopentane-isohexane glass at -190° resulted in disappearance of the absorption maximum of **3b** at 330 nm and



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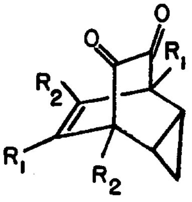

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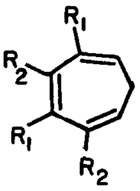
a, $R_1 = R_2 = H$

b, $R_1 = H$; $R_2 = t\text{-Bu}$
$R_1 = t\text{-Bu}$; $R_2 = H$

c, $R_1 = R_2 = Cl$



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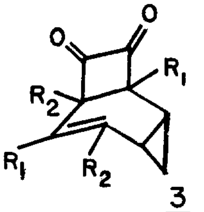

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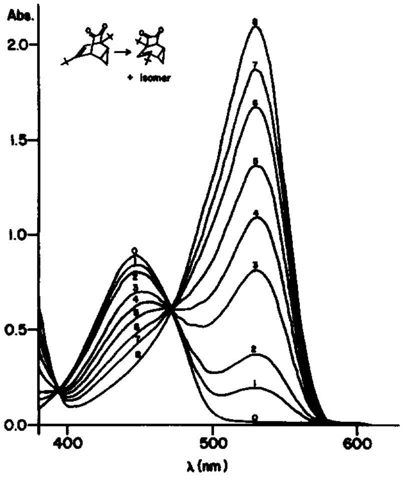
appearance of a new maximum at 280 nm due to the formation of di-t-butylnorcaradiene (**1b**). As can be seen in Figure 2 this reaction proceeded with isosbestic behaviour (isosbestic points at 250 and 305 nm). Warming to about -160° and recooling resulted in appearance of the absorption spectrum of 2,4-di-t-butylcycloheptatriene[5] (**4b**) as shown by the dashed spectrum in the Figure. Similar behaviour was observed with the tetrachloro compound **3c** with isosbestic points at 227 and 303 nm; the absorption maximum of 2,3,4,5-tetrachloronorcaradiene was observed at 300 nm ($\epsilon \sim 3500$). Warming to -160° and recooling resulted in appearance of the spectrum of 2,3,4,5-tetrachlorocycloheptatriene[6]. Low temperature irradiations monitored by infrared spectroscopy showed disappearance of the characteristic carbonyl absorption of **3b** and **3c** and concomitant appearance of the absorption maximum of carbon monoxide at 2140 cm^{-1}. No new carbonyl bands were observed. Direct conversion of **2c** to **1c** at -190° could be achieved by irradiation at wavelengths above 380 nm due to the absence of a significant activation energy in these reactions[7] in contrast to unsubstituted or alkyl substituted diones.



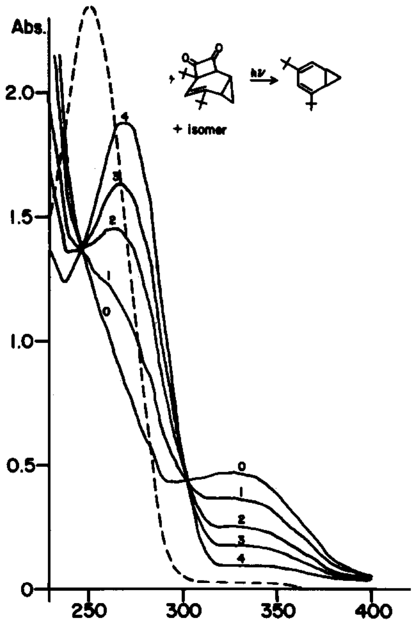


Fig. 1 (left). Progress of irradiation of **2b** at 404 nm in cyclohexane at room temperature. Fig. 2 (right). Progress of irradiation of **3b** at λ > 380 nm in 1:1:1 methylcyclohexane-isohexane-isopentane at 83K. The dotted line is the spectrum obtained after warming to 113 K and recooling.

Irradiation of diketones **2b** or **2c** in the ultraviolet (250-400 nm) did not produce the desired norcaradienes. This could be shown to arise from the fact that the substituted norcaradienes underwent photochemical reaction[8] in contrast to the parent compound which was photochemically stable.

The considerable difference in absorption spectra between the substituted norcaradienes and the cycloheptatrienes produced by their thermal rearrangement allowed measurement of the kinetics of isomerization much more easily than in the case of norcaradiene itself. Thus the isomerization of **3b** was followed at 255 and 280 nm with identical results and the isomerization of **3c** at 300 nm. In all cases good first order kinetic behaviour was observed. Rates of isomerization of **1b** were measured over the range 90-102 K and of **1c** at 93-105 K to give the following Arrhenius expressions and activation parameters:

1b→4b $k = (6.0\pm0.5)\mathrm{x}10^{9}\varepsilon^{(-5600\pm1000)/RT}$ $\Delta S^{\neq}_{298} = -14$ e.u., $\Delta G^{\neq}_{298} = 9.8$ kcal/mole.

1c→4c $k = (7.2\pm0.5)\mathrm{x}10^{7}\varepsilon^{(-5100\pm1000)/RT}$ $\Delta S^{\neq}_{298} = -22$ e.u., $\Delta G^{\neq}_{298} = 7.2$ kcal/mole.

The relative rates of isomerization at 100 K were 1:0.93:0.15 for **1a**, 1b, and **1c** respectively. As can be seen from the activation parameters above, these differences are mainly due to variations in the preexponential term in the Arrhenius expressions rather than to differences in activation energies.

References and Notes

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8. These photoreactions are the subject of further study.

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