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

Wolter Ten Hoeve and Hans Wynberg*

Department of Organic Chemistry, The University, Nijenborgh 16, 9747 AG Groningen, The Netherlands

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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**.

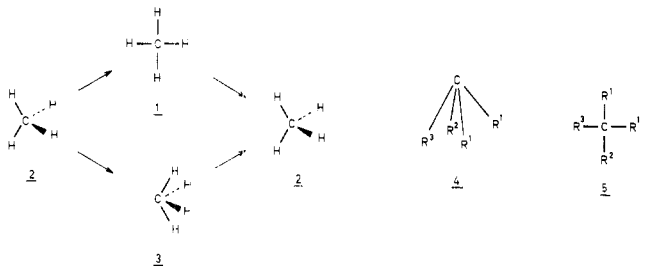
The concept of the tetrahedral tetracoordinate carbon atom has been familiar to chemists for more than a century. In recent decades this concept has undergone modifications by the successful synthesis of a large number of strained compounds.[1] These compounds were previously thought to be incapable 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

(1) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311.

(2) Hoffmann, R. *Pure Appl. Chem.* **1971**, *28*, 181.

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

Scheme I

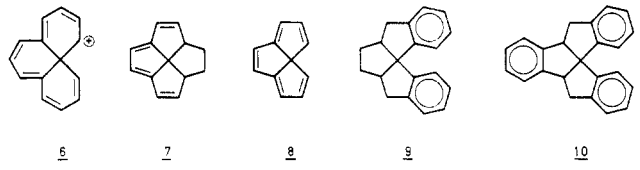


difference between a tetrahedral and the corresponding planar structure. In the case of methane, this energy difference has been calculated to be ca. 100–250 kcal/mol.[3] Since a C–H bond has an energy content of 104 kcal/mol, planar methane, **1**, might not easily be isolated as a stable entity, bond breaking probably occurring during automerization (degenerate enantiomerization) of tetrahedral methane, **2** (Scheme I). Although such bond breaking may lead to automerization via radical coupling, this automerization might never involve any planar methane. Another possibility for automerization of methane proceeds along pyramidal methane, **3**.

Pyramidal methane has been calculated to be ca. 10 kcal/mol more stable than planar methane; however, in several other compounds the energy difference between the pyramidal and planar structures appeared to be negligible.[4] A feature of a pyramidal carbon compound is that three different substituents (with the two identical substituents lying side by side) are a sufficient criterion for chirality; i.e., structure **4** is chiral. This new type of chirality[5] would be an elegant test for a pyramidal structure, and it makes possible, in principle, an easy distinction between planar and pyramidal structures (the planar structure **5** is achiral).

In selected compounds the energy difference between the tetrahedral and planar structure (or the equally interesting pyramidal structure) is much smaller, and in these compounds the planar structure might be as stable as the tetrahedral structure (e.g., in 3,3-dilithiocyclopropene),[6] or the planar structure might be a thermally accessible transition state or intermediate (as can be evident from a racemization experiment in suitable cases). These compounds can be selected on the ground that a planar carbon atom has an sp^2 hybridization; i.e., only one 2s and two 2p atomic orbitals are used for σ bonding to the four ligands. The remaining nonbonding 2p orbital is perpendicular to the plane of the molecule, and it contains two electrons. Therefore, factors which stabilize a planar arrangement are π-accepting groups (e.g., CN, $2n$-π-electron systems), σ-donating groups (e.g., Li, SiH_3), and the inclusion of the planar carbon atom in the composition of a small ring.[4b,6] Since for a pyramidal carbon atom the same stabilizing factors are operative, one cannot decide beforehand whether a (synthesized) compound will be planar or pyramidal. For the sake of convenience we devote our attention solely to planar carbon compounds.

Although synthetic approaches to planar carbon compounds are still in their infancy, some preliminary work has been concerned with the preparation of the benzo[*d*]naphthalene cation **6**[7] and the unsaturated tetracyclic



compound 7.[8] Both structures are highly attractive from a planar carbon point of view, since the central quaternary carbon atom might have a planar arrangement. In this paper we describe some approaches to derivatives of the unsaturated system **8**. Although **8** is not expected to contain a planar tetracoordinate carbon atom, it may be that the planar structure can exist as an intermediate during racemization of chiral derivatives of **8** (because of the expected small energy difference between tetrahedral chiral **8** and planar achiral **8**). Our approach consists of the preparation of dibenzo-annulated **9** and of tribenzo-annulated **10** as well as the preparation of some derivatives. These compounds may lend themselves to further unsaturation around the central, quaternary carbon atom, thereby finally leading to derivatives of **8**.

Dibenzo-Annulated Tricycles. In theory, the synthesis of compounds derived from **9** can be accomplished via an acid-catalyzed dehydration of the dibenzylcyclopentanone **11** (Scheme II). Such dehydrations, involving two cyclizations, have been reported for the ketone **12** (using phosphorus oxychloride in benzene at 80 °C)[9] and for the 1-indanones **13** (with polyphosphoric acid at 100 °C),[10] leading to the spirane **14** and the triptindans **15** and **16**, respectively. In these cases an activating methoxy group was present, which facilitates the desired cyclization. In the case of 2,2-dibenzyl-1-indanone (**13**) the cyclization which should afford triptindan could not be accomplished. Application of an analogous reaction to the cyclopentanone **17** (which is prepared in two steps from cyclopentanone and *m*-anisaldehyde, via aldol condensation[11] and subsequent hydrogenation of the condensation product **18**), i.e., by heating **17** with phosphorus oxychloride and a catalytic amount of *p*-toluenesulfonic acid in benzene, furnished two isomeric spiranes, namely, the tricycles **19** and **20** (Scheme III). The formation of these two isomers is easily understood in view of the mechanism, which involves protonation of the carbonyl group followed by electrophilic aromatic substitution at ortho and para positions with

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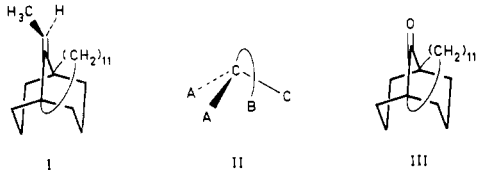
(4) (a) Minkin, V. I.; Minyaev, R. M.; Zacharov, I. I. *J. Chem. Soc., Chem. Commun.* **1977**, 213. (b) Minkin, V. I.; Minyaev, R. M.; Zacharov, I. I.; Avdeev, V. I. *Zh. Org. Khim.* **1978**, *14*, 3. (c) References 895 and 902 in ref 1; see also p 5426 in ref 6.

(5) In an extended form, this type of chirality is also present in the paddlane I, wherein flipping of the polymethylene bridge is not possible. In its basic form this compound can be represented as shown in structure II. Although the ketone III is known (cf.: Mori, T.; Kimoto, K.; Kawanishi, M.; Nozaki, H. *Tetrahedron Lett.* **1969**, 3653), compounds such as the paddlane I have not yet been synthesized. We predict that paddlane I is chiral and propose the name pyramidal chirality for this type of chirality.



I II III

(6) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5419.

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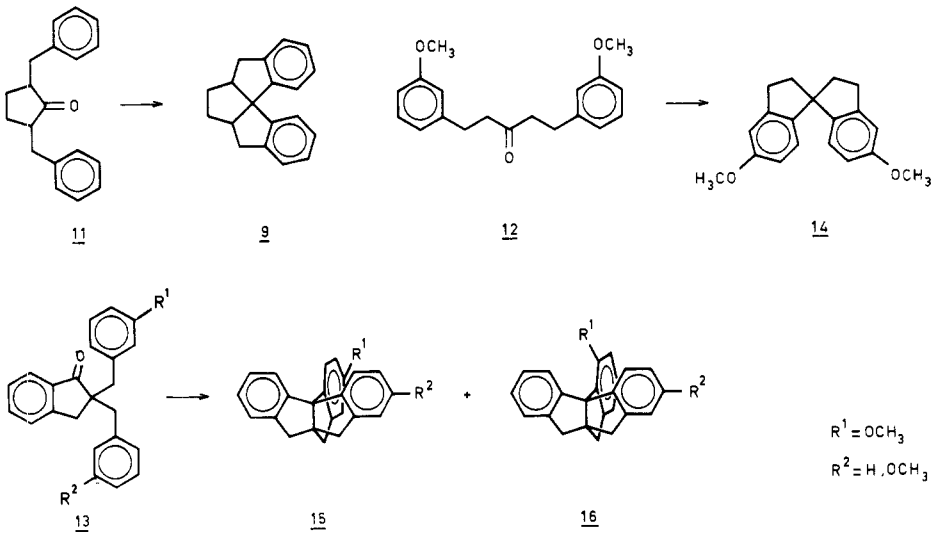
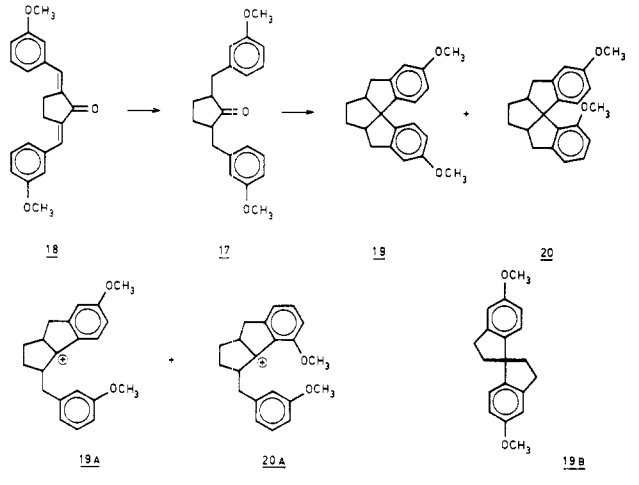
(11) Buu-Hoi, N. P.; Xuong, N. D. *Bull. Soc. Chim. Fr.* **1958**, 758.

Scheme II



11 9 12 14 13 15 16

Scheme III



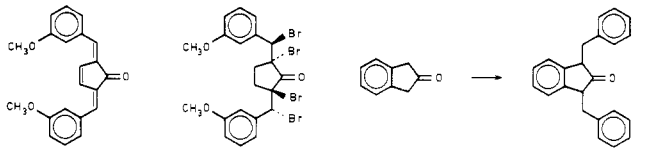
18 17 19 20 19A 20A 19B

respect to the methoxy group. This leads to the cations **19A** and **20A**, **19A** being favored because of less steric hindrance. A second cyclization will lead to **19** (from **19A**) and **20** (from **19A** and **20A**), as a result of para–para and ortho–para (para–ortho) substitution, respectively. The ^{13}C NMR and ^{1}H NMR spectra of the tricycles **19** and **20** (isolated in 54 and 18% yields, respectively) were in accord with the structures in Scheme III. From the projection formula **19B**, wherein the former cyclopentanone ring is perpendicular to the plane of the paper, it can be readily seen that **19** contains a C_2 axis. Hence, one would expect 11 signals in the ^{13}C NMR spectrum of **19**, as are in fact observed. In contrast, **20** lacks such symmetry, and therefore its ^{13}C NMR spectrum is expected to show 21 signals, of which 10 are observed. As expected, the ^{1}H NMR spectrum of **19** shows two coinciding methoxy signals, whereas the ^{1}H NMR spectrum of **20** shows two distinct methoxy signals.

The parent compound, 2,2′-ethylene-1,1′-spirobiindan (**9**) can be obtained analogously, however, under more drastic conditions than were necessary for the cyclization of **17**. Stirring ketone **11**,[12] prepared by hydrogenation of dibenzalcyclopentanone,[13] with polyphosphoric acid at ca. 160 °C for about 15 h effected the desired cyclization, thereby affording **9** in 79% yield.

(12) Borsche, W. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 46.
(13) Cornubert, R.; de Demo, M.; Joly, R.; Louis, P.; Strébel, A. *Bull. Soc. Chim. Fr.* **1938**, *5*, 1490.

Having a suitable synthesis for tricycles **9**, **19**, and **20** in hand, we carried out some experiments to introduce unsaturation in these tricycles via functionalization of the parent cyclopentanones. To that end the cyclopentenone **21** was prepared via allylic bromination–dehydrobromi-



21 22 23 24

nation of **18** with *N*-bromosuccinimide.[14] Attempts to selectively protect one of the double bonds in **21** failed, however. Also an attempt to cyclize the tetrabromo derivative **22** was unsuccessful.[15] Since the starting dienone **18** will have the *E,E* configuration,[16] this unsuccessful cyclization could be anticipated. As bromination will proceed in a trans fashion, the cyclization will be possible only when the tetrabromide adopts the highly unfavorable synperiplanar conformation.

Tribenzo-Annulated Tricycles. Instead of introducing an olefinic double bond in the tricycles **9**, **19**, or **20** (e.g., via the cyclopentenone **21**), this unsaturation might be introduced more conveniently by annulating a benzene ring to the 3,4-position of the cyclopentanones **11** or **17**. The starting compund for the tricycles described in this section will therefore be 2-indanone (**23**).[17] Aldol condensation with benzaldehyde, followed by hydrogenation, should lead to 1,3-dibenzyl-2-indanone (**24**). However, aldol condensation of 2-indanone is successful only with reactive aldehydes.[18] Therefore, access to **24** is not possible in this manner. As alkylation of the homopiperidine enamine of 2-indanone, **25B**, with benzyl bromide was reported recently to give a 57% yield of 1-benzyl-2-indanone,[19] we applied this enamine alkylation to obtain the doubly alkylated 1,3-dibenzyl-2-indanone (**24**). Enamines **25A–C**[20] were prepared in over 90% yield by the

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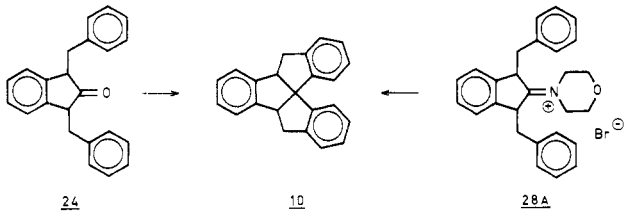
(15) Vorländer, D.; Hobohm, K. *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 1836.
(16) Tanaka, H.; Yamada, K.; Kawazura, H. *J. Chem. Soc., Perkin Trans. 2* **1978**, 231.
(17) Horan, J. E.; Schiessler, R. W. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. 5, p 647.
(18) Harmon, R. E.; Subbarao, H.-A. N.; Gupta, S. K.; Slomp, G. *J. Org. Chem.* **1973**, *38*, 1395. Friedländer, P.; Herzog, W.; Voss, G. v. *Ber. Dtsch. Chem. Ges.* 1922, 55, 1591.
(19) Jensen, B. L.; Michaud, D. P. *Synthesis* **1977**, 848.

reaction of 2-indanone with morpholine, homopiperidine, and pyrrolidine, respectively. Alkylation of **25A** with benzyl bromide was performed by heating in acetonitrile (Scheme IV). During this heating period a precipitate had formed which proved to be the iminium salt **28A** (12% yield), arising by dialkylation of the starting enamine. This dialkylation, a common side reaction in enamine alkylations,[21] can occur because the iminium salt **26A** can be dehydrobrominated by the starting enamine **25A** to give the enamine **27A** which is subsequently alkylated to afford **28A**. Since only the dialkylated salt precipitates, this dialkylation is very advantageous. The iminium salt **26A** which was also present in the reaction mixture, could be obtained pure afterward (72% yield). The salt **26A** was converted to the enamine **27A** by stirring a suspension of **26A** in benzene for 1 h with a slight excess of triethylamine. During this period triethylammonium hydrobromide precipitates, and the enamine **27** goes into solution (obtained in 81% yield after evaporation and filtration). This procedure for the iminium salt (enamine conversion) is far preferable over the usual methods (such as treatment with a solution of potassium hydroxide)[22] since it avoids hydrolytic conditions and because of its simplicity. Alkylation of the enamine **27A** proceeded readily to give the dialkylated iminium salt **28A** in 64% yield. The ketone **24** could be obtained by hydrolysis of the latter salt, but it could not be obtained pure (rapid discoloration). This conversion of **28A** to ketone **24** was, however, superfluous as will be described below. The related iminium salts, **26B** and **26C** could be obtained in an entirely analogous way, in 75 and 84% yields, respectively, by starting from the enamines **25B** and **25C** (no evidence was present that the dialkylated salts **28** had been formed). Subsequent dehydrobromination gave the enamines **27B** and **27C**, the alkylation of these with benzyl bromide afforded the dialkylated salts **28B** and **28C**, and hydrolysis of the salt **28B** gave the ketone **24**.

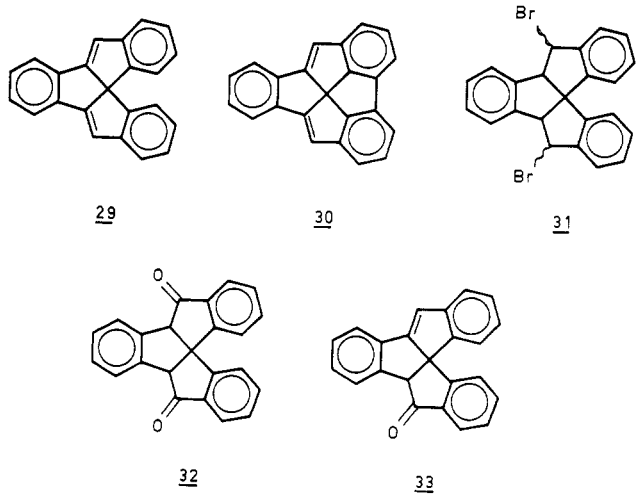
An attempt was made to prepare the dibenzyl ketone **24** directly via twofold alkylation of the starting morpholine enamine **24A** in the presence of the Hünig base *N,N*-diisopropylethylamine. After hydrolysis, the crude product contained the desired ketone **24**, which could not be obtained as a single product, however. The final cyclization of 1,3-dibenzyl-2-indanone (**24**) to 2,2′-*o*-phenylene-1,1′-spirobiindan (**10**) proceeded in the desired manner. Ini-



24 10 28A

tially, **24** was treated with polyphosphoric acid at 170 °C to give the expected doubly cyclized product **10**, the C_2 symmetry of which was confirmed by ^{13}C NMR spectroscopy. It was found, however, that **10** could be obtained in a more convenient way, namely, by heating the morpholine iminium salt **28A** with polyphosphoric acid at 170 °C. The product **10** was obtained as an oil (66% yield), crystallizable from hexane or ethanol/ethyl acetate. Rather surprising was the behavior of the iminium salts **28B** and **28C**: after the compounds were heated with polyphosphoric acid and after workup and evaporation of the organic layer, there was virtually no residue. This probably means that no cyclization has occurred in these instances. An explanation for this failure seems to be the following: since pyrrolidine and homopiperidine are much stronger bases than morpholine[23] (the difference in base strength being about 10^3), they will preferably donate their lone electron pair to an electrophilic center. This indicates that in **28B,C** the contribution of the resonance form $C{=}N^+$ is much more important than that of the $C^+{-}N$ form, whereas in **28A** the $C^+{-}N$ contribution is relatively greater. Since only the $C^+{-}N$ form allows cyclization to occur, this explains the difference in behavior of **28A** and **28B,C**. In the literature we did not find an example wherein an iminium salt was used for cyclization as a substitute for a ketone.[24]

Introduction of an Olefinic Linkage. Tricycle **10** might serve as a good precursor to compound **29** via functionalization of the benzylic positions. In **29** the



29 30 31 32 33

double bonds are stabilized by the presence of aromatic rings, and therefore this compound will have a greater stability than the parent olefin **8**. Furthermore, **29** can serve as a precursor to the even more interesting **30** via coupling of two phenyl groups. Access to **29** was investigated via functionalization of the benzylic positions of **10**. This approach to **29** was explored in two ways. (i) Bromination of **10** with ca. 2 equiv of *N*-bromosuccinimide gave a mixture of dibromides, which can be represented largely by formula **31**, on the basis of its further reactions (see below). Several attempts were made to prepare **29** from the dibromide via elimination with base;[25] however, indefinite products were obtained (e.g., potassium *tert*-butoxide in Me_2SO at 20 °C or DBU in carbon tetrachloride at 80 °C). (ii) Benzylic oxidation of **10** with chromium trioxide in acetic acid[26] furnished the diketone **32** (by ^1H NMR spectroscopy the yield was determined to be 20–30%). The ^1H NMR spectrum of the crude product showed only three signals in the δ 0–7 region, namely, a singlet at δ 4.15, arising from the diketone, and two small

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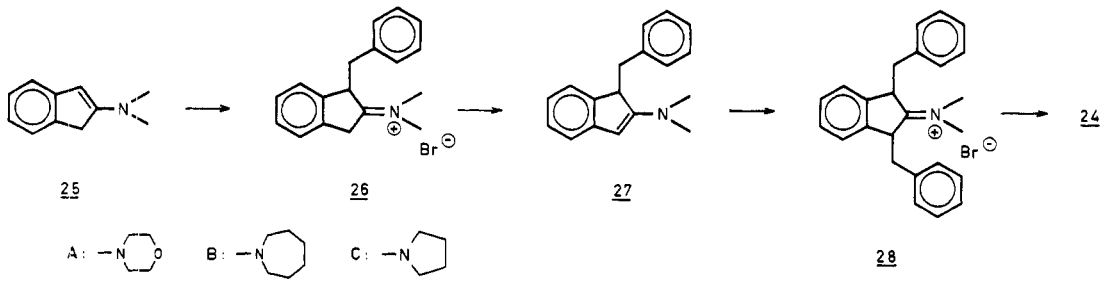
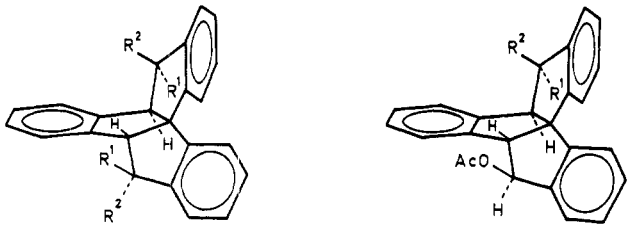
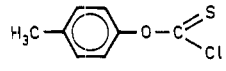
Scheme IV



singlets of equal intensity at δ 4.3 and 6.25. These two singlets possibly arise from the keto olefin **33**; however, no attempt was made to isolate this product. A rather curious feature of the oxidation was that only with dry chromium trioxide did the reaction succeed. Attempts to prepare the bis(tosylhydrazone)[27] or the dihydrazone[28] of the diketone (as precursors to **29**) proved to be unsuccessful.

Secondary routes to **29** were then explored via conversion of the dibromide **31** and the diketone **32** to the diols **34** and **35**, respectivley. Lithium aluminium hydride reduction of the diketone gave the cis–cis diol **34** mixed with some cis–trans and/or trans–trans diol. The configuration of this cis–cis diol was based on the ^{1}H NMR spectrum of the product which showed the expected large coupling constants of 8 Hz for the aliphatic protons. Furthermore, lithium aluminium hydride is expected to attack the ketone from the less hindered side, and this would also give the cis–cis diol (compare the stereoformulas **34–38**). The trans–trans diol **35**, mixed with some cis–trans and/or cis–cis diol, was obtained by solvolysis of the dibromide **31**, using mercuric oxide, water, and perchloric acid in DME.[29] The small coupling constants of 2.5 Hz for the aliphatic protons confirmed its structure. These diols are potentially good precursors to compound **29**, for instance via a twofold dehydration. For this purpose the diols **34** and **35** were treated with a mixture of acetic acid and concentrated sulfuric acid.[30] This gave a mixture of the trans–trans diacetate **36** (major product) and the cis–trans diacetate **37** (minor product). Since from **34** as well as **35** the same mixture of diacetates was produced, this reaction probably proceeds via a carbonium ion. Instead of giving a strained olefin (i.e., E_1 reaction), this carbonium ion combines with acetic acid to give an acetate (i.e, S_N1 reaction). On steric grounds, the formation of the trans–trans diacetate will be favored over formation of the cis–trans diacetate. The ^{1}H NMR spectra of **36** and **37** were in accord with their structures. For instance, **36** shows one acetyl signal and small coupling constants between the aliphatic ring protons, whereas **37** shows two acetyl signals and two sets of aliphatic ring protons with small and large coupling constants, respectively. Furthermore, saponification of the crude mixture of diacetates gave back the diol, which consisted mostly of the trans–trans isomer. The trans–trans diacetate **36** can serve as a precursor to **29**. In **36** two syn eliminations seem possible because the respective hydrogen atom and acetoxy group are synperiplanar to each other.[31] The mass spectra of **36** and **37** showed this feature also: no peak was present at *m/e* 410 (mass of diacetates), but the parent peak was at *m/e* 350 (loss of acetic acid), and a rather intense peak was observed at *m/e* 290 (mass of the bis compound). The drastic conditions needed for acetate pyrolysis made it impossible to isolate a pure product after heating the mixture of diacetates at 450 °C under vacuum. A related attempt to prepare **29** was made via the thiocarbonate route.[32] However, attempted pyrolysis of the product, obtained from the reaction of the thiocarbonyl chloride **38**[33] with the diol **35** (assumed to be a mixture of bisthiocarbonates) gave only nonidentifiable products (200 °C, vacuum). Since it appeared from these experiments that **29** is either too unstable to permit isolation or that it has not been formed at all, ways were sought to stabilize the double bonds in **29**. To that end the diol **35** was treated with an excess of aluminium chloride in benzene. This produced the diphenyl-substituted analogue **39** in 61% yield, the ^{1}H NMR spectrum of which showed that it was either the cis–cis or the trans–trans isomer (a coupling constant of J = 5 Hz was observed for the aliphatic protons). Its ^{13}C NMR spectrum confirmed the C_2 symmetry. A similar Friedel–Crafts alkylation was possible with the easily accessible dibromide **31**. Treatment of **31** with an excess of aluminium chloride in benzene gave rise to a mixture of **39**, a new compound **40**, and diphenylmethane (**40** was present in minor amounts in the Friedel–Crafts reaction of the diol). Treatment of this mixture with aluminum





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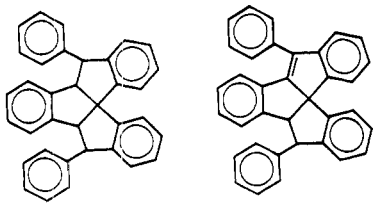

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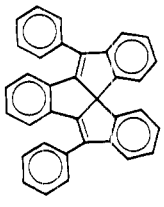

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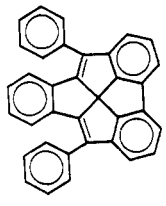

42

chloride in benzene led to disappearance of **39** and an increase of **40** and diphenylmethane. Therefore, **40** must have been formed from **39**, as was also indicated by separate treatment of **39** with aluminium chloride in benzene (leading to a mixture of **40** and diphenylmethane). The formation of **40** appeared to be serendipitous. All data confirm the structure shown below. For instance, **40** has an M^+ peak at m/e 444 (whereas **39** has its M^+ peak at m/e 446), its UV spectrum showed the expected strong absorption above 300 nm, its ^1H NMR spectrum showed two slightly broadened singlets (hence the two aliphatic protons will be almost perpendicular to each other), and its ^{13}C NMR spectrum showed the absence of symmetry in **40** and the presence of only three aliphatic carbon atoms. The surprising feature of the Friedel–Crafts reaction is that dehydrogenation of the diphenyl derivative **39** must have occurred under the reaction conditions.[34] At this moment we are puzzled about the presence of considerable amounts of diphenylmethane in the reactions mentioned above. Diphenylmethane must have formed from the olefin **40**, since separate treatment of **40** with aluminum chloride in benzene gave rise to a mixture of **40** and diphenylmethane.

Molecular models of **40** showed that its olefinic linkage is slightly distorted, whereas introduction of another olefinic linkage produces the highly distorted compound **41**. Nevertheless, the combined stabilizing power of three aromatic rings, as shown by the surprisingly easy synthesis of **40**, may compensate the strain produced by the nonplanarity of the olefinic bonds in **41**. This nonplanarity is caused by the fact that the central carbon atom has a tetrahedral arrangement. Relief of the strain in **41** is most easily accomplished by the coupling of two phenyl rings and by changing the geometry of the central carbon atom from tetrahedral to planar. Thereby, **42** is produced with a planar carbon atom. The synthesis of the latter compounds, **41** and **42**, will be the subject of further research.

Experimental Section

General Methods. Melting points were determined on a Mettler FP apparatus and are uncorrected. Infrared spectra were recorded on a Unicam SP 200 infrared spectrophotometer. Ultraviolet spectra were measured on a Beckman DB-G spectrophotometer. ^1H NMR spectra were recorded on a 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 at (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.

2,5-Bis(*m*-methoxybenzyl)cyclopentanone (17) and 2,5-Dibenzylcyclopentanone (11). A mixture of dianisalcyclopentanone **18** or dibenzalcyclopentanone and ethyl acetate (ca. 10 mL/g of the dienone) was hydrogenated for ca. 20 h in a Parr apparatus at a pressure of 2–3 atm and with palladium on carbon as the catalyst (5% Pd, ca. 1 g of catalyst/15 g of the dienone). The crude product consisted of a mixture of the expected ketone **17** or **11** and the corresponding alcohols. This mixture was oxidized in the usual way with the Jones reagent[35] to give, after distillation, the pure ketones **17** and **11** in about 80% yield: ^1H NMR of **17** (CCl_4) δ 1.1–3.2 (m, 10 H), 3.7 (s, 6 H), 6.5–7.2 (m, 8 H); ^1H NMR of **11** (CCl_4) δ 1.1–3.2 (m, 10 H), 7.0 (s, 10 H); IR of **17** and **11** (neat) 1740 (C=O), 1620 and 1520 cm^{-1} (aryl); bp (**17**) ca. 175 °C (0.07 mm). Anal. Calcd for $C_{21}H_{24}O_3$ (**17**): C, 77.75; H, 7.46. Found: C, 78.01, 78.17; H, 7.68, 7.68.

5,5′-Dimethoxy-2,2′-ethylene-1,1′-spirobiindan (19) and 5,7′-Dimethoxy-2,2′-ethylene-1,1′-spirobiindan (20). A mixture of the ketone **17** (4.39 g, 13.5 mmol), phosphorus oxychloride (24 mL), *p*-toluenesulfonic acid (0.2 g), and benzene (60 mL) was heated under reflux for 22 h. The reaction mixture was poured into ice–water (100 mL), the layers were separated, and the aqueous layer was extracted with two portions of benzene. The combined benzene layers were washed with water, dried, and evaporated. The crude product was chromatographed on a short alumina column (25–50 g, activity I, neutral, carbon tetrachloride as eluent) to give a colorless residue (3.5 g) after evaporation. Recrystallization from hexane gave 0.74 g of the pure isomer **20** (2.4 mmol, 18%). The filtrate on cooling gave 0.82 g of the pure isomer **19**. Kugelrohr distillation of the residue gave another 1.40 g of **19** with a boiling point of 165 °C (0.04 mm). The total amount of **19** obtained was 2.22 g (7.3 mmol, 54%): ^1H NMR of **19** (CCl_4) δ 1.1–3.5 (m, 10 H), 3.7 (s, 6 H), 6.5 (br s, 6 H); mass spectrum, m/e 306; ^1H NMR of **20** (CCl_4) δ 1.1–3.7 (m), 3.4 (s), and 3.6 (s) (16 H), 6.2–7.1 (m, 6 H); mass spectrum, m/e 306; ^{13}C NMR of **19** ($CDCl_3$) δ 158.9 (s), 144.0 (s), 142.9 (s), 124.7 (d), 113.2 (d), 109.0 (d), 72.6 (s), 54.9 (q), 53.1 (d), 38.1 (t), 33.6 (t); ^{13}C NMR of **20** ($CDCl_3$) δ 158.6 (s), 156.6 (s), 144.1 (s), 142.3 (s), 137.5 (s), 128.2 (d), 123.7 (d), 117.2 (d), 112.6 (d), 109.3 (d), 108.9 (d), 72.1 (s), 55.0 (q), 53.1 (d), 50.2 (d), 38.3 (t), 37.4 (t), 34.9 (t), 34.8 (t); IR (neat, crude product) 1620, 1600, and 1500 cm^{-1} (aryl), no C=O present. Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found for **19** (mp 69–70 °C): C, 82.34, 82.21; H, 7.15, 7.17. Found for **20** (mp 136.5–137.5 °C): C, 82.47, 82.21; H, 7.28, 7.16.

2,2′-Ethylene-1,1′-spirobiindan (9). The ketone **11** (5.08 g, 19.2 mmol) was heated for 24 h at about 170 °C with 80 g of polyphosphoric acid (purchased from Merck). Water was added to the cooled reaction mixture, and the product was extracted with benzene. The benzene layer was washed with water, dried, and evaporated. After chromatography over a short alumina column (activity I, neutral, carbon tetrachloride as eluent), 3.72 g of the slightly yellow solid **9** was obtained (15.1 mmol, 79%). Recrystallization from hexane gives the colorless product: mp 99.0–99.7 °C; ^1H NMR (CCl_4) δ 1.2–3.6 (m, 10 H), 6.5–7.4 (m, 8 H); IR (crude product, neat) 1620, 1600, and 1500 cm^{-1} (aryl), no C=O present. Anal. Calcd for $C_{19}H_{18}$: C, 92.62; H, 7.37. Found: C, 92.56, 92.54; H, 7.30, 7.16.

Di-*m*-anisalcyclopent-3-en-1-one (21). The ketone **18** (25.0 g, 78.1 mmol) was heated under reflux (by irradiating with a Philips 250-W IR lamp) with *N*-bromosuccinimide (20.0 g, 112.4 mmol) and carbon tetrachloride (400 mL). After about 20 min of heating with the lamp, the reaction started and went on for 10 min (evolution of hydrogen bromide). After being irradiated for 1 h the reaction mixture was cooled and filtered. The residue,

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(35) See: "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. 5, p 310.

obtained by evaporation of the filtrate, was recrystallized from a mixture of ethanol and chloroform to give 11.62 g (36.5 mmol, 47%) of **21**: mp 134.5–135 °C; ^{1}H NMR ($CDCl_3$) δ 3.8 (s, 6 H), 6.7–7.5 (m, 12 H). Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.17, 78.96; H, 5.71, 5.59.

Tetrabromodi-*m*-anisalcyclopentanone 22. To a solution of 6.0 g of the ketone **18** (18.8 mmol) in 50 mL of chloroform was added bromine (6.6 g, 41.2 mmol). The mixture was stirred overnight, and the precipitate which had formed was sucked off and washed with chloroform to afford 5.0 g of the colorless product (7.8 mmol, 42%). It can be recrystallized from benzene: mp 166–166.5 °C dec; IR (Nujol) 1760 (C=O), 1620, 1600, and 1500 cm^{-1} (aryl). Anal. Calcd for $C_{21}H_{20}Br_4O_3$: C, 39.41; H, 3.15; Br, 49.94. Found: C, 39.81, 39.84; H, 3.10, 3.12; Br, 49.33, 49.31.

Enamines of 2-Indanone (25A–C). The enamines were prepared as described in ref 20. In the case of morpholine, the enamine **25A** crystallized from the reaction solution and was obtained in 95% yield. In the case of pyrrolidine and homopiperidine, the reaction solution was evaporated, and dry methanol was added to the residue. The enamines were filtered off and washed with dry methanol. After being dried in a desiccator, **25B** and **25C** were obtained in yields of 91 and 92%, respectively, as yellow solids: ^{1}H NMR of **25A** ($CDCl_3$) δ 2.95–3.2 (m, 4 H), 3.3 (s, 2 H), 3.65–3.9 (m, 4 H), 5.5 (s, 1 H), 6.6–7.3 (m, 4 H); ^{1}H NMR of **25B** ($CDCl_3$) δ 1.72–2.1 (m, 4 H), 3.0–3.4 (m, 6 H), 5.1 (s, 1 H), 6.5–7.3 (m, 4 H).

Alkylation of Enamines of 2-Indanone. Synthesis of Iminium Salts 26A–C and 28A. A mixture of the morpholine enamine **25A** (27.61 g, 0.137 mol) and benzyl bromide (35 g, 0.205 mol) was heated under reflux in 200 mL of acetonitrile for 7 h (under a nitrogen atmosphere). After the mixture was allowed to stand overnight, the iminium salt **28A** was filtered off and washed with acetonitrile; yield 7.85 g (0.017 mol, 12%). The filtrate was evaporated, and the residue was crystallized from 120 mL of acetone/benzene (1:1) to afford 36.73 g of the iminium salt **26A** (0.099 mol, 72%).

Analogously, the homopiperidine enamine **25B** (9.63 g, 45.2 mmol) was heated for 6 h with benzyl bromide (14.0 g, 81.9 mmol) in 75 mL of acetonitrile. After the mixture cooled overnight, the salt **26B** was filtered off (9.69 g), and the filtrate was evaporated. Acetone was added to the residue to furnish another 3.30 g of **26B**, total yield 12.99 g (33.8 mmol, 75%).

In a similar way, the reaction mixture, obtained by refluxing a mixture of the pyrrolidine enamine **25C** (8.0 g, 43.2 mmol), benzyl bromide (12 g, 70.2 mmol), and acetonitrile (75 mL), was evaporated, and the residue was crystallized from a mixture of acetone (15 mL) and benzene (10 mL) to afford 12.93 g (36.4 mmol, 84%) of the salt **26C**: ^{1}H NMR of **26A** ($CDCl_3$) δ 2.6–3.1 (br) and 3.1–3.3 (d, J = 7 Hz) (3 H), 3.6–4.6 (m, 9 H), 5.0–5.3 (br t, 1 H), 6.4–7.3 (m, 9 H).

Enamines of 1-Benzyl-2-indanone (27A–C). The iminium salt **26A** (33.73 g, 90.7 mmol) was stirred under nitrogen with triethylamine (12.0 g, 118.8 mmol) and benzene (300 mL) for about 1 h at room temperature. The mixture was filtered, the solid was washed with benzene, and the filtrate was evaporated to give 21.37 g of the slightly red enamine **27A** (73.4 mmol, 81%). This product, which is pure enough for the next step, can be recrystallized from a mixture of benzene and petroleum ether (bp 60–80 °C) to give the colorless **27A**, mp 102.5–103.5 °C.

Analogously, **27B** (14.9 g, 49.2 mmol, 99%) was obtained as a slightly brown oil by stirring the iminium salt **26B** (19.13 g, 49.8 mmol) with triethylamine (9.2 g, 91 mmol) and benzene (150 mL). This product could not be obtained crystalline and was used as such in the next step.

The enamine **27C** was obtained in the following way (treatment with triethylamine was not performed with the salt **26C**). To a solution of the iminium salt **26C** (21.2 g, 59.6 mmol) in methanol (150 mL) was added a 10% sodium hydroxide solution (60 mL). The enamine was extracted with chloroform. After the extract was washed with water (50 mL), dried, and evaporated, a dark brown oil remained which was chromatographed on an alumina column (ca. 50 g, activity I, neutral) with benzene as the eluent. Evaporation of the eluate gave 11.5 g of the enamine **27C** (41.8 mmol, 70%) as a slightly brown solid. Although **27C** can be obtained colorless by performing the elution over alumina under nitrogen, recrystallization from a mixture of benzene and petroleum ether (bp 60–80 °C) gave rise to discoloration (enamines **27B** and **27C** both discolor rapidly in solution, whereas **27A** is somewhat more stable): ^{1}H NMR of **27A** ($CDCl_3$) δ 2.5–4.0 (m, 11 H), 5.5 (s, 1 H), 6.6–7.3 (m, 9 H); ^{1}H NMR of **27B** (CCl_4) δ 1.3–1.9 (m, ca. 8 H), 2.1–2.6 (m, 0.5–1 H), 3.0–3.9 (m, ca. 6.5 H), 5.1 (s, 0.6 H), 6.3–7.2 (m, 9 H) (presumably the more substituted enamine is present, ca. 40%); ^{1}H NMR of **27C** (CCl_4) δ 1.3–1.9 (m, 4 H), 2.7–3.9 (m, ca 7.5 H), 5.0 (s, ca. 0.5 H), 6.4–7.2 (m, 9 H) (presumably the more substituted enamine is present, ca. 50%). Anal. Calcd for $C_{20}H_{21}NO$ (**27A**): C, 82.44; H, 7.26; N, 4.81. Found: C, 82.40, 82.57; H, 7.22, 7.31; N, 4.71, 4.79.

Alkylation of Enamines of 1-Benzyl-2-indanone. Synthesis of Iminium Salts 28A–C. The morpholine enamine **27A** (9.6 g, 33.0 mmol) was heated for 7 h with benzyl bromide (13.0 g, 76.0 mmol) and acetonitrile (100 mL) in a nitrogen atmosphere. The reaction mixture was evaporated, and a mixture of acetone and benzene (40 mL, ratio of 1:2) was added to the residue. After the mixture was cooled to 0 °C, there was obtained 7.98 g of the iminium salt **28A**. Another 1.83 g was obtained from the filtrate after ca. 5 days at 0 °C. A total yield of 9.81 g (21.2 mmol, 64%) of **28A** was obtained.

Analogously the homopiperidine enamine **27B** (9.0 g, 29.7 mmol) was treated with benzyl bromide (12.0 g, 70.2 mmol) in acetonitrile (75 mL). After evaporation and addition of acetone (50 mL) to the residue, there was obtained 7.70 g of the salt **28B** (16.2 mmol, 55%).

From 8.0 g of the pyrrolidine enamine **27C** (29.1 mmol) and benzyl bromide (8.0 g, 46.8 mmol) in 70 mL of acetonitrile, there was obtained 8.97 g of the salt **28C** (20.1 mmol, 69%). The latter two yields are based on only one or two experiments; they might be improved: ^{1}H NMR of **28B** ($CDCl_3$) δ 1.2–2.3 (br m, 8 H), 3.3–4.2 (m, 8 H), 4.6–4.9 (br t, 2 H), 6.4–7.4 (m, 14 H); ^{1}H NMR of **28C** ($CDCl_3$) δ 2.0–2.6 (m, 4 H), 3.0–4.8 (m, 10 H), 6.4–7.3 (m, 14 H).

1,3-Dibenzyl-2-indanone (24). The iminium salt **28A** (1.5 g, 3.2 mmol) was stirred for 15 h under nitrogen with acetic acid (7.5 mL) and water (25 mL). Water was added, and the product was extracted with benzene. After the extract was washed with water, dried, and evaporated, the ketone **24** was obtained (0.94 g, 93%). The ketone decomposed on attempted vacuum distillation and could not be obtained crystalline. On being allowed to stand the ketone discolors rapidly. It was also obtained from the iminium salt **28B** in the same way. The conversion of the salt **28C** to the ketone **24** was not performed: ^{1}H NMR (CCl_4) δ 2.4–3.3 (m, 6 H), 6.5–7.2 (m, 14 H); IR (neat) 3100, 1620, and 1500 (aryl), 1750 cm^{-1} (C=O).

2,2′-*o*-Phenylene-1,1′-spirobiindan (10). The iminium salt **28A** (7.85 g, 17.0 mmol) was heated with stirring at 160–180 °C for 16 h with 80 g of polyphosphoric acid. Water was added to the cooled reaction mixture, and the product was extracted with benzene. The benzene layer was washed with water, dried, and evaporated. After chromatography over a short alumina column (activity I, neutral, carbon tetrachloride as the eluent) 3.32 g of the slightly yellow product was obtained (11.3 mmol, 66%). Further purification can be done by Kugelrohr distillation [230 °C (0.05 mm)] or by crystallization from hexane or ethanol/ethyl acetate. The pure product has the following: mp 107.5–108 °C; mass spectrum, m/e 294; ^{1}H NMR ($CDCl_3$) δ 2.8–3.2 (dd, 2 H), 3.35–4.2 (m, 4 H), 6.7–7.4 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 148.8 (s), 146.4 (s), 142.6 (s), 126.9 (d), 124.3 (d), 74.1 (s), 57.4 (d), 39.0 (t) [by use of a spectrum width of 500 Hz, the doublets at δ 126.9 and 124.3 were shown to consist of three doublets (the decoupled spectrum showed two sets of three signals)]; IR (neat) 3100, 1600, and 1500 cm^{-1} (aryl), no C=O present; UV (c 1.905 × 10^{-4}, n-hexane) λ_{max} 276 nm (ε 4400), 270 (3800), 263 (2400). Anal. Calcd for $C_{23}H_{18}$: C, 93.84; H, 6.16. Found: C, 93.83, 93.71; H, 6.24, 6.25.

Bromination of 10 (Dibromide 31). The tricycle **10** (0.31 g, 1.05 mmol) was heated under reflux for 15 min with *N*-bromosuccinimide (0.39 g, 2.2 mmol), carbon tetrachloride (20 mL), and dibenzoyl peroxide (ca. 10 mg). The cooled reaction mixture was filtered and then evaporated to give the bromide in quantitative yield.

2,2′-*o*-Phenylene-3,3′-dioxo-1,1′-spirobiindan (32). The tricycle **10** (2.15 g, 7.3 mmol) was dissolved in glacial acetic acid. Chromium trioxide (5.1 g, dried under vacuum at 100 °C) was

added, and the mixture was warmed to 50–60 °C. After some time, an exothermic reaction starts (cooling was necessary in order to prevent the temperature of the reaction mixture from rising above ca. 80 °C) which subsides after a few minutes. The reaction mixture was subsequently stirred for 0.5 h at 50–60° C and then poured into water (100 mL), and the products were extracted with chloroform (3 × 50 mL). The combined chloroform layers are washed with water, saturated sodium bicarbonate solution, and water, respectively, dried, and evaporated to give 1.58 g of product which, by ^{1}H NMR analysis, consisted of about 40% of a ca. 3:1 mixture of **32** and **33**. After chromatography over a short alumina column (activity I, neutral, benzene as the eluent) and crystallization from ethanol, the diketone **32** could be obtained: mp 202–203 °C; mass spectrum, *m/e* 322; ^{1}H NMR ($CDCl_3$) δ 4.15 (s, 2 H), 7.0–7.8 (m, 12 H); IR (CH_2Cl_2) 3100, 1600, and 1500 (aryl), 1720 cm^{-1} (C=O). Anal. Calcd for $C_{23}H_{14}O_2$: C, 85.70; H, 4.38. Found: C, 85.23, 85.27; H, 4.33, 4.42.

2,2′-*o*-Phenylene-3,3′-dihydroxy-1,1′-spirobiindan. (a) Cis–Cis Isomer (34). To a suspension of the diketone **32** (0.85 g, 2.6 mmol) in ether (50 mL) was added lithium aluminum hydride (0.5 g). The mixture was heated under reflux for 3 h and then ethyl acetate was added. After addition of dilute hydrochloric acid, the product was extracted with ether. The ether layer was washed with water, 10% sodium bicarbonate solution, and water, dried, and evaporated to give the diol in quantitative yield. The diol was used directly in subsequent steps: ^{1}H NMR ($CDCl_3$) δ 2.7–2.9 (br s, 2 H), 4.05 (d, *J* = 8 Hz, 2 H), 5.45 (d, *J* = 8 Hz, 2 H), 6.6–7.5 (m, 12 H). Some signals at positions of the aliphatic protons of the trans–trans diol were also present (ca. 15%).

(b) Trans–Trans Isomer (35). The dibromide **31** (prepared from 5.0 g of the tricycle **10**, 17.0 mmol), dissolved in some dimethoxyethane, was added to a mixture of mercuric oxide (8 g), 70% perchloric acid (8.5 mL), dimethoxyethane (70 mL), and water (7.5 mL) (prepared as described in ref 29). After being stirred for 45 min, the reaction mixture was poured into water (200 mL), and the diol was extracted with benzene (2 × 150 mL). The combined benzene fractions were washed with water (200 mL), dried, and evaporated to provide 12 g of a product, consisting fo the diol **35** and of mercury salts which were removed during the purification of the diacetates: ^{1}H NMR ($CDCl_3$) δ 2.7–3.0 (br s, 2 H), 3.8 (d, *J* = 2.5 Hz, 2 H), 5.15 (d, *J* = 2.5 Hz, 2 H), 6.8–7.6 (m, 12 H). Some signals at positions of the aliphatic protons of the cis–cis diol were also present (ca. 25%).

2,2′-*o*-Phenylene-3,3′-diacetoxy-1,1′-spirobiindan (36 and 37). The crude diol **35** (12 g, see above) was dissolved in acetic acid (200 mL). To this solution was added concentrated sulfuric acid (15–20 mL), and the mixture was stirred for 0.5 h and then poured into water (500 mL). The product was extracted with benzene (2 × 150 mL), and the benzene layer was washed with water (2 × 250 mL). After the benzene layer was dried and evaporated, a residue was obtained which was chromatographed on ca. 50 g of alumina (activity I, neutral) in order to remove the mercury salts. Elution with ca. 300 mL of toluene gave ca. 5 g of crude product, and subsequent elution with chloroform gave ca. 1 g of product, partly consisting of mercury salts (addition of ethanol dissolved the salts and left 0.22 g of the diacetate **36** behind). To the crude product (ca. 5 g) was added ether, and 1.8 g of pure **36** remained undissolved. The filtrate was evaporated and recrystallized from ethanol to afford 0.77 g of **37** (1.88 mmol, 11%) mixed with ca. 15% **36**: mass spectrum, *m/e* 350, 290 (relative intensity 2:1). The filtrate was combined with the formerly mentioned ethanol solution, evaporated, and chromatographed on a slightly deactivated alumina column (eluent toluene) to give a product which, after recrystallization from hexane and some ethanol, furnished 0.87 g (2.12 mmol, 12%) of a mixture of **36** and **37** (ca. 1:1). The total yield of trans–trans diacetate **36** was 2.02 g (4.92 mmol, 29%). Recrystallization from ethanol/chloroform and sublimation [200 °C (0.005 mm)] gave analytically pure material: mp 212.5–215.5 °C; mass spectrum, *m/e* 350, 290 (relative intensity 1:1); ^{1}H NMR of **36** ($CDCl_3$) δ 2.15 (s, 6 H), 3.9 (d, *J* = 2 Hz, 2 H), 6.2 (d, *J* = 2 Hz, 2 H), 6.9–7.6 (m, 12 H); ^{1}H NMR of **37** ($CDCl_3$) δ 1.5 (s, 3 H), 2.05 (s, 3 H), 3.9 (br s, 1 H), 4.3 (d, *J* = 7 Hz, 1 H), 6.15 (br s, 1 H), 6.65 (d, *J* = 7 Hz, 1 H), 6.8–7.6 (m, 12 H). Anal. Calcd for $C_{27}H_{22}O_4$ (**36**): C, 79.01; H, 5.40. Found: C, 79.06, 78.74; H, 5.41, 5.32.

Saponification of **36** (0.5 g, 1.22 mmol) by stirring for 16 h with a mixture of potassium hydroxide (0.55 g), water (8 mL), ethanol (15 mL), and ether (10 mL) gave after normal workup 0.35 g of the diol **35** (1.07 mmol, 88%). According to the ^{1}H NMR spectrum, ca. 20% of the cis–cis isomer (and/or cis–trans isomer) was present.

2,2′-*o*-Phenylene-3,3′-diphenyl-1,1′-spirobiindan (39). The diol **35** (0.35 g, 1.07 mmol) was stirred for 2.5 h with powdered aluminium chloride (0.85 g) and benzene (80 mL). The reaction mixture was poured into water, and the layers were separated. The benzene layer was washed with water, dried, and evaporated. The residue on recrystallization from ethanol/chloroform gave slightly yellow **39** (0.29 g, 0.65 mmol, 61%), which on Kugelrohr distillation [200 °C (0.01 mm)] gave the colorless product: mp 185.5–186 °C; mass spectrum, *m/e* 446; IR (KBr) 3100, 1620, 1520, 1500 cm^{-1} (aryl); UV (c 3.139 × 10^{-4}, *n*-hexane) λ_{max} 278 nm (ε 3400), 271 (3200), 264 (2500); ^{1}H NMR ($CDCl_3$) δ 4.05 (d, *J* = 5 Hz, 2 H), 4.45 (d, *J* = 5 Hz, 2 H), 6.8–7.4 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 149.6 (s), 146.0 (s), 145.7 (s), 145.0 (s), 128.7 (d), 128.2 (d), 127.8 (d), 127.5 (d), 126.5 (d), 125.5 (d), 125.1 (d), 124.7 (d), 72.9 (s), 68.3 (d), 59.3 (d). Anal. Calcd for $C_{35}H_{26}$: C, 94.13; H, 5.87. Found: C, 93.83, 94.08; H, 5.85, 5.90.

2,2′-*o*-Phenylene-2,3-dihydro-3,3′-diphenyl-1,1′-spirobiindene (40). The dibromide **31** (0.58 g; obtained from 0.31 g, 1.05 mmol, of tricycle **10** and 0.395 g, 2.22 mmol, of *N*-bromosuccinimide) was stirred for 3 h with powdered aluminum chloride (1.0 g) and benzene (30 mL). Workup as described for the synthesis of **39** gave a residue consisting of a mixture of **40** and diphenylmethane in nearly equal amounts as shown by ^{1}H NMR spectroscopy (in other experiments variable amounts of **39** were also present). Recrystallization from ethanol/chloroform gave 0.27 g of pure **40** (0.61 mmol, 58% based on **10**). The analytically pure product can be obtained after chromatography on a short alumina column (activity I, neutral, toluene as eluent) and subsequent sublimation [220 °C (0.01 mm)]. This gives an almost colorless product with a melting point of 226.5–227 °C and a mass spectral peak at *m/e* 444. Diphenylmethane was identified by its mass spectrum (*m/e* 168), ^{1}H NMR spectrum, and ^{13}C NMR spectrum: IR (KBr) 3150, 1620, and 1520 cm^{-1} (aryl); UV (*c* 0.372 × 10^{-4}, *n*-hexane) λ_{max} 335 nm (ε 15 000), 251 (23 000); ^{1}H NMR ($CDCl_3$) δ 4.0 (s, 1 H), 5.0 (s, 1 H), 6.5–7.7 (m, 22 H); ^{13}C NMR ($CDCl_3$) δ 155.8 (s), 154.4 (s), 150.4 (s), 147.2 (s), 146.8 (s), 145.0 (s), 143.2 (s), 135.6 (s), 134.6 (s), 129.5 (d), 128.5 (d), 128.4 (d), 128.2 (d), 127.9 (d), 127.8 (d), 127.6 (d), 127.4 (d), 127.0 (d), 126.6 (d), 125.4 (d), 125.0 (d), 124.7 (d), 123.7 (d), 122.0 (d), 120.9 (d), 76.4 (s), 59.1 (d), 56.7 (d). Anal. Calcd for $C_{35}H_{24}$: C, 94.56; H, 5.44. Found: C, 94.08, 94.19; H, 5.21, 5.27.

Registry No. 9, 73559-04-3; **10**, 73559-05-4; **11**, 52186-05-7; **17**, 73559-06-5; **18**, 73559-07-6; **19**, 73559-08-7; **20**, 73559-09-8; **21**, 73559-10-1; **22**, 73559-11-2; **24**, 73574-35-3; **25A**, 23929-00-2; **25B**, 23929-03-5; **25C**, 39157-79-4; **26A**, 73559-12-3; **26B**, 66209-38-9; **26C**, 73559-13-4; **27A**, 73559-14-5; **27B**, 73559-15-6; **27C**, 24017-07-0; **28A**, 73559-16-7; **28B**, 73559-17-8; **28C**, 73559-18-9; **31**, 73559-19-0; **32**, 73559-20-3; **33**, 73559-21-4; **34**, 73559-22-5; **35**, 73609-90-2; **36**, 73559-23-6; **37**, 73609-91-3; **39**, 73559-24-7; **40**, 73574-38-6; dibenzalcyclopentanone, 895-80-7.