THE JOURNAL OF Organic Chemistry

VOLUME 45, NUMBER 15

JULY 18, 1980

Synthetic Approaches to Planar Carbon. 1

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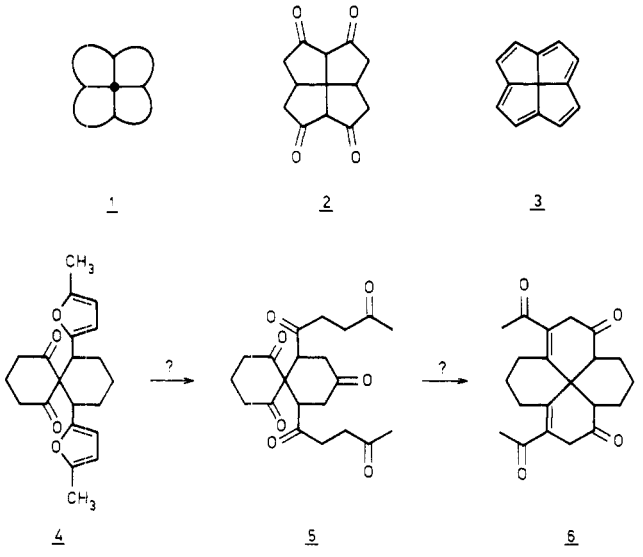
Received February 11, 1980

An approach to fenestranes, which are potentially good precursors to planar carbon compounds, was investigated via suitably functionalized spiranes **7** and **8**. Acidic hydrolysis of **8** led to the doubly hydrolyzed spirane **15**. The synthesis of a fenestrane such as **17**, via two intramolecular aldol condensations in **15**, appeared to be unsuccessful. Treatment of **7** with acid gave rise to a rearrangement: with boron trifluoride in ether three products, **20**, **21**, and **22**, were formed, whereas with hydrochloric acid compound **18** could be isolated. The structure of **21** was assessed via X-ray structure determination, thereby giving insight into the mechanism of the rearrangement of **7**.

Only a limited number of fenestranes (general structure **1**) have been reported.[1-5] These fenestranes deserve attention as possible precursors to planar carbon structures.[6,7] For instance, the [5.5.5.5]fenestrane **2** might lead



ultimately to the attractive, possibly planar, compound **3**. Although at present a synthesis of a planar carbon compound seems a rather elusive goal, the extension of the number of fenestranes may stimulate synthetic as well as theoretical considerations about planar carbon structures.

The presence of what might be called a double spiro unit has prevented an easy access to fenestranes. In this paper we describe some attempts to prepare fenestranes which are suitably functionalized to allow conversion to a planar carbon system. Our approach consisted of an acid-catalyzed hydrolysis of the furan rings in a system such as **4** to yield the doubly ring-opened spirane **5**, which might give the [6.6.6.6]fenestrane **6** after intramolecular aldol condensation and dehydration. Our efforts have focussed on the spiranes **7** and **8**, the synthesis of which is depicted in Scheme I. A double Michael reaction between the 1,3-pentadienone **9** and dimedone (5,5-dimethyl-1,3-cyclohexanedione) or 1,3-indandione, respectively, readily gave the triketones **10** and **11**. When dimedone was used as a Michael donor,[8] the addition was performed in ethanol with sodium hydroxide as a catalyst. This gave *cis*-**10** in 69% yield. The cis configuration was deduced from the ^{1}H NMR spectrum of the product, which showed mutual coupling of the equatorial protons α to the carbonyl group of the cyclohexanone ring.[9] When 1,3-indandione was used as a Michael donor,[10] the addition could be performed in acetic acid. Heating a mixture of the 1,3-pentadienone **9** and 1,3-indandione for 1 h gave a 66% yield of a mixture of *cis*- and *trans*-**11** (ratio of ca. 1:9), whereas heating overnight furnished the same mixture, however, in a ratio of 9:1 (68% yield).[9] This trans–cis isomerization could equally well be effected by treating *trans*-**11** with sodium methoxide in methanol. The cis and trans configurations of the isomers of **11** were based on the differences in symmetry, shown by the respective ^{1}H NMR and ^{13}C NMR spectra.[9] The carbonyl group in the cyclohexanone moiety

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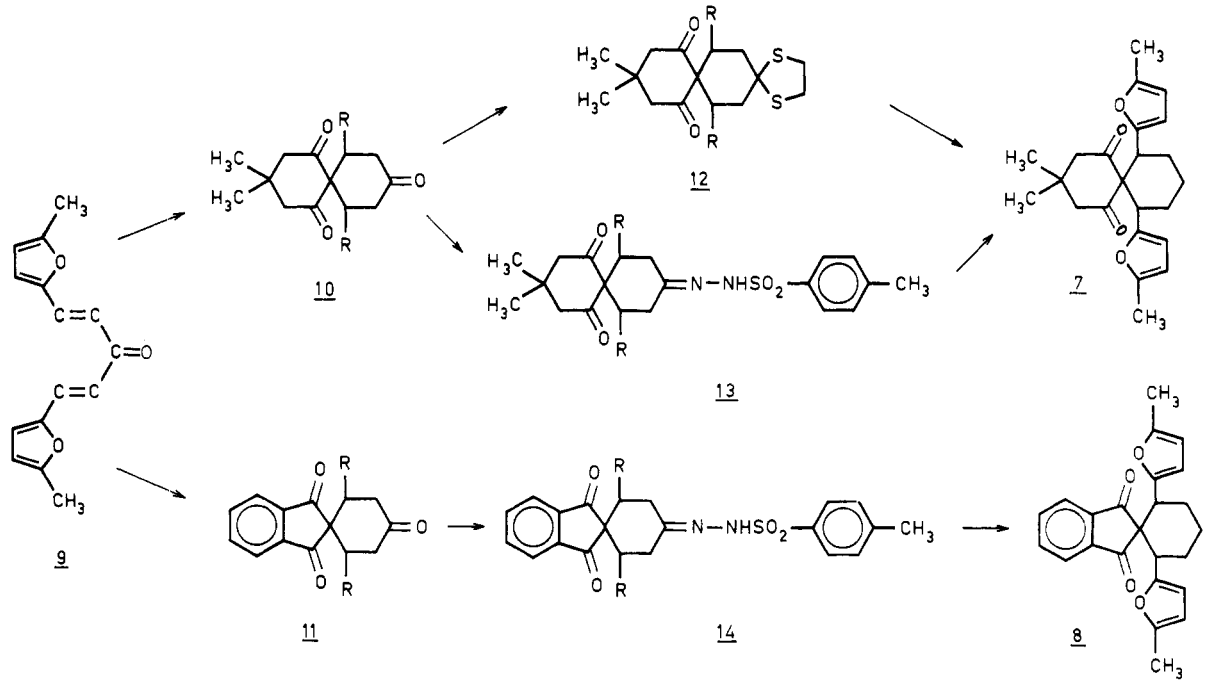
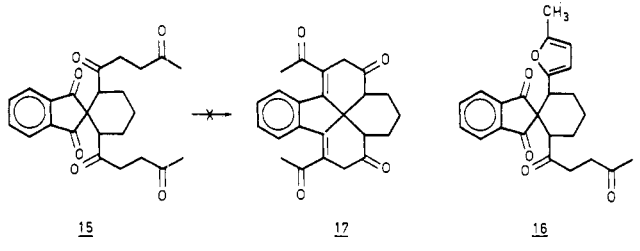
Scheme I



of **10** and **11** was subsequently transformed to a methylene group. This was done in order to circumvent retrograde Michael reaction and/or unwanted aldol condensations after hydrolysis of the 5-methylfuryl units. In the case of **10** this transformation was performed in two ways: (a) thioacetalization readily gave **12** (78% yield), which on desulfurization gave *cis*-**7** in 47% yield (**7** was contaminated with some thioacetal); (b) reduction of the tosylhydrazone **13** (obtained in 88% yield) with sodium borohydride in methanol[11] gave *cis*-**7** in 75% yield. The cis configuration of **7** was deduced from the symmetry, shown by its ^{13}C NMR spectrum (*cis*-**7** will contain a plane of symmetry). With the latter and more convenient method, the spirane **8** was prepared. *cis*-**11** readily gave the tosylhydrazone **14** in 98% yield; however, formation of the tosylhydrazone of *trans*-**11** was accompanied by partial epimerization to afford *cis*-**14** in 38% yield and *trans*-**14** in 56% yield. This epimerization must have been catalyzed by the basic tosylhydrazide. Since sodium borohydride reduction of **14** gave inferior results, this reduction was performed with catecholborane[12] to provide *cis*-**8** in 68% yield and *trans*-**8** in 48% yield, respectively.

Attempted Fenestrane Synthesis. (a) Using Spirane 8 as Precursor. Hydrolysis of the furan rings in **8** to form 1,4-diketone units was performed under the usual acidic conditions.[13] Heating *cis*- or *trans*-**8** with a mixture of concentrated hydrochloric acid and ethanol gave the doubly hydrolyzed product **15** in 67% yield. This hydrolysis proceeded with epimerization, since both *cis*- and *trans*-**8** gave the same isomer. The ^{13}C NMR spectrum showed that a plane of symmetry was present in **15**, thus establishing that this spirane is a cis isomer. As a byproduct of the hydrolysis of **8**, the partially hydrolyzed product **16** was isolated in 17% yield. In the next step **15** had to be cyclized to a fenestrane by two intramolecular aldol condensations. Although successful intramolecular aldol condensations have been described for compounds which are related to **15**,[14-16] we were not able to prepare a fenestrane such as **17**. In most cyclization attempts either no reaction took place (L-proline in DMF or Me_2SO at 20 °C,[17] pyrrolidine in benzene at 80 °C[18]) or some **16** was present (*p*-toluenesulfonic acid in benzene at 80 °C,[19] L-proline and perchloric acid in acetonitrile at 80 °C[17]). Under mildly basic conditions (sodium hydroxide in water and ethanol at 20 °C) reaction took place, leading to a complicated mixture of products from which no pure products could be isolated.



(b) Using Spirane 7 as Precursor. In contrast to the hydrolysis of spirane **8** the reaction of **7** with a mixture of concentrated hydrochloric acid and methanol did not lead to the product resulting from direct hydrolysis of the 5-methylfuryl units. A colorless compound, **18**, was obtained in 36% yield by crystallization of the crude product. The spectroscopic data of **18** were not compatible with a fenestrane structure derived from **6**. Since these spectroscopic data did not provide us with an acceptable structure for **18**, additional information had to be obtained. To that end the related spirane **4** was prepared via catecholborane reduction of the tosylhydrazone, prepared from *trans*-**19**.[9] Hydrolysis of **4** with concentrated hydrochloric acid and

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Table I. Relevant Spectroscopic Data of Compounds 7, 18, 20, 21, and 22[a]

	^{13}C NMR, δ	MS, m/e	IR (CH_2Cl_2), cm^{-1}	UV, λ_{max}, nm (ε)
7	212, 210, 153, 150, 108 (d), 106 (d), 68	368	1700, 1680	248 (3000)
18	210, 210, 196, 166, 112, 85, 83, 78 (d)	386	1700, 1620	266 (14 000)
20	197, 166, 147, 128 (d), 126, 111, 101 (d), 84 (d), 82, 77			
21	196, 168, 151, 146, 125, 117, 102 (d), 86, 82 (d), 78	368	1650	267 (11 000)
22	197, 167, 151, 150, 127, 120 (d), 118, 112, 105 (d), 76 (d), 65	368	1640	268 (21 000)

[a] Only low-field ^{13}C NMR signals are shown, i.e., signals above δ 60. These signals are singlets, unless otherwise stated by the multiplicity shown in parentheses.

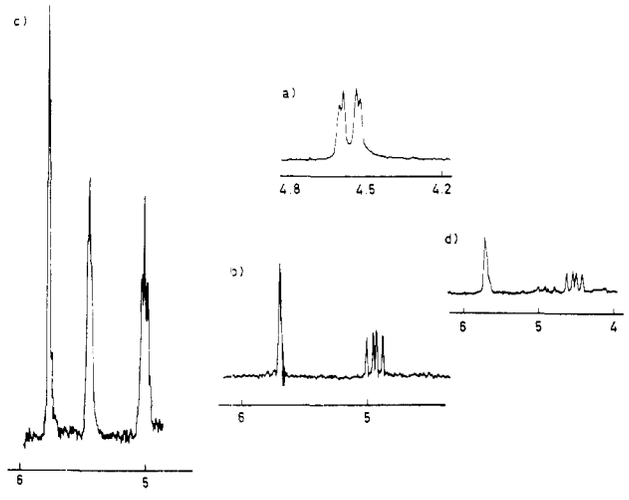
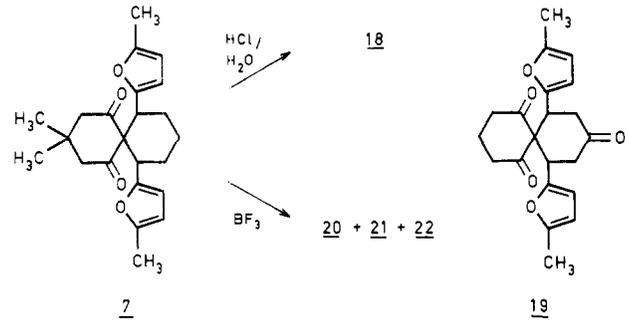
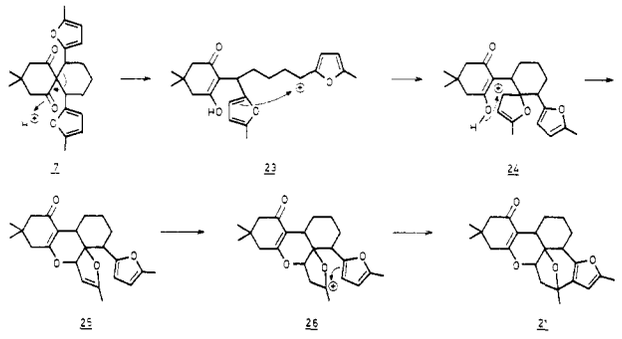


Figure 1. Lower field part of the 100-MHz ^{1}H NMR spectra of (a) **18**, (b) **21**, and (c) **22** and of the 60-MHz ^{1}H NMR spectrum of (d) **20**.

methanol gave a mixture of products, from which no pure product could be isolated, however. Other information, regarding the structure of **18**, was obtained by treatment of **7** with an excess of boron trifluoride in ether. A rearrangement took place under these conditions, leading to a mixture of three products, **20**, **21**, and **22**, together with some starting compound. The relative quantities of these three isomers differed somewhat in each experiment, although **20** was always present in small amounts; **21** and **22** could be obtained pure after chromatography, but **20** was contaminated with **21**. Again, the structures of these products were not evident from their spectroscopic data (see Figure 1 and Table I for relevant data). From the ^{1}H NMR and ^{13}C NMR spectra of **20** and **21** it was concluded that they were closely related isomers and that they contained a furan ring. From the ^{1}H NMR and ^{13}C NMR spectra of **22** it was concluded that **22** contained a 5-methylfuryl group. The UV spectra of compounds **18**, **21**, and **22** showed that these contained an α,β-unsaturated carbonyl unit. The interrelationship of compounds **18**, **20**, **21**, and **22** was assessed in the following ways. (a) Acidic hydrolysis of a mixture of **20** and **21** (consisting largely of **21**) gave a product which consisted mainly of **18**. Presumably a furan ring had been hydrolyzed to give **18**, and, therefore, knowledge of the structure of **21** will furnish the structure of **18**. (b) Treatment of **22** with an excess of boron trifluoride in ether gave a product consisting of a mixture of **21** and **22** in nearly equal amounts. Similarly, treatment of **21** gave a mixture of **21** and **22** (ratio of ca. 2:1), whereas treatment of a mixture of **20** and **21** (consisting largely of **21**) with boron trifluoride in ether gave a mixture of **20**, **21**, and **22** wherein, by ^{1}H NMR spectroscopy, the amount of **20** had remained unchanged. Upon consideration of these interrelations, it seemed that (X-ray) structure determination of one of the four unknown compounds would give information about the structure of the other compounds and provide a mechanism to account for the formation of the respective compounds. Since **21** was the only compound that could be crystallized well, this compound was chosen for X-ray crystallography. This furnished the structure for **21**, which is shown in Scheme II.[20]



Scheme II

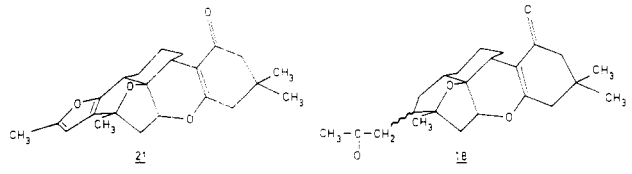


Mechanism of the Rearrangement

After determination of the structure of **21**, a reasonable mechanism accounting for the formation of this compound could be envisioned (Scheme II). The first step involves acid-catalyzed ring opening of one of the spirane rings in the starting spirane **7** (for the sake of convenience the H^+-catalyzed reaction is schematized). This leads to an intermediate carbonium ion **23**, which is stabilized by a 5-methylfuryl group. The carbonium ion then adds intramolecularly to the other furan ring, thus leading to **24**, which undergoes enol ether formation to form **25**. Protonation of **25** gives the intermediate **26**, which affords **21** after C–C bond formation and proton abstraction. Since the formation of **24** is accompanied by formation of a cyclohexane ring with four different substituents, **24** is a mixture of several isomers. After the following ring closures one of these isomers leads to **21**, whereas another isomer may lead to **20** via the same pathway (**20** will then be closely related to **21**, as a stereoisomer of the latter). The structure of **22** remains an open question. For instance, structure **25** of Scheme II does not conform completely to the ^{1}H NMR and ^{13}C NMR data. Therefore, **22**

(20) Spek, A. L.; Duisenberg, A. J. M., to be submitted for publication.

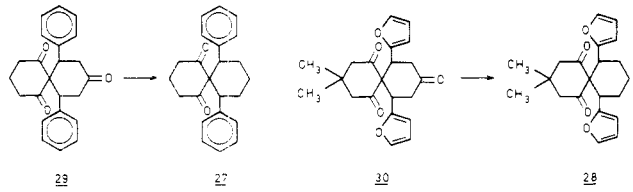
has possibly arisen from one of the intermediates in Scheme II via reversible reactions. Because compound **18** was formed by hydrolysis of **21**, its structure can be represented by the one shown below. The structures of **18**, **20** (as a stereoisomer of **21**), and **21** are in full accord with the spectroscopic data; e.g., the typical O—C=C—C=O system is expected[21] to have an IR absorption at 1640 cm^{-1}, a UV absorption for this system can be calculated[22] to be at 267 nm (with $\epsilon > 10\,000$), and the ^{13}C NMR resonance for the β-carbon atom of this type of α,β-unsaturated ketone is expected to be at ca. 170 ppm (e.g., 1,3-cyclohexanedione methyl ether has this resonance at 173.5 ppm[23]). The other signals in the ^{13}C NMR as well as in the ^1H NMR spectra of **18**, **20**, and **21** are also consistent with the proposed structures. For instance, in the ^1H NMR spectra the vinylic proton of compounds **20** and **21**, coupling with a methyl group, is present at δ 5.7. Furthermore, the characteristic proton α to the oxygen of the enol ether function in **18**, **20**, and **21** (one of the vinylic



protons in the former 5-methylfuryl group) is present at δ 4.5–5.0 as the lower field portion of an AMX system (Figure 1).

Conclusions

The purported synthesis of fenestranes of the type **6** and **17** could not be achieved via the route described in this paper. However, the acid-catalyzed rearrangement of the spirane **7**, giving rise to a new type of tetracyclic compound, is intricate and unprecedented. The scope of this rearrangement has only been casually explored up to now. Before the structures of **18**, **20**, and **21** became known, insight into the mechanism of the rearrangement was sought by chemical means. To that end the spiranes **27**[24] and **28** were prepared via sodium borohydride reduction



of the tosylhydrazones of the triketones **29** and **30**.[8] However, **27** and **28** did not give any rearrangement upon treatment with boron trifluoride in ether. Since we did not aim to investigate the scope of the rearrangement, other conditions were not tried.

Experimental Section

General Methods. Melting points (uncorrected) were determined on a Mettler FP apparatus. Infrared spectra were recorded on a Unicam SP200 infrared spectrophotometer. Ultraviolet spectra were measured on a Beckman DB-G spectrophotometer. ^1H NMR spectra were recorded on an Hitachi Perkin-Elmer R-24B spectrometer. A Varian XL-100 instrument was used for the ^{13}C NMR and 100-MHz ^1H NMR spectra. Tetramethylsilane (Me_4Si) was used as an internal standard in the ^1H NMR spectra, and chemical shifts are denoted in parts per million relative to Me_4Si (δ 0). Chloroform-*d* ($CDCl_3$) was used as an internal standard in the ^{13}C NMR spectra, and chemical shifts are denoted in parts per million relative to $CDCl_3$ (δ 77.0). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Microanalyses were performed in the analytical section of our department. Mass spectra were obtained on an AEI MS-902 instrument by Mr. A. Kiewiet.

7,11-Bis(5-methylfur-2-yl)-3,3-dimethylspiro[5.5]undecane-1,5,9-trione (10). A mixture of dienone **9** (5.7 g, 23.6 mmol), dimedone (3.65 g, 26.1 mmol), sodium hydroxide (0.07 g), and 96% ethanol (35 mL) was heated under reflux for 5 h. The reaction mixture was left at room temperature for 3 days, and then crystals were sucked off and washed with ethanol to give 4.3 g of slightly yellow spirane **10**. From the filtrate there could be obtained another 1.87 g of product after partial evaporation. The product (6.17 g, 16.2 mmol, 69%) is pure enough for further reactions. It was purified by recrystallization from ethanol to give a colorless product: mp 161–163 °C; ^1H NMR ($CDCl_3$, 100 MHz) δ 0.50 (s, 6 H), 2.06 (s, 2 H), 2.13 (s, 2 H), 2.21 (s, 6 H), 2.40–2.60 (dd, 2 H), 3.25–3.70 (dd, 2 H), 3.70–3.90 (dd, 2 H), 5.80–5.95 (m, 4 H); the signals centered around δ 2.50 (dd) showed broadening due to mutual coupling of the equatorial protons at positions 8 and 10 in **10**; UV (c 0.106 mg/mL, dioxane) λ_{max} 249 nm (ϵ 4200); IR (KBr) 3100 (C=CH), 1680 (C=O), 1020, 940, and 800 cm^{-1} (furan). Anal. Calcd for $C_{23}H_{26}O_5$: C, 72.23; H, 6.85. Found: C, 72.53, 72.33; H, 6.96, 6.82.

Thioacetal of the Spiro[5.5]undecane-1,5,9-trione 10 (12). A 3.0-g sample of spirane **10** (7.9 mmol) was stirred for 1.5 h at room temperature with glacial acetic acid (30 mL), 1,2-ethanedithiol (3 mL), and boron trifluoride etherate (3 mL). After the mixture cooled, the product was filtered off, washed with ethanol, and dried. This gave 2.81 g of colorless **12** (6.1 mmol, 78%). It was purified by recrystallization from ethanol and some chloroform: mp 200–201 °C; ^1H NMR (CCl_4) δ 0.4 (s, 6 H), 1.6 (s, 2 H), 1.8–2.15 (m, 10 H), 2.6–3.3 (dd, 2 H), 3.1 (s, 4 H), 3.3–3.55 (dd, 2 H), 5.4–5.6 (m, 4 H); IR (KBr) 3100 (C=CH), 1680 (C=O), 1020, 950, and 790 cm^{-1} (furan). Anal. Calcd for $C_{25}H_{30}O_4S_2$: C, 65.47; H, 6.59; S, 13.98. Found: C, 65.22, 65.48; H, 6.86, 6.75; S, 13.63, 13.64.

***p*-Toluenesulfonylhydrazone of the Spiro[5.5]undecane 10 (13).** A mixture of spirane **10** (2.02 g, 5.29 mmol), tosylhydrazide (1.08 g, 5.81 mmol), and ethanol (10 mL) was heated under gentle reflux for 0.75 h. After the reddish mixture cooled, the tosylhydrazone precipitated, and it was filtered off and washed with ethanol until colorless to give 2.55 g (4.64 mmol, 88%) of product. The product was recrystallized from ethanol and some acetone: mp 179–180 °C; ^1H NMR ($CDCl_3$) δ 0.35 (s, 3 H), 0.5 (s, 3 H), 1.8–3.5 (m, 13 H), 5.4–5.7 (m, 4 H), 6.8–7.7 (m, 5 H); IR (KBr) 3300 (NH), 1710 and 1690 (C=O), 1020 and 800 cm^{-1} (furan). Anal. Calcd for $C_{30}H_{34}N_2O_6S$: C, 65.43; H, 6.22; N, 5.09; S, 5.82. Found: C, 65.14, 65.11; H, 6.27, 6.20; N, 5.14, 5.14; S, 5.57, 5.48.

7,11-Bis(5-methylfur-2-yl)-3,3-dimethylspiro[5.5]undecane-1,5-dione (7). (i) From Thioacetal 12. Raney nickel catalyst W-5[25] was prepared from sodium hydroxide (80 g), nickel–aluminum alloy (63 g), and water (300 mL). After the washings with water it was washed with absolute ethanol (2 × 250 mL) and with dioxane (250 mL). It was then heated under reflux for 6 h with thioacetal **12** (3.03 g, 6.61 mmol) and dioxane (300 mL). After the mixture was filtered while hot, the catalyst was washed with hot dioxane (2 × 150 mL). The combined filtrates were evaporated, and the residue was recrystallized from ethanol to give 1.15 g (3.13 mmol, 47%) of **7** (contaminated with some starting material).

(ii) From Tosylhydrazone 13. A 4.42-g sample of **13** (8.04 mmol) was heated under reflux for 6 h with sodium borohydride (8.7 g) and methanol (70 mL). Water (50 mL) was added to the reaction mixture, the liquid was evaporated to ca. 50 mL, another portion of water (50 mL) was added, and this aqueous solution was extracted with benzene (3 × 75 mL). The benzene fractions

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were combined and washed with saturated sodium bicarbonate solution (2 × 50 mL) and with water (2 × 50 mL). Drying and evaporation of the organic layer gave the crude product which was recrystallized from ethanol to afford 2.21 g of slightly yellow **7** (6.01 mmol, 75%). The product was obtained colorless by elution with benzene over a short acidic alumina column (activity I, ca. 25 g): mp 189.0–189.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.40 (s, 6 H), 1.5–2.6 (m) and 2.2 (s) (16 H), 3.1–3.4 (dd, 2 H), 5.65–5.85 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 212.3 (s), 209.8 (s), 153.0 (s), 149.8 (s), 107.8 (d), 105.9 (d), 67.6 (s), 54.1 (t), 52.7 (t), 43.9 (q), 28.8 (d), 28.2 (s), 25.5 (t), 24.9 (t), 13.0 (q); UV (*c* 0.129 mg/mL, dioxane) λ_{max} 249 nm (ε 2800); IR (KBr) 3100 (C=CH), 1700 and 1680 (C=O), 1020, 950, and 800 cm^{-1} (furan); mass spectrum, *m/e* 368. Anal. Calcd for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 75.13, 75.21; H, 7.63, 7.61.

7,11-Bis(5-methylfur-2-yl)spiro[5.5]undecane-1,5-dione (4). (i) Tosylhydrazone of 19. A 7.11-g sample of *trans*-**19** (20.1 mmol) was dissolved in hot ethanol (ca. 50 mL), tosylhydrazide (4.8 g, 25.8 mmol) was added, and the mixture was heated under gentle reflux for 0.25 h. The reddish solution gave, after cooling and scratching, 8.66 g of the tosylhydrazone, which was obtained colorless after washing with ethanol and which had a melting point of 197–199 °C. From the filtrate there could be obtained another 0.48 g of the tosylhydrazone for a total yield of 9.14 g (17.5 mmol, 87%).

(ii) Reduction of the Tosylhydrazone. To a solution of the tosylhydrazone (8.60 g, 16.5 mmol) in chloroform there was added under a nitrogen atmosphere and at 0 °C catecholborane (3.5 mL). The mixture was stirred at room temperature for 2 h, sodium acetate trihydrate (9.0 g) was added, and the mixture was heated under reflux for 2 h. After being allowed to stand overnight, the reaction mixture was washed with water (25 mL), saturated sodium bicarbonate solution (25 mL), and water (25 mL). Drying and evaporation of the organic layer gave a dark residue which was chromatographed on an acidic alumina column. Elution with benzene gave 2.24 g of colorless **4** (6.6 mmol, 40%). It was purified by recrystallization from ethanol; mp 116.7–116.9 °C.

In this reduction of the tosylhydrazone of **19** the other method (sodium borohydride in methanol) which might give better yields was not performed (reduction of **13** with catecholborane gave lower yields than reduction of **13** with sodium borohydride in methanol): ^{1}H NMR ($CDCl_3$) δ 1.0–2.5 (m) and 2.2 (s) (18 H), 3.2–3.5 (dd, 2 H), 5.8 (s, 4 H). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.04, 74.00; H, 6.97, 6.92.

2,6-Bis(5-methylfur-2-yl)spiro[cyclohexane-1,2′-indan]-1′,3′-dione (8). (A) Cis Isomer. (i) Tosylhydrazone of *cis*-11. A mixture of *cis*-**11** (3.0 g, 7.73 mmol), tosylhydrazide (1.67 g, 8.98 mmol), and ethanol (40 mL) was heated under gentle reflux for 0.75 h. During this heating period the tosylhydrazone had already begun to precipitate. It was filtered off after cooling of the mixture and washed with ethanol to give the colorless product (4.23 g, 7.61 mmol, 98%).

(ii) Reduction of the Tosylhydrazone. *cis*-**14** was reduced as described above in the synthesis of **4** by using 14.74 g of the tosylhydrazone. After the chloroform layer was dried and evaporated, a residue was obtained which was recrystallized from ethanol to give 4.76 g of *cis*-**8**. The filtrate was evaporated and chromatographed on an acidic alumina column (ca. 50 g, activity I) with benzene as eluent. The eluate was evaporated, and the residue was recrystallized from ethanol to give 1.97 g of the product. The total yield was 6.73 g of *cis*-**8** (18.0 mmol, 68%): mp 134.5–134.8 °C; mass spectrum, *m/e* 374; ^{1}H NMR ($CDCl_3$) δ 1.8–2.85 (m) and 1.8 (s) (12 H), 3.2–3.5 (dd, 2 H), 5.45 (br d, 2 H), 5.7 (d, 2 H), 7.4–7.9 (m, 4 H). Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.85, 76.63; H, 5.96, 5.91.

(B) Trans Isomer. (i) Tosylhydrazone of *trans*-11. A mixture of *trans*-**11** (7.15 g, 18.4 mmol), tosylhydrazide (4.1 g, 22.0 mmol), and 75 mL of ethanol was heated at about 60 °C for 0.5 h. The slightly red solution was cooled overnight at 0 °C to afford 3.90 g of *cis*-**14** (7.0 mmol, 38%) as was deduced from the fact that its reduction with catecholborane gave rise to *cis*-**8**. The filtrate was partly evaporated and cooled again at 0 °C. This gave 5.78 g (10.4 mmol, 56%) of *trans*-**14**.

(ii) Reduction of the Tosylhydrazone. A 5.78-g sample of *trans*-**14** (10.4 mmol) in chloroform (75 mL) was treated at 0 °C with 2.8 mL of catecholborane. After the mixture was stirred for 5 h at room temperature, 6.5 g of sodium acetate trihydrate was added. The reaction mixture was stirred overnight at room temperature and then heated under reflux for 1.5 h. Workup as described above gave a product which was purified by column chromatography and then recrystallized from ethanol to afford 1.85 g of *trans*-**8** (4.9 mmol, 48%). It contained some *cis*-**8** (ca. 10%) as was deduced from the ^{1}H NMR spectrum: mp 96.0–96.2 °C; mass spectrum, *m/e* 374; ^{1}H NMR ($CDCl_3$) δ 1.7–2.6 (m) and 2.0 (s) (12 H), 3.2–3.8 (m, 2 H), 5.6 (br d, 2 H), 5.75 (d, 2 H), 7.4–8.0 (AA′BB′, 4 H). Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.69, 76.91; H, 5.90, 6.08.

2,6-Bis(1,4-dioxopentyl)spiro[cyclohexane-1,2′-indan]-1′,3′-dione (15) and 6-(1,4-dioxopentyl)-2-(5-methylfur-2-yl)spiro[cyclohexane-1,2′-indan]-1′,3′-dione (16). *cis*-**8** (7.28 g, 19.5 mmol) was heated under reflux for 3 h with ethanol (200 mL) and concentrated hydrochloric acid (200 mL). The yellow solution was evaporated to about 200 mL and then extracted with benzene (2 × 200 mL). The benzene extracts were washed with saturated sodium bicarbonate solution (2 × 75 mL) and with water (75 mL), dried, and evaporated. The residue was recrystallized from ethanol to give 4.85 g of **15**. The filtrate from this crystallization was evaporated, dissolved in a small volume of benzene, and then chromatographed on a silica column (BDH, 60–120 mesh, ca. 75 g) with ether as the eluent. This gave 1.28 g of **16** (3.3 mmol, 17%) which was recrystallized from ethanol (mass spectrum, *m/e* 392). Further elution with ether/methanol (ca. 10:1) gave a yellow oil which, after recrystallization from ethanol, gave 0.52 g of **15**. The total yield of **15** was 5.37 g (13.1 mmol, 67%): mass spectrum, *m/e* 410; ^{1}H NMR of **15** ($CDCl_3$) δ 1.9–3.3 (m) and 2.0 (s) (22 H), 7.6–8.0 (m, 4 H); ^{1}H NMR of **16** ($CDCl_3$) δ 1.6–3.9 (m), 1.7 (s) and 2.0 (s) (18 H), 5.3 (br d, 1 H), 5.6 (d, 1 H), 7.4–7.9 (m, 4 H); ^{13}C NMR of **15** ($CDCl_3$) δ 208.1 (s), 205.7 (s), 202.6 (s), 200.2 (s), 143.9 (s), 140.4 (s), 134.9 (d), 133.2 (d), 121.8 (d), 121.5 (d), 57.2 (d), 52.7 (s), 36.1 (t), 34.2 (t), 29.0 (q), 25.0 (t), 24.1 (t); IR of **15** (CH_2Cl_2) 1720 (C=O), 1610 cm^{-1}; mp (for **15**) 126.9–127.3 °C; mp (for **16**) 138.5–140 °C. Anal. Calcd for $C_{24}H_{26}O_6$ (**15**): C, 70.23; H, 6.38. Found: C, 69.87, 69.95; H, 6.32, 6.39. Anal. Calcd for $C_{24}H_{24}O_5$ (**16**): C, 73.45; H, 6.16. Found: C, 73.49, 73.33; H, 6.23, 6.20.

Rearrangement and Hydrolysis of 7 with Hydrochloric Acid. Synthesis of 18. Spirane **7** (1.5 g, 4.08 mmol) was heated under reflux for 1.5 h with methanol (30 mL) and concentrated hydrochloric acid (15 mL). The reaction mixture was cooled and extracted with benzene (4 × 40 mL). The combined benzene extracts were washed with water (2 × 50 mL), dried, and evaporated. The residual brown oil was crystallized from a mixture of ethanol and petroleum ether (bp 60–80 °C) to afford 0.56 g of the feathery compound **18** (1.45 mmol, 36%). After recrystallization from the same solvent mixture, **18** had a melting point of 157.5–158.5 °C. The analytically pure material was obtained after sublimation [160–165 °C (0.02 mm)]: mp 183.5–185 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 1.0–3.15 (m), 1.0 (s), 1.05 (s), 1.3 (s), and 2.15 (s) (28 H), 3.25 (dd, 1 H), 4.5 (dd, *J* = 1.5 and 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 206.2 (s), 205.2 (s), 196.0 (s), 166.2 (s), 111.6 (s), 84.6 (s), 82.9 (s), 77.8 (d), 56.4 (d), 56.1 (d), 50.1 (t), 43.7 (t), 42.1 (t), 38.0 (t), 32.6 (d), 32.0, 30.7, 30.0 (q), 28.2, 27.4, 24.3 (q), 23.6 (t), 22.5 (t) (due to overlapping only a part of the signals could be assigned); IR (CH_2Cl_2) 1700 (C=O), 1620 cm^{-1} (O—C=C—C=O); UV (*c* 0.031 mg/mL, methanol) λ_{max} nm 266 (ε 14000); mass spectrum (exact mass), M^+ peak calculated at *m/e* 386.209, found 386.209. Anal. Calcd for $C_{23}H_{30}O_5$: C, 71.48; H, 7.82. Found: C, 71.36, 71.31; H, 7.84, 7.79.

Rearrangement of 7 with Boron Trifluoride. Synthesis of 20, 21, and 22. Spirane **7** (4.0 g, 10.87 mmol) was stirred for 4 h with ether (12 mL), dichloromethane (7 mL), and boron trifluoride etherate (16 mL). The reaction mixture was poured into water, and the products were extracted with benzene. The benzene layer was washed with a saturated sodium bicarbonate solution and with water, dried, and evaporated. The ^{1}H NMR spectrum of the crude product showed a **20/21/22** ratio of ca. 1:3:3. This crude product was chromatographed on an alumina column (acidic, deactivated by standing in open air, 200 g) by elution with benzene–ether mixtures, with increasing amounts of ether. The starting material was eluted first, **20** (contaminated with some **21**) second (390 mg, 1.06 mmol, 10%), a mixture of **20** and **21** (640 mg, 1.74 mmol, 16%, ratio of ca. 1:2) third, **21** (820 mg, 2.23 mmol, 20%) fourth, and finally **22** (910 mg, 2.47 mmol, 23%).

Compound **20** could not be obtained in a pure state. Compound **21** crystallized very well from ethanol. Compound **22** was obtained as a colorless solid by adding ether to the product obtained via column chromatography (giving the product with a melting point of 188–190 °C). Recrystallization of this solid was unsuccessful, however, and analytically pure material was obtained by sublimation at ca. 185 °C (0.04 mm), giving the product with a melting point of 197–200 °C. The data for the compounds are as follows: ^{1}H NMR of **20** (impure product, $CDCl_3$) δ 0.6–3.2 (m), 0.95 (s), 1.05 (s), 1.2 (s), 1.45 (s), and 2.15 (s) (26 H), 4.55 (dd, J = 5 and 7 Hz, 1 H), 5.7 (br s, 1 H); ^{1}H NMR of **21** (100 MHz, $CDCl_3$) δ 0.95–2.45 (m), 1.0 (s), 1.1 (s), 1.45 (s), and 2.2 (s) (23 H), 2.6–2.85 (dd, 1 H), 2.9–3.2 (2 t, 2 H), 4.95 (dd, J = 5 and 8 Hz, 1 H), 5.7 (q, J = 1 Hz, 1 H); ^{1}H NMR of **22** (100 MHz, C_6D_6) δ 0.7–2.3 (m), 0.9 (s), and 2.05 (s) (23 H), 2.9–3.1 (br dd, 1 H), 3.15–3.35 (br dd, 1 H), 5.0 (br, J = 2.2 and 5 Hz, 1 H), 5.45 (br, J = 1.4 and 5 Hz, 1 H), 5.75 (q, J = 1 Hz, 1 H); ^{13}C NMR of **20** ($CDCl_3$, obtained by subtraction of the spectrum of **21** from the spectrum of **20** plus **21**) δ 196.6 (s), 166.0 (s), 147.4 (s), 128.1 (d), 126.5 (s), 111.4 (s), 101.6 (d), 83.8 (d), 82.4 (s), 77.2 (s), 54.2, 50.6, 42.6, 40.9, 31.7, 29.5, 23.8, 21.8, 20.2; ^{13}C NMR of **21** ($CDCl_3$) δ 196.0 (s), 167.8 (s), 150.6 (s), 146.3 (s), 124.7 (s), 117.4 (s), 102.0 (d), 85.5 (s), 82.0 (d), 77.9 (s), 53.9 (t), 50.4 (t), 45.9, 43.0, 32.5, 32.3 (d), 29.3 (t), 26.8 (t), 24.2 (t), 21.5 (q), 13.4 (q); ^{13}C NMR of **22** ($CDCl_3$) δ 196.8 (s), 167.4 (s), 150.6 (s), 150.4 (s), 127.2 (s), 120.4 (d), 117.9 (s), 112.2 (s), 105.3 (d), 75.7 (d), 65.5 (s), 50.5 (t), 48.4 (d), 41.9 (t), 38.2 (d), 32.3 (t), 32.1, 28.4, 28.0, 24.8, 23.7, 13.1 (q); IR of **21** (CH_2Cl_2) 1650 cm^{-1} (O—C=C—C=O); IR of **22** ($CHCl_3$) 1640 (O—C=C—C=O), 930 cm^{-1} (furan); mass spectrum of **21** and **22**, m/e 368; UV of **21** (c 0.018 mg/mL, methanol) λ_{max} nm 267 (ϵ 11 000); UV of **22** (c 0.011 mg/mL, methanol) λ_{max} nm 268 (ϵ 21 000); mp (**21**) 221–224 °C. Anal. Calcd for $C_{23}H_{28}O_4$ (**21**): C, 74.97; H, 7.66. Found: C, 74.63, 74.85; H, 7.63, 7.60. Anal. Calcd for $C_{23}H_{28}O_4$ (**22**): C, 74.97; H, 7.66. Found: C, 74.77, 74.77; H, 7.63, 7.61.

7,11-Diphenylspiro[5.5]undecane-1,5-dione (27). From *cis*-**29** (9.5 g, 27.5 mmol) and tosylhydrazide (6.0 g, 32.3 mmol) in 80 mL of ethanol was easily obtained the tosylhydrazone (13.86 g, 27.0 mmol, 98%) by heating for 0.5 h under reflux and then cooling the mixture. The colorless tosylhydrazone is reduced with 30 g of sodium borohydride in 400 mL of methanol as described for the synthesis of **7** to afford after crystallization of the crude product from ethanol 3.16 g of the desired spirane **27**: 9.5 mmol (35%); ^{1}H NMR ($CDCl_3$) δ 0.25–0.8 (m, 2 H), 1.4–3.0 (m, 10 H), 3.1–3.5 (dd, 2 H), 6.8–7.3 (m, 10 H).

7,11-Bis(2-furyl)-3,3-dimethylspiro[5.5]undecane-1,5,9-trione (30). A 21.4-g sample of difurfurylideneacetone (100 mmol), obtained in the same way as dienone **9**, was heated under reflux for 2.5 h with dimedone (14.2 g, 101 mmol) and sodium hydroxide (0.44 g) in ethanol (150 mL). After the mixture was cooled for a few hours at 0 °C, there was obtained 13.47 g of the spirane **30**. From the filtrate there could be obtained another 6.03 g of product after cooling for 2 days at 0 °C. The spirane **30** was washed with ethanol until slightly yellow: total yield 19.50 g (55.1 mmol, 55%); ^{1}H NMR ($CDCl_3$) δ 0.5 (s, 6 H), 2.0 (s, 2 H), 2.05 (s, 2 H), 2.3–2.7 (dd, 2 H), 3.2–3.85 (dd, 2 H), 3.7–4.1 (dd, 2 H), 5.95–6.1 (d, 2 H), 6.15–6.3 (m, 2 H), 7.25 (br s, 2 H).

7,11-Bis(2-furyl)-3,3-dimethylspiro[5.5]undecane-1,5-dione (28). A 24.82-g sample of spirane **30** (70.1 mmol) was heated under gentle reflux for 0.5 h with tosylhydrazide (14.0 g, 75.3 mmol) in ethanol (400 mL). The reddish reaction mixture was evaporated, and ethanol (100 mL) was added to the oily residue. The tosylhydrazone precipitated on scratching and cooling of the mixture. It was filtered off and washed with ethanol until almost colorless. The yield was 27.41 g (52.5 mmol, 75%). The tosylhydrazone was then reduced to the spirane **28** in the same way as described for the synthesis of **7** with 49 g of sodium borohydride in 550 mL of methanol. The crude product, obtained after workup, was chromatographed on an acidic alumina column (activity I, ca. 100 g) with benzene as the eluent. After recrystallization from ethanol there was obtained a total amount of 7.5 g of **28** (22.3 mmol, 43%): mp 176.5–177.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.4 (s, 6 H), 1.3–2.8 (m), 1.75 (s), and 2.1 (s) (10 H), 3.2–3.6 (dd, 2 H), 5.85–5.95 (d, 2 H), 6.05–6.2 (m, 2 H), 7.05–7.2 (m, 2 H). Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 73.87, 73.98; H, 6.95, 6.92.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON).

Registry No. *trans*-**4**, 73611-51-5; *cis*-**7**, 73611-52-6; *cis*-**8**, 73611-53-7; *trans*-**8**, 73611-54-8; **9**, 69239-15-2; *cis*-**10**, 73611-55-9; *cis*-**11**, 69239-06-1; *trans*-**11**, 73611-56-0; *cis*-**12**, 73611-57-1; *cis*-**13**, 73611-58-2; *cis*-**14**, 73611-59-3; *trans*-**14**, 73611-60-6; **15**, 73611-61-7; **16**, 73611-62-8; **18**, 73622-49-8; *trans*-**19**, 73611-63-9; *trans*-**19** tosylhydrazone, 73611-64-0; **21**, 73611-65-1; *cis*-**27**, 73611-66-2; **28**, 73611-67-3; **30** tolsylhydrazone, 73611-68-4; *cis*-**29**, 69239-09-04; *cis*-**29** tosylhydrazone, 73611-69-5; **30**, 856-81-5; dimedone, 126-81-8; 1,2-ethanedithiol, 540-63-6; difurfurylideneacetone, 886-77-1; 1,3-indandione, 606-23-5.

Synthetic Approaches to Planar Carbon. 2

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Received February 11, 1980

Access to planar carbon compounds has been investigated via tricyclic compounds such as **9**, **10**, **19**, and **20**. These tricycles could be obtained via acid-catalyzed dehydration of the ketones **11**, **17**, and **24**. Compound **10** could also be obtained by treatment of the iminium salt **28A** with acid. Ketone **24** and iminium salt **28A** were prepared by starting from the morpholine enamine of 2-indanone (**25A**) via two sequential alkylations with benzyl bromide. Several derivatives of **10** were prepared, none of them serving as a precursor to the olefin **29**. Surprisingly, treatment of the dibromide **31** with aluminium chloride in benzene gave rise to the olefin **40**.

The concept of the tetrahedral tetracoordinate carbon atom has been familiar to chemists for more than a century. In recent decades this concept has undergone modifications by the successful synthesis of a large number of strained compounds.[1] These compounds were previously thought to be incapable of existence because of the distortion of the tetrahedral geometry around certain carbon atoms. Among distorted geometries, planar carbon (e.g., planar methane, **1**) must be classified as a highlight.[2] Not unexpectedly, planar carbon compounds have not yet been synthesized, and these compounds have existed up to now mainly as targets of theoretical interest. During the past 10 years, calculations have been performed on a large variety of compounds in order to estimate the energy

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0022-3263/80/1945-2930$01.00/0