122. The Photochemistry of 5,6-Dimethylidene-2-norbornanone. Synthesis and *Diels-Alder* Reactivity of 2,3-Dimethylidenebicyclo[2.1.1]hexane[1])

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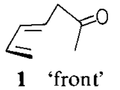
(16.IV.80)

Summary

2,3-Dimethylidenebicyclo[2.1.1]hexane (**4**) was isolated from direct irradiation (253.7 nm) of 5,6-dimethylidene-2-norbornanone (**3**). Quenching experiments at 253.7 nm, as well as direct and sensitized irradiations at > 300 nm suggested that a high vibrationally excited S_1- or a S_2-state is required for the photodecarbonylation of **3** in contrast with other β,γ-unsaturated ketones for which α-cleavage occurs with lower excitation-energy. The new diene **4** reacted toward tetracyanoethylene ($k^{II}_{39,5°}$ ($l\,mol^{-1}\,s^{-1}$) $= (3.1 \pm 0.34) \cdot 10^{-3}$ in toluene and $(6.2 \pm 0.11) \cdot 10^{-3}$ in benzene) only 60 times more slowly than 2,3-dimethylidenenorbornane (**5**) and *ca.* 850 times as fast as 2,3-dimethylidene-*syn*-1,4,5,6-tetramethylbicyclo[2.1.1]hexane (**9**).

Introduction. - The photochemistry of β,γ-unsaturated carbonyl compounds has been studied widely [2-5]. Three types of reactions can be observed: (1) the carbonyl reactions (α-cleavage *(Norrish I)*, γ-hydrogen transfer *(Norrish II)*, reduction, ketene elimination, etc.), (2) the olefin reactions (cycloadditions, cyclizations, *cis-trans* isomerizations, reduction, *etc.*) and (3) the bichromophoric reactions (1,2- and 1,3-acyl shifts, intramolecular oxetane formation, *etc.*). The photoreactions of $\beta,\gamma,\delta,\varepsilon$-unsaturated ketones in which the carbonyl function looks at the 'front' of the diene, as depicted in **1**, have been illustrated abundantly [2] [6]. The photochemistry of bichromophoric systems [7] in which an homoconjugated carbonyl group looks at the 'back' of a diene, as depicted in **2**, has received little attention[3]). The 5,6-dimethylidene-2-norbornanone (**3**) [9] is one example of such a system. We report here an exploratory study on its photochemistry.



1 'front'

2 'back'

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[1]) Interactions between non-conjugated chromophores, Part 12; Part 11, see [1].

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[3]) The photolysis ($\lambda > 300$ nm) of 2,3-dimethylidene-7-norbornanone yields CO and the 2,3-dimethylidene-1,4-cyclohexanediyl diradical [8].

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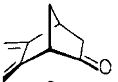
Photolysis of 5,6-dimethylidene-2-norbornanone. - Contrary to 2,3-dimethylidene-7-norbornanone [8] and to other β,γ- and $\beta,\gamma,\delta,\varepsilon$-unsaturated ketones [2] [6], the keto-diene **3** is little photoreactive. Under direct irradiation at $\lambda > 300$ nm (pyrex, high-pressure Hg lamp, -50 to $+30°$) only slow polymerization of **3** was observed (quantum yield < 0.02) in pentane, acetone or methanol. Addition of triplet sensitizers such as acetophenone or xanthone [10] did not affect the outcome of the photolysis. Irradiation at 253.7 nm (low-pressure Hg lamp, quartz) in pentane, ether, methanol, toluene or acetone yielded the 2,3-dimethylidenebicyclo-[2.1.1]hexane (**4**) and untractable polymers. The photo-decarbonylation $\mathbf{3} \rightarrow \mathbf{4}$ was not quenched with O_2, *cis*-1,3-pentadiene, 9,10-benzophenanthrene or azulene, thus suggesting a singlet reactive state S_2- or a vibrationally excited S_1-state.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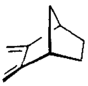
4

Cyclohepta-3,5-dienones are known to undergo α-cleavage under $\lambda_{\text{irr}} > 300$ nm, probably via a $S_1(\text{n},\pi^*)$-state [6]. In **3**, the $S_1(\text{n},\pi^*)$- and $T_1(\text{n},\pi^*)$-states do not lead to any observable decarbonylation. The 2,3-dimethylidenenorbornane (**5**) cyclizes to give the cyclobutene **6** upon direct irradiation at 253.7 nm with a relatively low quantum yield [11]. The analogous cyclobutene **7** could not be detected upon irradiation of **3** under the above conditions. However, it can not be excluded that **7** is consumed by fast reopening into **3** (if true, this would imply that the homoconjugated carbonyl group in **7** activates the electrocyclic ring opening, *cf.* [11]) or by a *Diels-Alder* reaction with **3** or **4** to generate various adducts. We failed, however, to detect any dimer of **3** or adduct of **7**+**4** in the polymeric material that was formed competitively with **4** ($\lambda_{\text{irr}} = 253.7$ nm), neither in the polymer formed under direct or sensitized irradiations at $\lambda > 300$ nm. Also no products of an oxa-di-π-methane rearrangement which has to occur *via* **8** could be detected. Control experiments established that the diene **4** was also polymerized under direct irradiation at 253.7 nm with a quantum yield of 0.10 ± 0.03, not very different from that of the photodecarbonylation $\mathbf{3} \rightarrow \mathbf{4}$ (0.30 ± 0.08). A quantum yield of 0.75 ± 0.08 was measured for the disappearance of **3** at 253.7 nm.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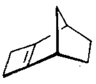
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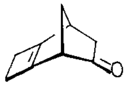
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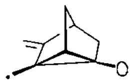
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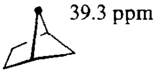
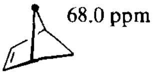
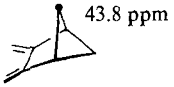
The structure of **4** was deduced from its spectral data, combustion analysis and reactivity toward tetracyanoethylene (TCE). A typical UV. absorption spectrum was observed for the planar *s-cis*-butadiene moiety [12] with $\lambda_{\max} = 238.5$ nm. This corresponds to a somewhat higher transition energy than for the diene **5** ($\lambda_{\max} = 248$ nm [13]) and 2,3-dimethylidenebicyclo[2.2.2]octane ($\lambda_{\max} = 252$ nm [14]). If the small differences observed are not due to *Franck-Condon* effects of the $V \leftarrow N$ transition, one could attribute them to changes in the 1,4-interactions between the two ethylenic chromophores [15]. The distance between the two olefinic CH_2-groups is expected to be larger in **4** than in **5** and 2,3-dimethylidene-bicyclo-



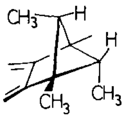




[2.2.2]octane [16]. Another possible interpretation would be to invoke the different abilities of puckered cyclobutane [17], cyclopentane [18] and cyclohexane [19] rings to hyperconjugate with the exocyclic diene in **4**, **5** and 2,3-dimethylidene-bicyclo[2.2.2]octane, respectively.

The endocyclic double bond in 2-norbornene derivatives exerts in the ^{13}C-NMR. spectrum a remarquable downfield shift effect of 10-17 ppm on the γ-carbon C(7) relative to the corresponding saturated analogs [12a] [20]. This so-called 'norbornene effect' is not observed in acylic, monocyclic hydrocarbons [21] and in the bicyclo[2.2.2]octane series [22]. A downfield shift effect of *ca.* 29 ppm is observed on the δ_C of the γ-carbon atoms C(5,6) by introducing an endocyclic double bond in bicyclo[2.1.1]hexane [23]. In contrast, 2-methylidenenorbornane [24] and 2,3-dimethylidene-norbornane [12a] [25] display a δ_C for C(7) very similar to that of norbornane. Similarly, we find that methylidene groups at C(2,3) of the bicyclo[2.1.1]hexane system don't affect significantly the δ_C of C(5,6).

***Diels-Alder* reactivity of 2,3-dimethylidene-bicyclo[2.1.1]hexane.** - *Hogeveen et al.* [26] have shown that the cyclobutane bridged diene **9** has a remarkably low *Diels-Alder* reactivity ($k^{\mathrm{II}} = 2 \cdot 10^{-6}$ lmol^{-1} s^{-1} toward tetracyanoethylene (TCE) in benzene at 20°), whereas the bicyclobutane bridged diene **10** is an extremely reactive diene. The non-substituted analog **4** was found to yield the expected adduct with TCE in benzene (67°, 24 h, see exper. part) in 90% yield. Kinetic measurements gave a second order rate constant $k^{\mathrm{II}}_{\mathrm{toluene}} = (3.1 \pm 0.34) \cdot 10^{-3}$ lmol^{-1} s^{-1} at 39.5° (average of 3 independent runs under pseudo-first order conditions, 40-150 fold excess of **4**). Thus, the diene **4** is only *ca.* 60 times less reactive than **5** toward TCE in toluene at 40° [27]. A second order rate constant $k^{\mathrm{II}}_{\mathrm{benzene}} = (6.2 \pm 0.11) \cdot 10^{-3}$ lmol^{-1} s^{-1} was measured for the cycloaddition of **4** to TCE at 39.4°. After extrapolation to 20° ($k^{\mathrm{II}}_{\mathrm{benzene}} \simeq 1.7 \cdot 10^{-3}$ lmol^{-1} s^{-1}, assuming for **9** $\Delta S^{\ddagger} = -27$ calmol^{-1} K^{-1} [27] as an upper limit, one estimates **4** to be *ca.* 850 times more reactive than the *syn*-tetramethylated derivative **9** toward TCE. It appears, therefore, that steric hindrance to the approach of the dienophile due to the *syn*-methyl groups at C(5,6) in **9** might be a part of the *Diels-Alder* reactivity difference between the dienes **9** and **10**. Nevertheless, we agree with *Hogeveen et al.* [26] that steric hindrance alone cannot explain the observed difference in reactivity of these dienes.



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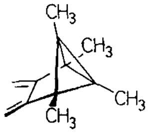

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The lower *Diels-Alder* reactivity of **4** compared with that of **5** might be attributed to a larger distance between the methylidene groups in **4** than in **5** [28]. This argument, probably, does not apply to the reactivities of **9** and **10**. Another interpretation invoking the different ability of the puckered cyclobutane [17] and cyclopentane [18] ring to hyperconjugate with the diene function in **4** and **5**, respectively, cannot be ruled out yet.

We are grateful to the *Swiss Science Foundation* (FN 2.891-0.77), to the *Fonds Herbette* (Lausanne) and to the *Commission Fédérale des bourses pour étudiants étrangers* (Zürich) for generous support.

Experimental Part

General Remarks. Melting points (m.p.) and boiling points (b.p., not corrected), *Tottoli* apparatus; IR. spectra ($\tilde{\nu}$ [cm^{-1}]), *Beckman* IR-20A spectrometer; UV. spectra, *Pye Unicam* SP 1800 instrument (λ_{max}[nm](ε), sh. = shoulder; Mass spectra (MS.) in electron ionization mode, CEC 21-490 *Bell-Howell* and *Hewlett-Packard* HP 5980A spectrometers (*m/z*[amu](% base peak)); ^{1}H-NMR. spectra, *Bruker* WP 80 CW (δ ppm, apparent coupling constant *J* [Hz], number of protons, tentative attribution); *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, br. = broad, $\delta_{TMS} = 0.0$ ppm; ^{13}C-NMR. spectra, *Bruker* WP 60 spectrometer (15.08 MHz, spectrum width: 3750 Hz, 4096 points, FT Mode): δ ppm, multiplicity, $^1J_{C,H}$. Elementary analysis were performed by the microanalytical laboratory of the University of Geneva (Dr. *K. Eder*). Analytical gas chromatography, *Hewlett-Packard* 5710A; preparative gas chromatography, *Carlo Erba* Fractovap 2400 V chromatograph.

Photoreactors. For $\lambda = 253.7$ nm: Tauschlampe *Hanau* TNN 15/32 or *Gräntzel* (Karlsruhe) Reaktor 400, low pressure Hg lamp (quartz vessel); for $\lambda > 300$ nm, *Philips* HPK 125 W, pyrex vessels. Stirring was made magnetically or by bubbling dry He or N_2 through the solutions. Sensitisers: acetophenone, xanthone, *(Fluka, puriss p.a.);* quenchers: azulene, *cis*-1,3-pentadiene, 9,10-benzophenanthrene *(Fluka, puriss p.a.).*

2,3-Dimethylidene-bicyclo[2.1.1]hexane (**4**). A pentane (450 ml) solution of the keto-diene **3** [9] was degassed at 20° with dry N_2 for 30 min. After cooling to −30°, the stirred solution was irradiated (253.7 nm, *Hanau* TNN 15/32) in a quartz vessel for 24 h. The slightly yellow solution contained *ca.* 28% of **3**, 26% of **4** and 46% of polymers (partially precipitated at −30°). The solution was concentrated by distillation. The residue was combined with 4 other residues obtained under the same conditions. Distillation afforded 490–500 mg of the crude diene **4** (36% based on reacted **3**), b.p. 130°/720 Torr, and 675 mg unreacted **3** (28%), b.p. 80°/2 Torr. The diene was purified by preparative gas chromatography (FFAP 10%, *Alltech Associates* or SE30 10% on WAW Chromosorb, 60/80 mesh). - UV. (isooctane): 247 (sh.), 238.5 (8100), 231 (sh.), 222 (sh.). - IR. ($CDCl_3$): 3090, 3000, 2960, 2890, 1670, 1430, 1210, 1150, 865, 815. - ^{1}H-NMR. ($CDCl_3$): 5.20 (*s*, 2 H); 4.95 (*s*, 2 H); 2.95 (*t*, 2 H, $^3J_{H(1,4),H(5,6\text{-}syn)} \cong 0.0$, $^3J_{H(1,4),H(5,6\text{-}anti)} \cong 2.5$, H(1,4)); 2.02 (*m*, 2 H, $^2J_{H(5,6\text{-}syn),H(5,6\text{-}anti)} \cong 3.5$, $^4J_{H(5,6\text{-}syn),H(6,5\text{-}anti)} \cong 2.0$, $^3J_{H(5,6\text{-}anti),H(1,4)} \cong 2.5$, H(5,6-*anti*)); 1.33 (*d*×*d*, 2 H, $^2J_{H(5,6\text{-}syn),H(5,6\text{-}anti)} \cong 3.5$, $^4J_{H(5,6\text{-}syn),H(6,5\text{-}anti)} \cong 2.0$, H(5,6-*syn*)). - ^{13}C-NMR. ($CDCl_3$): 151.6 (*s*), 97.4 (*t*, 158), 48.2 (*d*, 143), 43.8 (*t*, 144). - MS. (70 eV): 107 (5), 106 (60), 91 (100), 78 (45).

C_8H_{10} (106.17) Calc. C 90.51 H 9.49% Found C 90.71 H 9.63%

Tetracyanoethylene adduct of **4**. The diene **4** (57 mg, 0.53 mmol) and freshly sublimed TCE (54.6 mg, 0.47 mmol) in anhydrous benzene (3 ml) were heated to 67° for 24 h under stirring. The adduct precipitated at 10°. Yield: 90 mg (90%), colourless crystals, m.p. 220° (dec.). - UV. (CH_3CN): 227.5 (3490). - IR. (KBr): 2990, 2960, 2880, 2250, 1660, 1430, 1220. - ^{1}H-NMR. (CD_3COCD_3): 3.75 (br. *s*, 4 H); 2.78 (*m*, 4 H); 2.50 (*m*, 2 H). - MS. (70 eV): 234 (0.6), 106 (16), 105 (15), 91 (100), 78 (27), 51 (19), 39 (25).

$C_{14}H_{10}N_4$ (234.266) Calc. C 71.78 H 4.30 N 23.92% Found C 71.92 H 4.22 N 24.02%

Kinetic measurements of the tetracyanoethylene addition to **4** (*cf.* [27]). The disappearance of the TCE/toluene and TCE/benzene (solvent) charge-transfer complex at 405 and 384 nm, respectively, was recorded as a function of time.

Quantum Yields were determined in the vessels used for the preparative irradiations. Potassium ferrioxalate [29] was used as actinometer [30].

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