Rappelons qu'en formulant les règles de calcul des coefficients des IE, nous indiquons, partout où il est possible, deux valeurs. Sauf indication contraire, la première correspond à deux atomes de parité différente, et la seconde, à des atomes de même parité. Si les deux atomes de l'IE sont monovalents, on utilisera $n_A = 1$, et si l'un des atomes est polyvalent, on utilise $n_A = 2, 3$ ou 4 suivant le nombre d'électrons de l'atome polyvalent.

Pour le développement de la méthode graphique ce résultat est évidemment remarquable. Bien qu'il soit impossible de prévoir avec certitude le comportement des systèmes à plusieurs atomes polyvalents, on peut malgré tout s'attendre à ce qu'une généralisation semblable se présente aussi pour les systèmes plus compliqués.

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161. 2,3,5,6-Tetramethylidene-Bicyclo[2.2.1]Heptane

(Preliminary Communication¹))

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(11. VI. 75)

Summary. Preparation of the title compound **1** is described. An important transannular effect between the two unconjugated *s-cis*-butadiene chromophores is observed by comparison of the UV. spectra of the tetramethylidenenorbornane **1** and the dimethylidenenorbornane **3**. The differences observed between the UV. spectra of 2,3,5,6-tetramethylidene-7-oxanorbornane **2** and **1** are also discussed briefly.

'Through space' and 'through bond' interactions have been found to affect spectroscopic and chemical properties of molecules containing non-conjugated chromophores in a rigid conformation [1]. Difficulties arise when analysing the UV. absorption spectra of unconjugated dienes where $\sigma \rightarrow \pi^*$ bands can overlap $\pi \rightarrow \pi^*$ bands [2]. Those difficulties can be avoided in practice when studying the interaction between butadiene chromophores whose separate V ← N transition energies ($\pi_2 \rightarrow \pi_3^*$) are usually much smaller than the other $\sigma \rightarrow \pi^*$ transition energies. Recently, we prepared the 2,3,5,6-tetramethylidene-7-oxanorbornane (**2**) whose UV. absorption spectrum indicated an important transannular effect between the two unconjugated *s-cis*-butadiene [3]. In order to test the importance of the σ-skeleton hyperconjugation with the π-system ('through bond' interaction) and of an eventual perturbation due to the oxygen n-orbitals, the comparison of ether **2** with the cor-

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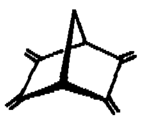
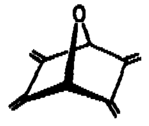
[1] A full paper will appear later in this journal.

responding hydrocarbon **1** was necessary. We present here a synthesis of this tetraene and discuss briefly its electronic spectrum taken in solution.



1



2

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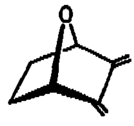

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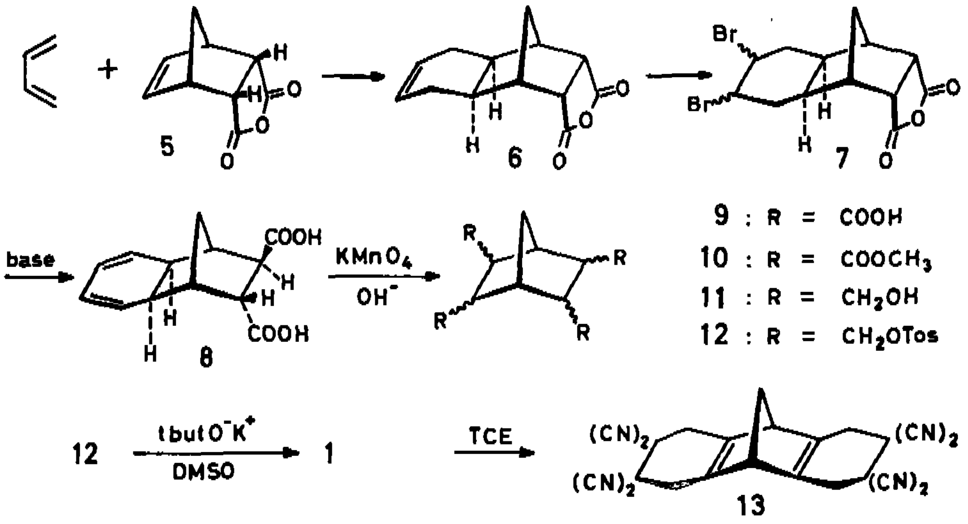
The key product in the preparation of **2** was a 7-oxanorbornane-2,3,5,6-tetracarboxylate derivative which is obtained readily by *Diels-Alder* addition of di(methoxycarbonyl)acetylene to alkyl 3,4-furanedicarboxylate, followed by catalytic hydrogenation [3]. Due to fast sigmatropic shifts [4], a corresponding cyclopentadienedicarboxylate is expected to yield a mixture of unwanted adducts besides the desired product under similar conditions. We found that alkyl 2,3,5,6-norbornanetetracarboxylates (**10**) can be prepared according to the *Scheme 1*.

Scheme 1



Diels-Alder cycloaddition of butadiene to the anhydride **5** is known to furnish the *exo*-tricyclic compound **6** [5] (200°; 48 h; yield: 22–25%). **6** adds one mole of bromine in CH_2Cl_2 at $-15°$ and yields a mixture of dibromides **7** (95%). Elimination of hydrobromic acid (*t*-BuOK/THF; $-20°$; 5 h) followed by hydrolysis (H_2O/Na_2CO_3) furnishes the cyclohexadiene derivative **8**. By oxidative cleavage of this diene ($KMnO_4$ 5%/NaOH 5%) a 2,3,5,6-norbornanetetracarboxylic acid (**9**) is obtained (40% based on **7**). Esterification by diazomethane in acetone/ether yields the corresponding tetraester **10** (86%). The exact steric structure of **9** and **10** has not yet been established. $LiAlH_4$ reduction of **10** (THF; 60°; 5 h) yields the tetrol **11** (74%) which is esterified into the oily tetratoluenesulfonate **12** (56%). Treatment of **12** in *t*-BuOK/DMSO (20°/4–5 h) furnishes a volatile, pentane soluble mixture that contains the expected 2,3,5,6-tetramethylidenenorbornane (**1**) besides several non-identified products. **1** is isolated (5%; by preparative GC.) as a colorless, cristalline

Table 1. *Physical and spectroscopic properties of compounds* **1**, **7**, **8**, **9**, **10**, **11**, **12** and **13**

	m.p. [°C]	IR. [cm^{-1}]	UV. λ_{max} (ε) [nm] sh = *shoulder*	^1H-NMR. δ [ppm] (number of H; multiplicity; $J_{H,H}$ in Hz)	MS. (70 eV) m/e^+ [amu] (relative intensity)
1	28–30	3150; 2960[a]) 2940; 2860 1630; 1460 1250; 910	264 (sh, 3150)[b]) 252 (sh, 7900) 244 (sh, 9400) 235 (12500) 228 (12000) 220 (sh, 8900)	5.2 (4; *s*); 4.95 (4; *s*)[c]) 3.4 (2; *t*; 2.5) 1.65 (2; *t*; 2.5)	145 (7); 144 (27); 143 (17) 131 (7); 130 (7); 129 (40); 128 (33) 127 (13); 117 (20); 116 (13) 115 (27); 105 (17); 104 (10) 92 (33); 91 (100); 79 (70); 74 (50) 73 (63); 70 (50); 61 (100)
7	156–157	3020; 2980[d]) 2970; 2920 1860; 1780 1480; 1230 1080; 900; 620	End absorption ε_{220} = 800[e])	4.7 (1; *m*); 4.25 (1; *m*)[c]) 3.5 (2; *m*; 4.; 3.) 2.6 (2; *m*); 2.05 (4; *d*; 2.) 1.9 (2; br. *s*); 1.75 (2; *m*)	382; 380; 378; 344; 342 (<1%) 299 (100); 297 (100); 281 (6) 280 (6); 279 (6); 278 (6); 217 (24) 181 (12); 171 (6); 145 (12) 143 (12); 117 (30)
8	243–245 (dec.)	3300–2500[d]) 1710; 1420 1230; 910		6.2 (4; *m*); 3.25 (4; *m*)[f]) 2.83 (2; *m*; 5.5; 2.) 1.47 (2; *m*)	non-volatile
9	164–166	3300–2500[d]) 1710; 1420 1230; 750	End absorption ε_{220} = 500[e])	2.75 (2; *m*); 2.55 (2; *m*)[g]) 2.4 (2; br. *s*) 1.6–1.2 (2; *m*)	non-volatile
10	b.p. = 85–90/0.5 Torr	2960; 2940[a]) 2840; 1750 1720; 1200 1070	End absorption ε_{230} = 250[e])	3.75 (6; *s*); 3.68 (6; *s*)[c]) 2.9 (2; *m*); 2.4 (2; *m*) 2.2 (2; *m*); 1.35 (2; *m*)	326 (3); 325 (10); 324 (3); 311 (2) 310 (3); 297 (6); 296 (10); 293 (2) 271 (23); 264 (14); 221 (37) 194 (14); 163 (100); 151 (43)
11	oil	3300; 2940[h]) 2900; 1040	End absorption	6.0 (4; br. *s*); 3.9 (8; *m*)[i]) 3–1.2 (8; *m*)	non-volatile
12	amorphous	2940; 2920[a]) 1600; 1440 1350; 1160	259 (5700)[e]) 222 (38000)	7.6 (16; *d-m*; 9.)[c]) 3.9 (8; *m*); 2.4 (12; br. *s*) 2.1–1.3 (8; *m*)	non-volatile
13	115–117	2960; 2980[d]) 2850; 2220 1640; 1440; 1230	240 (sh, 400)[e]) 216 (1500)	3.75 (8; br. *s*)[f]) 2.7 (2; *t*; 2.7) 1.35 (2; *t*; 2.7)	

[a]) In $CHCl_3$; [b]) In isooctane; [c]) In $CDCl_3$; [d]) In KBr; [e]) In ethanol 95%; [f]) In acetone-d_6; [g]) In CF_3COOH; [h]) As film; [i]) In pyridine. ^1H-NMR. reference: δ_{TMS} = 0.0 ppm (*s* = singulett; *d* = doublet; *t* = triplett; *m* = multiplet; br. *s* = broad singlet). Melting points (m.p.) are not corrected.

substance[2]. This tetraene is stable in degassed solutions at room temperature for several days. It polymerizes rapidly in presence of air or/and light. When **1** is dissolved in a CH_2Cl_2 solution of tetracyanoethylene (TCE) an intense, red colour develops immediately (charge-transfer complexe formation) that fades a few seconds later. The bis-adduct **13** is then formed and it precipitates.

IR.- and ^{1}H-NMR. spectra of **1** are characteristic of a substance having exocyclic *s-cis*-butadiene groups [6] and do not present, to a first approximation, any special effect due to homoconjugation (see the Table). The comparison of the UV. absorption spectra (see Fig. 1) of **1** and **3** shows that an important transannular interaction between the two unconjugated *s-cis*-butadiene chromophores affects the electronic properties of the rigid, bicyclic tetraene **1**[3].

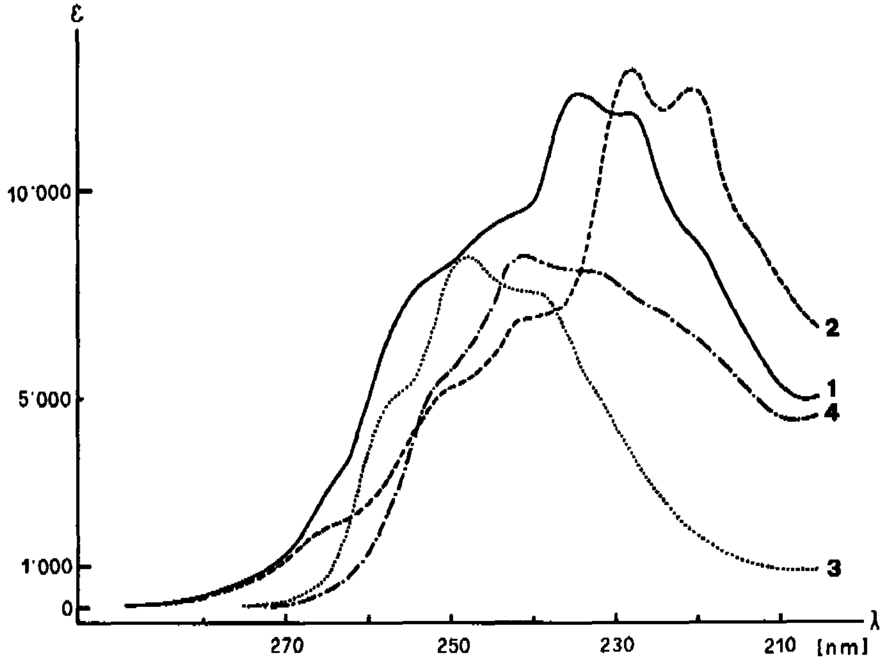


Fig. 1. *UV. absorption spectra of tetraenes* **1** *and* **2**, *and dienes* **3** *and* **4** (isooctane/20°)

In both tetraenes **1** and **2**, one observes a splitting of the bands expected for the V ← N transition of the *s-cis*-butadiene chromophores of **3** and **4**. From the spectra given in Fig. 1, the splitting is approximatively the same for **1** and **2**, thus indicating no important perturbation due to n-orbitals of the oxygen bridge in **2**[4]. Nevertheless,

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[2] The low yield in **1** obtained in this elimination contrastes with the good yield obtained when performing the same reaction in the preparation of the analog ether **2**. This is partially due to competitive processes forming cyclic ethers from **12**. The yields given here have not been optimized.

[3] Apparently, due to ring flexibility 1,2,4,5-tetramethylidenecyclohexane (λ_{max} = 224 nm; ε = 10500 [7]) and 1,2,5,6-tetramethylidenecyclooctane (λ_{max} = 228 nm; ε = 10000 [8]) do not present the similar effect in their UV. absorption spectra.

[4] A 'through space' interaction of the n-orbitals of oxygen with the π-system in **2** is expected to enhance the splitting of the V ← N transitions of the butadiene chromophores [10]. PE. spectra, gas phase and glass phase UV. spectra should make this point clearer.

it is remarkable that the blueshift of 700–1300 cm^{-1} observed on the V ← N transition when going from the hydrocarbon **3** to the ether **4** is also observed for the bands of **2** when compared with **1**. This observation can be explained by a diminished importance of the σ-skeleton hyperconjugative interaction with the π-system when the bicyclic ring is stabilized through the replacement of the CH_2- (7) by an oxygen-bridge [9].

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162. Carotinoidsynthesen über Sulfone; Synthese von Apocarotinoiden und Torularhodinester

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(22. V. 75)

Summary. The alkylation of conjugated arylsulfonyl ylids, prepared from the corresponding allylic sulfones (**2** or **8**), and allylic halides bearing terminal carbonylgroups (**3** or **4**) leads to polyene sulfones which readily undergo spontaneous elimination of the corresponding aryl sulfinates. By this method two apocarotenoids (**5** and **6**) and torularhodin ethyl ester (**9**) have been prepared.

Schon seit längerer Zeit sind Spaltungsreaktionen von Sulfonen unter basischen Bedingungen zu Olefinen und Sulfinaten bekannt [1]. Verschiedene Beispiele von Sulfinateliminierungen, ausgehend von Sulfonen, die in β-Stellung oder vinyloger β-Stellung zu einer Carbonylgruppe stehen, wurden ebenfalls veröffentlicht [2–4] und erfolgen besonders leicht. Beim Aufbau der hier beschriebenen Carotinoide sind wir einem Synthesekonzept gefolgt, das die Eliminierung von Sulfinat aus solchen besonders bevorzugten Stellungen gestattet. Dabei zeigten die angestrebten Polyensulfone mit komplett aufgebautem Kohlenstoffgerüst unter den angewandten Reaktionsbedingungen spontane Sulfinateliminierung unter Ausbildung der gewünsch-