The appearance of 2,4-dinitrophenol was measured at the wavelength of maximum absorption (368 nm).

Gel Filtration Chromatography. In order to effect a separation of 2,4-dinitrophenylcycloheptaamylose and other reaction products the following experiments were carried out.

β-Cyclodextrin (0.101 g, 8.92×10^{-5} mol) was dissolved in 90 mL of NaOH (10^{-3} M), and 2,4-dinitrofluorobenzene (0.0166 g, 8.92×10^{-5} mol) in 0.96 mL of dioxane was added.

The reaction mixture was stirred for 90 min, brought to pH 6–7 with a few drops of 0.1 M hydrochloric acid, and filtered to remove undissolved material. A 2.0-mL aliquot of the resulting solution was chromatographed by using a 1.5 × 28 cm column of Sephadex G-10 gel (Sigma).

The column was developed by eluting with distilled water. Consecutive 0.5-mL fractions were tested for the presence of cycloheptaamylose by thin-layer chromatography on silica gel using acetic acid/chloroform/water (80:10:10) as solvent.

Cycloheptaamylose was found to be present from the 6 to the 12–14 fractions taken after passage of the void volume, consistent with the molecular exclusion limits of Sephadex G-10. The 2,4-dinitrophenol was eluted after passing about 15 mL of water and the unreacted 2,4-dinitrofluorobenzene after about 30 mL of water. It is interesting to note that the 2,4-dinitrofluorobenzene is selectively retained by the Sephadex gel.

The ultraviolet absorption spectra of fractions 6–12 showed λ_{max} at 265 and 305 nm and were practically identical with the spectrum of 2,4-dinitroanisole. The thin-layer chromatography of these samples showed two compounds with R_f 0.22 and 0.38. The first one coincides with that of β-cyclodextrin.

A similar experiment was carried out by using 2,4-dinitrochlorobenzene, but in this case the reaction time was 33 h,[16] and the concentration of the solution contained 1×10^{-4} M 2,4-dinitrochlorobenzene, 0.01 M β-cyclodextrin, and 2.10^{-2} M NaOH.

A small amount of a compound having the same UV spectrum as that isolated from the reaction of 2,4-dinitrofluorobenzene appeared in fractions 7 and 8.

Equilibrium Constant for Complex Formation. To determine the equilibrium constant for complex formation between our substrates and CDOH, we used the partition coefficient method.[8] A solution prepared by dissolution of 2.47 mmol of 1 or 2 in 25 mL of benzene was mixed with 25 mL of water–dioxane (9:1 v/v) and stirred for 24 h. Then the two phases were separated by centrifugation for about 10 min, and 4 mL of the aqueous phase was withdrawn and diluted with NaOH (2.5 M) to hydrolyze the substrate. After the reaction was complete, the concentration of 2,4-dinitrophenol was determined by measuring its absorbance. The amount formed is equivalent to the amount of substrate dissolved in the water layer.

The ratio of concentration of the substrate in benzene (S_B) and in water (S_W) give the distribution constants (eq 9) 1.54×10^{-3} and 3.47×10^{-3} for 2,4-dinitrochlorobenzene and -fluorobenzene, respectively. The same determination was carried out at two

$$K_d = \frac{S_W}{S_B} \tag{9}$$

other initial concentrations in the benzene layer. The values of K_d obtained were independent of the concentration in the benzene layer within experimental error and also of the ratio of volumes of benzene and water.

The same determination was done but now by using a solution of 10^{-3} M β-cyclodextrin. The apparent equilibrium constant for complex formation was calculated from eq 10

$$K_{CD} = \frac{S_T - K_d(S_B)}{[(CDOH)_0 - S_T + K_d(S_B)]\, K_d(S_B)} \tag{10}$$

where S_T represents the total concentration of substrate in the water–dioxane–cyclodextrin solution, S_B is the concentration of the substrate in the benzene solution, and CDOH is the concentration of β-cyclodextrin in the water solution.

The concentration of β-cyclodextrin in water solution was determined by the phenol–sulfuric acid method,[17] and the value determined always coincides with the analytical concentration.

The value of K_{CD} thus determined was strongly dependent on the concentration of the substrate in the benzene layer and consequently in the water layer. As the concentration in the benzene layer increases K_{CD} decreases. For this reason, in our calculations we used the value of K_{CD} obtained for the lowest concentrations that give measurable amounts of substrate in the water layer, namely 4×10^4 M^{-1} and 2×10^3 M^{-1} for 2,4-dinitrochlorobenzene and -fluorobenzene, respectively.

Acknowledgment. This research is supported in part by the Consejo Nacional de Investigaciones Científicas y Tênicas, Argentina (CONICET) and the Consejo Provincial de Investigaciones Científicas y Tecnológicas, Córdoba, Argentina (CONICOR). M. Barra is a grateful recipient of a fellowship from the CONICET.

Registry No. 1, 70-34-8; 2, 97-00-7; CDOH, 7585-39-9.

(15) de Rossi, R. H.; de Vargas, E. B. *J. Am. Chem. Soc.* **1981**, *103*, 1533.

(16) This reaction time was chosen after calculating the time at which the concentration of product U in Scheme I should be maximum by using $k_{OH}^{CD} = 1.5 \times 10^{-4}$ M^{-1} s^{-1}, $k_u = 1.7 \times 10^{-3}$ M^{-1} s^{-1}; and $k_H = 4 \times 10^{-4}$ M^{-1} s^{-1}.

(17) Dubois, M.; Gilles, K. A.; Hamilton, H. K.; Reberts, P. A.; Smith, F. *Anal. Chem.* **1956**, *28*, 350.

Flash Vacuum Thermolysis of 5,6,8,9-Tetrahydro-4′-methylenespiro[7*H*-benzocycloheptene-7,1′-cyclohexa-2′,5′-diene]. The Intermediate Formation of [3,2]Orthoparacyclophane

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Received October 30, 1985

Flash vacuum thermolysis (FVT) of 5,6,8,9-tetrahydro-4′-methylenespiro[7*H*-benzocycloheptene-7,1′-cyclohexa-2′,5′-diene] (**2a**) at 520–650 °C yielded isomeric products **10** (26%), **12a** (14%), and **19** (3%) and 2,2′-dimethyldibenzyl (**17**, 22%). The formation of these products from the primary intermediate, the diradical **3a**, is discussed. It is concluded that **17** and **19** are formed via the intermediate [3,2]orthoparacyclophane (**1a**) which is unstable under FVT conditions. Attempts to investigate the regioisomer **2b** of **2a** were thwarted by the high reactivity of **2b** even at room temperature. FVT of **4a**, the 4′-keto precursor of **2a**, yielded **31** (60%); FVT of **4b** gave **17** (80%) and *p*-hydroxystyrene (**30**, 3%). In the thermolysis of **4**, cyclophanes are probably not involved.

In connection with our studies on the synthesis of short-bridged [*n*]para- and [*n*]metacyclophanes, we have reported that [8]- and [7]paracyclophane can be obtained by flash vacuum thermolysis (FVT) of methylenespiro-

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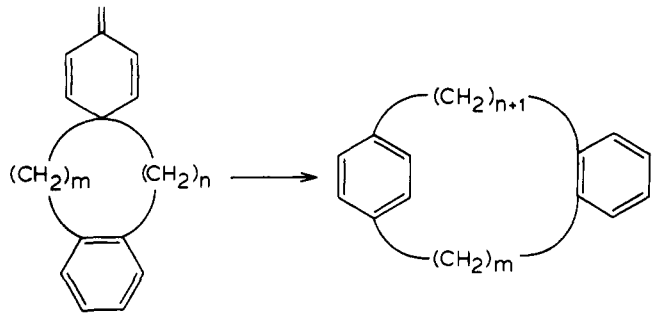
Scheme I



2 **1**

[a] $m = n = 2$. [b] $m = 1$, $n = 3$.

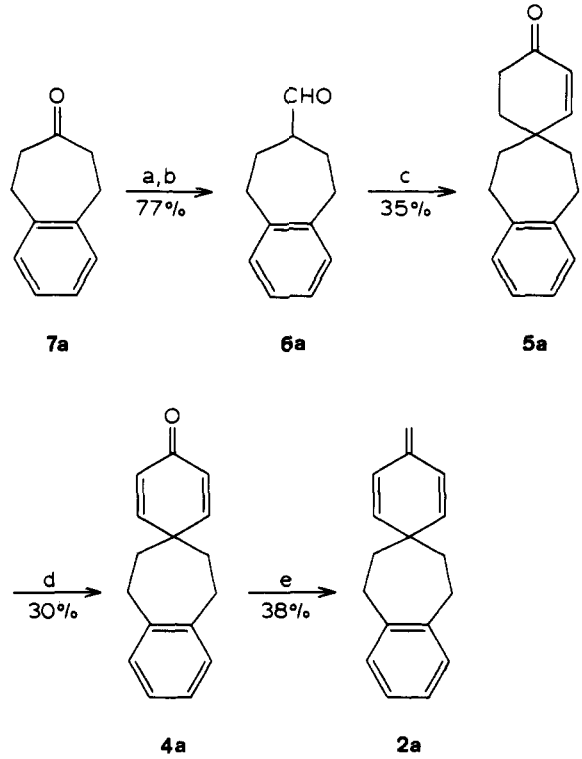
cyclohexadienes.[1] FVT of the corresponding spirocyclohexadienones gave a 9-hydroxy[7]metacyclophane[2a] or a β-hydroxybenzocycloalkane, depending on the chain length n.[2b] Diradicals formed by opening of the aliphatic spiro ring were postulated to be the primary intermediates. It appeared of interest to investigate the applicability of the FVT approach toward the synthesis of short-bridged [n,m]orthoparacyclophanes **1**, which to our knowledge, are unknown.[3] (Scheme I). Here we wish to report on the FVT of 5,6,8,9-tetrahydro-4′-methylenespiro[7*H*-benzocycloheptene-7,1′-cyclohexa-2′,5′-diene] (**2a**, $m = 2$, $n = 2$). Although the desired [3,2]orthoparacyclophane (**1a**) was not obtained, some of the isolated products indicate its intermediate formation, but under the severe conditions of FVT it rearranges or decomposes. We have also attempted the synthesis of **1b**, the regioisomer of **1a**, in order to investigate the influence of the position of the benzene ring. However, the required precursor **2b** ($m = 1$, $n = 3$) turned out to be thermally too unstable (vide infra).

Results and Discussion

Compound **2a** was prepared according to Scheme II from 6,7,8,9-tetrahydro-5*H*-benzocyclohepten-7-one (**7a**).[4] The latter was transformed to the aldehyde **6a** in 77% yield according to the method of Wittig[5] by reaction with (methoxymethylene)triphenylphosphorane in diethyl ether, followed by treatment with formic acid. The aldehyde **6a** was converted to the enone **5a** in 35% yield by the spiro annelation method of Kane and Jones.[6] Oxidation of **5a** with 1.4 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) provided **4a** in 30% yield after recrystallization.[6,7] Treatment[8] of **4a** with methylenetriphenylphosphorane in dimethyl sulfoxide yielded **2a** in 38% yield after recrystallization (Scheme II).

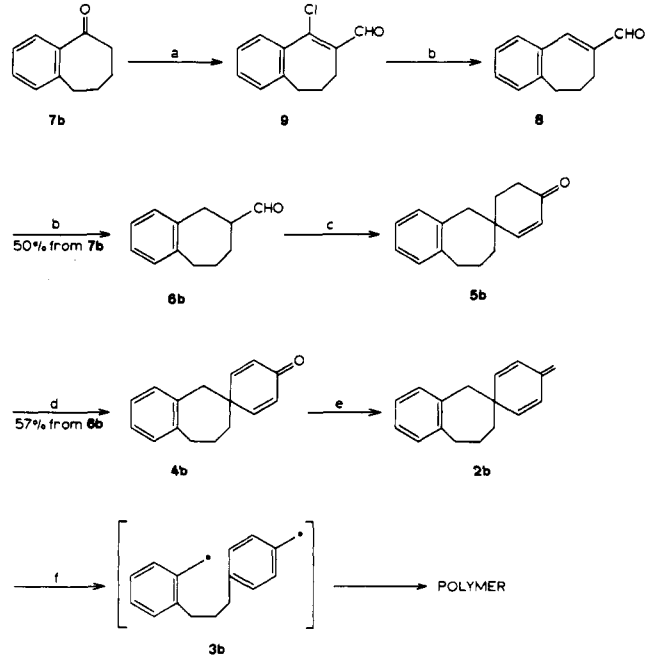
The regioisomer **2b** of **2a** was synthesized by a modified version of that applied for **2a** (Scheme III). Compound **7b** was transformed to the corresponding β-carboxaldehyde

Scheme II[a]



[a] (a) $Ph_3P{=}CHOMe$; (b) HCOOH; (c) piperidine, $MeCOCH{=}CH_2$, CH_3COOH, CH_3COONa, NaOH; (d) DDQ; (e) $Ph_3P{=}CH_2$.

Scheme III[a]

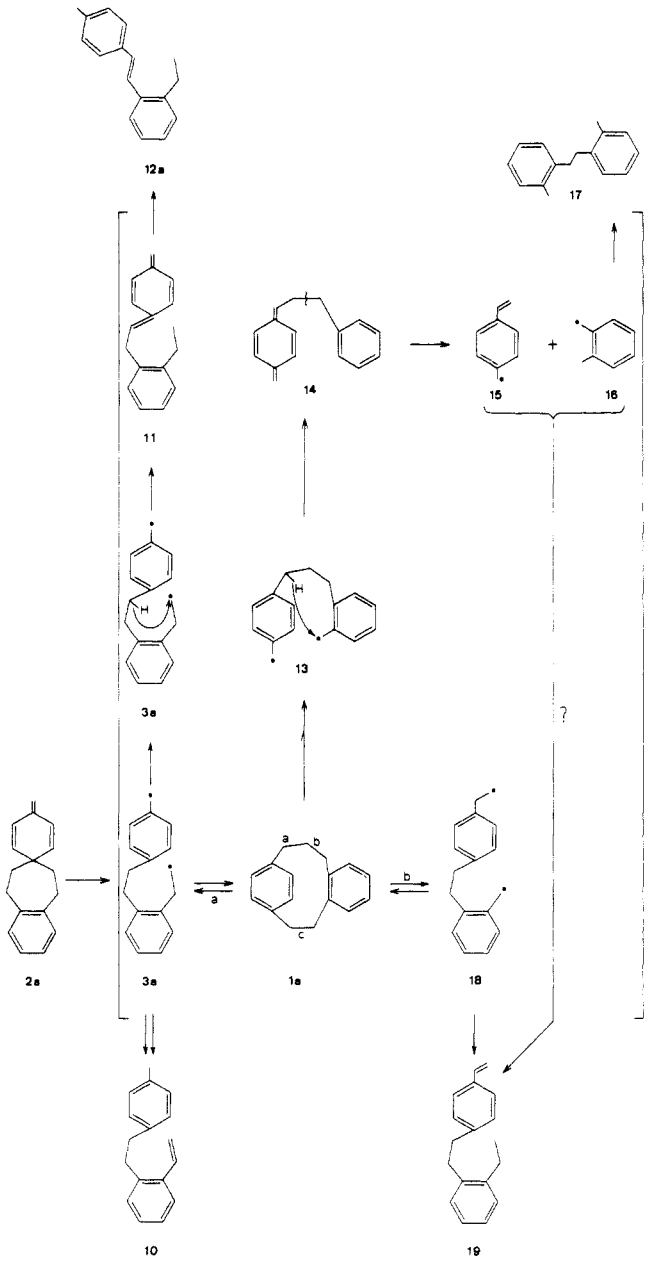


[a] (a) $POCl_3$, $HCONMe_2$; (b) H_2/Pd, K_2CO_3; (c) piperidine, $MeCOCH{=}CH_2$, CH_3COOH, CH_3COONa, NaOH; (d) DDQ; (e) $Ph_3P{=}CH_2$; (f) $T > 0$ °C.

6b by a three-step reaction sequence in 50% overall yield. First, **7b** was reacted with the Vilsmeier reagent, phosphorus oxychloride in dimethylformamide, leading to **9** according to the method of Virgillo et al.[9] By catalytic hydrogenation with 5% Pd/C, **9** was transformed into **6b**. However, dehalogenation and hydrogenation of the olefinic bond could not be accomplished in one step, probably

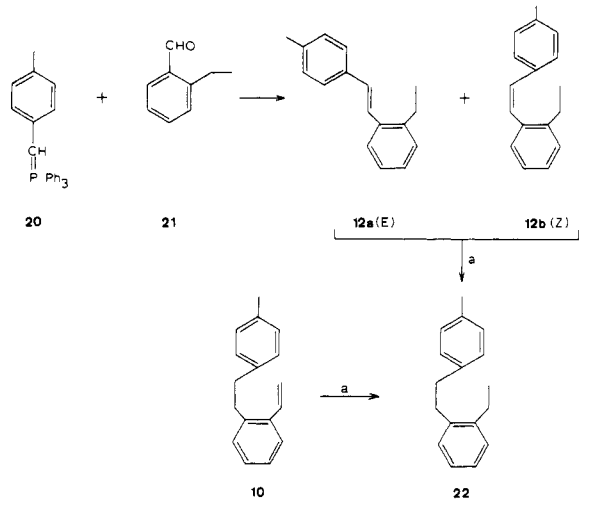
(1) Jenneskens, L. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron*, in press.
(2) (a) Jenneskens, L. W.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1984**, *40*, 3117. (b) Jenneskens, L. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron*, in press.
(3) For a review see: Keehn, P. M.; Rosenfeld, S. M. *Cyclophanes*; Academic Press: New York, 1983.
(4) (a) Allinger, N. L.; Szkrybalo, W. *J. Org. Chem.* **1961**, *27*, 722. (b) Fohlisch, B. *Synthesis* **1972**, 564.
(5) (a) Wittig, G.; Böll, W.; Krück, K. H. *Chem. Ber.* **1962**, *95*, 2514. (b) Adams, L. *Org. React.* (N.Y.) **1965**, *14*, 346.
(6) Kane, V. V.; Jones, M., Jr. *Org. Synth.* **1981**, *61*, 129.
(7) Van Straten, J. W. Ph.D. Thesis, Vrije Universiteit, Amsterdam, The Netherlands, **1978**.
(8) (a) Van Straten, J. W.; Turkenburg, L. A. M.; de Wolf, W. H.; Bickelhaupt, F. *Recl. J. R. Neth. Chem. Soc.* **1985**, *104*, 89. (b) Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.
(9) Virgillio, J. A.; Heilweil, E. *Org. Prep. Proced Int.* **1982**, *14*, 9.

Scheme IV



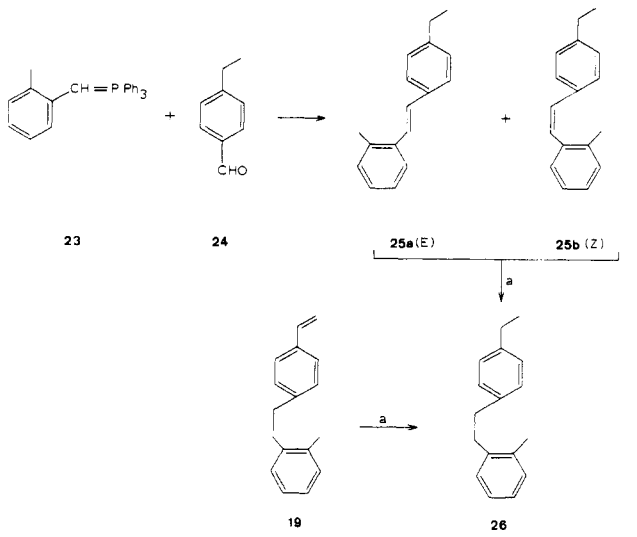
because chlorine deactivated the catalyst. Therefore, after reduction of the chlorine, yielding **8**, a second hydrogenation was necessary to obtain **6b**. Then, **6b** was transformed into the dienone **4b** in 57% yield as described for **6a**. Treatment of **4b** with methylenetriphenylphosphorane in dimethyl sulfoxide yielded only polymer after workup. However, in the ^{1}H NMR spectrum of the crude reaction mixture, some **2b** could be detected [δ 6.13 (AB system, (A) 6.24, (B) 6.02, J (AB) = 10 Hz, 4 H, 4.84 (br s, 2 H)]. These results suggest that in contrast to **2a**, **2b** is thermally extremely unstable. This is obviously caused by the fact that cleavage of the spirobond in **2a** leads to the diradical **3a** with one aliphatic and one benzylic radical, while that of **2b** leads to **3b** with two benzylic radicals. It is expected that the extra benzylic stabilization of ca. 15 kcal mol^{-1} in **3b** makes the latter cleavage reaction correspondingly easier. It is of interest to note **3b** is estimated[10] to be only

Scheme V[a]



[a] (a) H_2/Pd.

Scheme VI[a]



[a] (a) H_2/Pd.

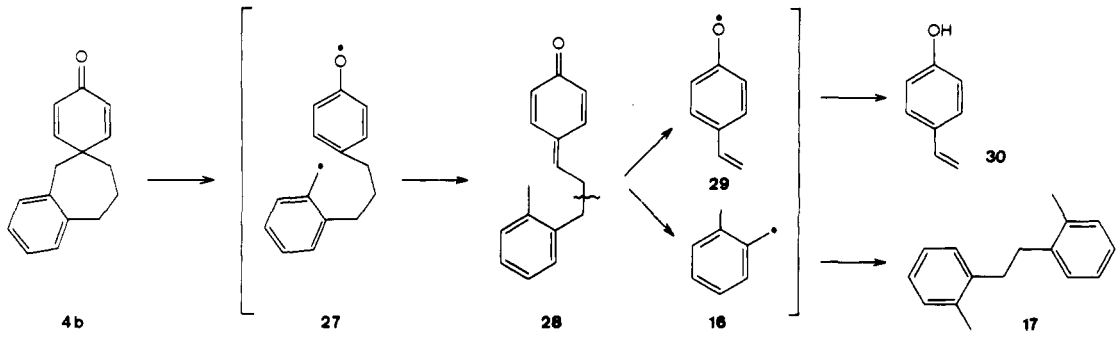
ca. 20 kcal mol^{-1} less stable than **2b**. Flash vacuum thermolysis (FVT) of **2a** in the temperature range of 520–600 °C yielded a pyrolysate with a recovery of ca. 55% by weight, which contained, besides starting material, several new products (^{1}H NMR, GLC, GCMS); at 650 °C only the new products were present. According to GLC and GCMS, four products were formed. Three products were isomeric with **2a** (GCMS, mol wt 222); the other product had a mol wt of 210. They were identified as **10** (26%), **12a** (14%), **19** (3%), and **17** (22%; 1 mol of **17** is formed from 2 mol of **2a**, vide infra), respectively (Scheme IV). Compound **12** was unambiguously identified through an independent synthesis by a Wittig reaction[11] from **20** and **21** (Scheme V). By separation of the *E* and *Z* isomers of **12** (**12a** and **12b**, respectively), it was deduced that FVT of **2a** yielded **12a**. The structure of **10** was confirmed by its catalytic hydrogenation of **22**, which was identical with the product obtained by hydrogenation of **12** (Scheme V).

The structure of **19** was established in a similar fashion as that of **12a**, by using **23** and **24** as starting materials for the independent identification, as elaborated in Scheme VI. It should be pointed out that **25** and **12** could be clearly distinguished by their ^{1}H NMR data (see Experi-

(10) $\Delta H°_f$ (**2b**) = 59.3 kcal mol^{-1} estimated from $\Delta H°_f$ (3,3-dimethyl-6-methylenecyclohexa-1,4-diene, MNDO: 34.5 kcal mol^{-1}) and group increments by Benson (Benson, S. W. *Thermochemical Kinetics* Wiley: New York, 1968). **3b** ($\Delta H°_f$ = 79.4 kcal mol^{-1}) has been calculated from group increments.

(11) Wittig, G.; Schöllkopf, N. *Chem. Ber.* **1954**, *87*, 1318.

Scheme VII



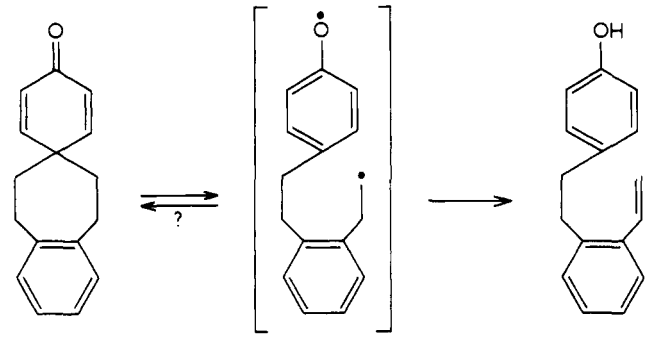
mental Section). Compound 17 was identified by comparison of its spectral data with an authentic sample (see Experimental Section).

We feel that the first step of FVT of **2a** is a homolytic scission of its spiro bond, leading to the diradical **3a** (Scheme IV). Similar diradicals have been postulated in FVT of methylenespirocyclohexadienes[1] and spirocyclohexadienones.[2] The diradical **3a** has several options to furnish spin-paired products.

First, we will discuss the formation of **10** from **3a**. β-Phenylethyl radicals are known to give styrene in high yield; the activation barrier for this process is relatively low. In a corresponding way, hydrogen transfer to the benzyl radical part of **3a** would furnish **10**. In this case, the transfer should be difficult for geometric reasons and an intermolecular process is unlikely under FVT conditions;[1] nevertheless, **10** is the main product of FVT of **2a**. Like the formation of **10**, that of **12a** can be explained from **3a** without invoking the intermediacy of **1a**. Intramolecular hydrogen transfer as indicated in Scheme IV yields the *p*-xylylene derivative **11b**, which isomerizes to **12a**; again the mechanism of hydrogen migration remains open.

Of special interest are the products **19** and **17**, because their formation can only be explained by invoking the intermediacy of **1a**. Of the aliphatic bonds of **1a**, bond c is expected to be cleaved most easily; cf., the easy cleavage of the corresponding dibenzylic bonds in [2,2]paracyclophane.[12] The cleavage of bond c yields the diradical **13** which by intramolecular hydrogen transfer as indicated in Scheme IV gives **14**. The latter has a weak allylic–benzylic bond; it is easily cleaved to give *o*-methylbenzylradicals (**16**) which will dimerize to **17**. We could not identify products derived from the other cleavage product, the *p*-vinylbenzyl radical **15**; however, it is expected to be rather reactive and susceptible to polymerization. This course of events gains credibility by the results obtained with **4b** (vide infra). Even without mechanistic reasoning, **19** is the most compelling piece of evidence for the intermediacy of **1a** because of its structural features, in particular the benzene ring substituted in para position by two two-carbon units. We rationalize its formation from **1a** by cleavage of the less activated bond b which is benzylic only with respect to one of the benzene rings. Cleavage of bond b leads to **18** which by hydrogen transfer yields **19**. The low yield of **18** reflects the relative difficulty of breaking bond b.[1] Bond a in **1a** is energetically comparable to b; its cleavage is the retroreaction of the formation of **1a** from **3a**, and it could eventually lead to **10** and **12a**. In view of the low yield of **19**, it is likely that not more than a fraction of **10** and **12a** is formed in this roundabout way from **1a**. An alternative, *inter*molecular mode of formation of **19** is conceivable which consists in the combination of **15** and **16**. However, as pointed out

Scheme VIII



above, no other products of **15** could be observed, presumably due to the high reactivity of this intermediate. Therefore, we consider this pathway less likely. It should be pointed out that this mode of formation, even if operative, would also require the intermediacy of **1a**.

As mentioned earlier, it would have been interesting to compare the behavior of **2b** (and of **1b**) under FVT conditions with that of **2a** (and **1a**), respectively. Unfortunately, **2b** was too unstable to be isolated in sufficiently pure form to warrant a further experimental investigation. However, FVT of **4b** yielded a mechanistically useful result. At 600 °C, **4b** gave **17** in 80% yield and *p*-hydroxystyrene (**30**) in 3% yield (Scheme VII). In this case, the benzylic spiro bond is the obvious candidate for cleavage to yield the diradical **27**. Intramolecular hydrogen transfer in **27** yields the quinomethane **28** which, in analogy to **14** (Scheme IV), is split at the allylic–benzylic bond to furnish the *p*-vinylphenoxy radical **29** and **16**. The latter dimerizes to **17**; the former picks up a hydrogen to give **30** in low yield, thus furnishing evidence for the fate of the second cleavage product which could not be obtained in the case of **14**. Compound **30** was synthesized independently by a Wittig reaction of *p*-hydroxybenzaldehyde with methylenetriphenylphosphorane.

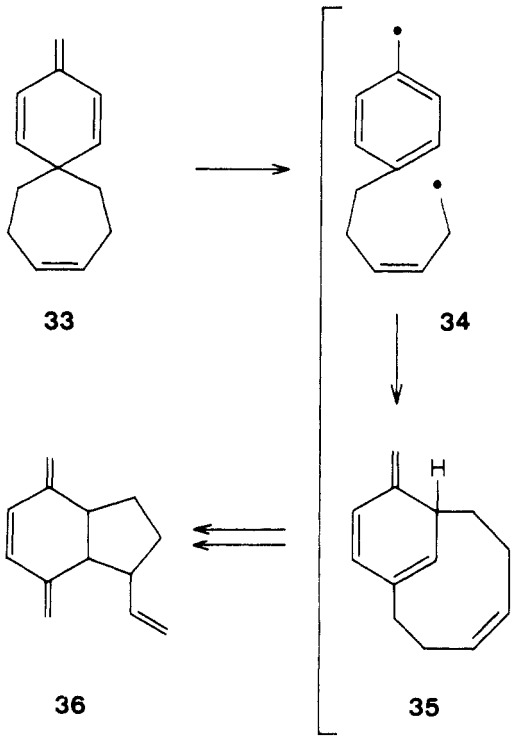
In contrast to **4b**, FVT of **4a** under similar conditions gave, besides starting material, only **31**, which may be considered as the "oxygen analogue" of **10** and is probably formed by hydrogen transfer within diradical **32** directly without intermediacy of a cyclophane (Scheme VIII).

Finally, it is interesting to note that the thermolysis of **2a** takes a course completely different from that of its nonbenzoannelated olefinic analogue **33** (Scheme IX) which has been investigated by Murray and Jones.[13] The most remarkable difference resides in the ring closure of the two analoguous primary radicals **3a** (Scheme IV) and **34** (Scheme IX). As discussed above, spin-pairing of **3a**

(12) Büchi, G.; White, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 2884.

(13) Murray, D.; Jones, M., Jr. *J. Org. Chem.*, in press; we thank Professor Jones for communicating his results prior to publication.

Scheme IX



occurs to some extent at the benzylic carbon atom to yield **1a**; in contrast, no cyclophane-derived products were observed from **34**. Rather, ring closure of **34** takes place at the ortho position of the benzylic radical part to give intermediate **35** with a metacyclophane skeleton, which is further transformed to **36**. It is not clear why **3a** does not, at least in part, show the same reaction pattern.

Experimental Section

Proton magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker WH 90 or WM 250 spectrometer as indicated. All products were analyzed by GCMS, on a Finnigan 4000 mass spectrometer. Exact mass measurements were performed with a Varian CH-5 DF mass spectrometer at an ionization potential of 70 eV. Infrared spectra were recorded on a Beckman 580B spectrometer. Gas chromatography was performed on an Intersmat 120 chromatograph (thermal conductivity detector) with hydrogen as the carrier gas (column 5% Carbowax on Chromosorb W, length 1.5 m). All boiling and melting points are uncorrected.

6,7,8,9-Tetrahydro-5*H*-benzocycloheptene-8-carbaldehyde (6a). To a vigorously stirred suspension of (methoxymethylene)triphenylphosphorane (32.5 mmol) in diethyl ether (110 mL), prepared according to the method of Wittig,[5] was added 4 g (25 mmol) of **7a**[4] in diethyl ether (20 mL) slowly at −40 °C. Then the temperature was slowly raised to room temperature, and stirred was continued overnight. After evaporation of the solvent, the residue was dissolved in *n*-pentane (100 mL) and stirred vigorously for 1 h. The precipitate of triphenylphosphine oxide was filtered off, and the filtrate was evaporated to dryness yielding crude 6,7,8,9-tetrahydro-7-(methoxymethylene)-5*H*-benzocycloheptene (4.2 g, 22 mmol, 88%) [^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.13 (s, 4 H), 5.84 (br s, 1 H), 3.57 (s, 3 H), 2.89–2.62 (m, 8 H); MS, *m/e* (rel intensity) 188 ($M^{\bullet+}$, 100]. The crude product was directly heated under reflux with 3 equiv of formic acid.[5] Distillation of the reaction mixture under reduced pressure gave **6a**, bp 70 °C, 0.05 mbar (3.3 g, 18.7 mmol, 85%): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 9.82 (s, 1 H), 7.40–7.26 (m, 4 H), 3.71–3.51 (m, 1 H), 3.23–1.38 (m, 8 H); MS, *m/e* (rel intensity) 174 ($\mathbf{6a}^{\bullet+}$, 26), 143 (16), 130 (31), 117 (100).

9-Chloro-6,7-dihydro-5*H*-benzocycloheptene-8-carbaldehyde (9). Compound **7b** (110 mmol)[14] was transformed into **9** by a Vilsmeyer formylation according to the procedure described in ref 9. Distillation of the crude product gave **9** bp 90 °C, 0.03 mbar (70 mmol, 64%): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 10.40 (s, 1 H) 7.76–7.65 (m, 1 H), 7.47–7.27 (m, 3 H), 2.73–2.59 (m, 2 H), 2.30–2.04 (m, 4 H); MS, *m/e* (rel intensity) 206 ($9^{\bullet+}$, 26), 208 (8), 171 ([**9**-Cl]$^+$, 25], 141 (100).

6,7,8,9-Tetrahydro-5*H*-benzocycloheptene-8-carbaldehyde (6b). Compound **9** (70 mmol), 1.0 g of 5% Pd/C, 13.8 g (100 mmol) of K_2CO_3, water (25 mL), and methanol (27 mL) were placed in an autoclave and hydrogenated at 10 bar and 60 °C during 5 h. After having cooled to room temperature, the solution was filtered, and the aqueous phase was extracted twice with ethylene dichloride (50 mL). The combined organic layer was dried ($MgSO_4$) and concentrated yielding 6,7-dihydro-5*H*-benzocycloheptene-8-carbaldehyde (**8**, 65 mmol, 93%) [^{1}H NMR ($CDCl_3$, 90 MHz) δ 9.57 (s, 1 H), 7.46–7.12 (m, 4 H), 5.30 (br s, 1 H), 2.99–2.85 (m, 2 H), 2.61 (t, ^3J (HH) = 6 Hz, 2 H), 2.14–1.88 (m, 2 H); MS, *m/e* (rel intensity) 172 ($8^{\bullet+}$, 50), 143 ([8-CHO]$^+$, 71), 128 (100)]. Compound **8** was directly subjected to another hydrogenation step as above. Distillation of the crude product after workup gave **6b**, bp 83–86 °C, 0.01 mbar (55 mmol, 85%): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 9.71 (br s, 1 H), 7.15–7.11 (m, 4 H), 2.88–2.76 (m, 4 H), 2.49–1.33 (m, 4 H); MS, *m/e* (rel intensity) 174 ($\mathbf{6a}^{\bullet+}$, 17), 145 ([**6b**-CHO]$^+$, 16), 128 (100).

General Procedure for Spiroannelation. Compounds **6a** and **6b** (ca. 15 mmol) were transformed into **5a** or **5b**, respectively, according to the spiroannelation method of Kane and Jones.[6] Both **5a** and **5b** were obtained as colorless crystals after recrystallization from petroleum ether 60–80.

5,6,8,9-Tetrahydrospiro[7*H*-benzocycloheptene-7,4′-cyclohex-2′-en]-1′-one (5a). The yield was 5.25 mmol (35%): mp 143–144 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.14 (s, 4 H), 6.40 (AB system, (A) 6.85, (B) 5.95, *J*(AB) = 10 Hz, 2 H), 2.96–2.73 (m, 4 H), 2.60–2.38 (m, 2 H), 2.19–1.94 (m, 2 H), 1.82–1.61 (m, 4 H); MS, *m/e* (rel intensity) 226 ($\mathbf{5a}^{\bullet+}$ 68), 198 (21), 117 (100); IR (KBr), 1675 cm^{-1} (C=O). HRMS calcd for $C_{16}H_{18}O$ 226.1358, found 226.1355.

5,7,8,9-Tetrahydrospiro[6*H*-benzocycloheptene-6,4′-cyclohex-2′-en]-1′-one (5b). The yield was 8.5 mmol (57%): mp 65–66 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.12 (m, 4 H), 6.27 (AB system, (A) 6.67, (B) 5.87, *J* (AB) = 10 Hz, 2 H), 2.94 (AB system, (A) 3.07, (B) 2.81, *J*(AB) = 14 Hz, 2 H), 2.87 (m, 2 H), 2.44 (m, 2 H), 2.04–1.56 (m, 6 H); MS, *m/e* (rel intensity) 226 ($\mathbf{5b}^{\bullet+}$), 118 (32), 105 (100); IR (KBr) 1683 cm^{-1} (C=O). HRMS calcd for $C_{16}H_{18}O$ 226.1358, found 226.1356.

General Procedure for the Oxidation with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Compound **5** (ca. 5 mmol) and DDQ (1.69 g, 7 mmol) were dissolved in dioxane (30 mL) and heated under a nitrogen atmosphere at 100 °C for 20 h. The reaction mixture was cooled to room temperature and poured into 100 mL of diethyl ether/*n*-pentane (1:1). The organic phase was washed twice with 5% sodium hydroxide (20 mL), water (20 mL), and brine (10 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by recrystallization from petroleum ether 60–80 yielding colorless crystals of 4.

5,6,8,9-Tetrahydrospiro[7*H*-benzocycloheptene-7,4′-cyclohexa-2′,5′-dien]-1′-one (4a). The yield was 1.5 mmol (30%): mp 214–216 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.17 (s, 4 H), 6.75 (AB system, (A) 7.20, (B) 6.40, *J*(AB) = 10.3 Hz, 4 H), 3.08–2.95 (m, 4 H), 1.84–1.71 (m, 4 H); MS, *m/e* (rel intensity) 224 ($\mathbf{4a}^{\bullet+}$, 100), 222 (50), 209 (50), 117 (81); IR (KBr) 1660 cm^{-1} (C=O). HRMS calcd for $C_{16}H_{16}O$ 224.1201, found 224.1212.

5,7,8,9-Tetrahydrospiro[6*H*-benzocycloheptene-6,4′-cyclohexa-2′,5′-dien]-1′-one (4b). The yield was 3.3 mmol (66%): mp 102–103 °C. ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.16 (m, 4 H), 6.51 (AB system, (A) 6.80, (B) 6.21, *J*(AB) = 10.1 Hz, 4 H), 3.04–2.89 (m, 4 H), 1.96–1.82 (m, 4 H); MS, *m/e* (rel intensity) 224 ($\mathbf{4b}^{\bullet+}$, 15), 117 (8), 105 (100); IR (KBr) 1671 cm^{-1} (C=O). HRMS calcd for $C_{16}H_{16}O$ 224.1201, found 224.1201.

5,6,8,9-Tetrahydrospiro-4′-methylene[7*H*-benzocycloheptene-7,1′-cyclohexa-2′,5′-diene] (2a). Compound **4a** (1.5 mmol) was transformed according to the procedure described in

(14) Compound **7b** was purchased from Aldrich.

(15) Jenneskens, L. W., de Wolf, W. H., Bickelhaupt, F. *Tetrahedron* 1984, *40*, 3117.

ref 8a to afford **2a** (0.13 g, 0.6 mmol, 38%): mp 101–103 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.13 (s, 4 H), 6.13 (AB system, (A) 6.23, (B) 6.03, J(AB) = 10 Hz, 4 H), 4.87 (br s, 2 H), 2.88–2.81 (m, 4 H), 1.72–1.65 (m, 4 H); MS, m/e (rel intensity) 222 (**2a**$^{\bullet+}$, 27), 117 (100); HRMS calcd for $C_{17}H_{18}$ 222.1409, found 222.1399.

5,7,8,9-Tetrahydrospiro-4′-methylene[6*H*-benzocycloheptene-6,4′-cyclohexa-2′,5′-diene] (2b). Compound **4b** (0.7 mmol) was dissolved in Me_2SO (1 mL) and added at room temperature to the methylenetriphenylphosphorane which had been generated from methyltriphenylphosphonium bromide (0.25 g, 0.7 mmol) and sodium hydride (0.7 mmol) in Me_2SO (2 mL). The reaction mixture was stirred at room temperature for 2 h, and a sample was quenched with water (1 mL) and extracted with toluene (1.5 mL); the toluene was dried (Na_2SO_4) and evaporated to dryness at room temperature. The residue was dissolved in $CDCl_3$; the ^{1}H NMR spectrum (see Results and Discussion) revealed the presence of **4b** and **2b** in a ratio of about 1:1. On attempted purification, **2b** decomposed and only **4b** was isolated. When the original reaction mixture was stirred overnight and worked up as described for the sample after 2 h, ^{1}H NMR spectroscopy revealed the absence of **2b** and the presence of broad, polymer-type signals in the product.

Flash Vacuum Thermolysis (FVT) of 2 and 4, Respectively. The FVT equipment has been described earlier.[15] In our experiments, a 28-cm aluminum oxide tube and a pressure of 0.04 mbar were applied. In a typical experiment ca. 0.1 mmol of **2** and **4** was evaporated into the hot zone at a rate of 40 mg per h, by using a sublimation furnace (Büchi GKR 50) to heat the sample bulb. The pyrolysate was trapped in a cold trap cooled with dry ice in acetone at −70 °C. After pyrolysis of the substrate, the pyrolysate was collected from the cold trap by washing with diethyl ether. The solvent was evaporated at reduced pressure; the residue was ca. 55% for **2a**, 60% for **4a**, and 40% for **4b**, respectively (by weight). Products were isolated by preparative GLC (5% Carbowax on Chromosorb W, length 1.5 m at 160 °C). The products were identified on the basis of their spectral data and by an independent chemical identification (vide supra).

2-Vinyl-4′-methyldibenzyl (10): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.53–7.50 (dd ^3J(HH) = 5 Hz, ^4J(HH) = 3.5 Hz, 1 H), 7.23–7.11 (m, 7 H), 7.03, 5.68 and 5.32 (ABC system, J(AC) = 17.3 Hz, J(BC) = 10.9 Hz, and J(AB) = 1.4 Hz, 3 H), 3.00–2.82 (AA′BB′ system, 4 H), 2.34 (s, 3 H); MS, m/e (rel intensity), 222 (**10**$^{\bullet+}$, 9), 207 (13), 130 (42), 105 (100).

(*E*)-2-Ethyl-4′-methylstilbene (12a): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.60 (m, 1 H), 7.32 (AB system, (A) 7.43, (B) 7.21 J(AB) = 8.1 Hz, 4 H), 7.17 (AB system, (A) 7.34, (B) 6.99, J(AB) = 16.1 Hz, 2 H), 7.20 (br s, 3 H), 2.80 (q, ^3J(HH) = 7.6 Hz, 2 H), 2.38 (s, 3 H), 1.26 (t, ^3J(HH) = 7.6 Hz, 3 H); MS, m/e (rel intensity) 222 (**12a**$^{\bullet+}$, 100), 207 (41), 192 (31), 178 (17), 130 (42), 115(42), 115 (42), 105 (38); HRMS calcd for $C_{17}H_{18}$ 222.1408, found 222.1399.

2,2′-Dimethyldibenzyl (17): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.20 (br s, 8 H), 2.87 (s, 4 H), 2.34 (s, 6 H); MS, m/e (rel intensity) 210 (**17**$^{\bullet+}$, 18), 105 (100); HRMS calcd for $C_{16}H_{18}$ 210.1408, found 210.1410.

2-Ethyl-4′-vinyldibenzyl (19): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.37–7.32 (dd, ^3J(HH) = 8.2 Hz, ^4J(HH) = 3.8 Hz, 1 H), 7.18–7.14 (m, 7 H), 6.72, 5.74 and 5.52 (ABC system, J(AC) = 17.5 Hz, J(BC) = 10 Hz, and J(AB) = 1.5 Hz, 3 H), 2.89 (brs, 4 H), 2.33 (s, 3H); MS, m/e (rel intensity) 222 (**19**$^{\bullet+}$, 100), 207 (41), 192 (30), 178 (16), 130 (37), 115 (42), 105 (35).

***p*-Hydroxystyrene (30):** ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.05 (AB system, (A) 7.27, (B) 6.83, J(AB) = 8 Hz, 4 H), 6.65, 5.58, and 5.09 (ABC system, J(AC) = 17 Hz, J(BC) = 11 Hz, J(AB) = unresolved, 3 H), 4.27 (s, 1 H); MS, m/e (rel intensity) 120 (**30**$^{\bullet+}$, 100), 94 (3), 91 (34), 65 (12); HRMS calcd for C_8H_8O 120.0575, found 120.0575.

2-Vinyl-4′-hydroxydibenzyl (31): ^{1}H NMR ($CDCl_3$, 90 MHz) δ 7.56–7.44 (m, 1 H), 7.22–7.07 (m, 7 H), 6.89, 5.64, and 5.29 (ABC system, J(AC) = 17.1 Hz, J(BC) = 11 Hz, J(AB) = ca. 1.5 Hz, 3 H), 4.62 (br s, 1 H), 3.07–2.76 (m, 4 H); MS, m/e (rel intensity) 224 (**31**$^{\bullet+}$, 15), 117 (9), 107 (100).

General Procedure for the Wittig Reaction. To a solution of (*p*-methylbenzylidene)triphenylphosphorane (**20**) or (*o*-methylbenzylidene)triphenylphosphorane (**23**) (ca. 20 mmol, respectively, prepared from the corresponding phosphonium salts according to ref 11, was added *o*-ethylbenzaldehyde (**21**) or *p*-ethylbenzaldehyde (**24**), respectively (ca. 20 mmol). The reaction mixture was stirred for 3 h at 60 °C. After having been cooled to room temperature, the reaction mixture was poured into 0.1 M HCl (100 mL). After the addition of an extra amount of water (100 mL), the aqueous phase was extracted twice with diethyl ether (75 mL). The combined organic phases were washed with saturated bicarbonate solution, dried ($MgSO_4$), and concentrated at reduced pressure. The residue was dissolved in *n*-pentane (100 mL) and stirred for 0.5 h. The precipitate of triphenylphosphine oxide was filtered off, and the filtrate was evaporated to dryness, yielding crude (**12** or **25**, respectively, in ca. 70% yield. It was established that both **12** and **25** were a mixture of *E*- and *Z*-isomers in a ratio of ca. 1:1 by GLC. Analytially pure samples were obtained by preparative GLC (5% Carbo-wax, length 1.5 m, 150 °C (**12**) and 110 °C (**25**), respectively). On the basis of their ^{1}H NMR data, the *E*- and *Z*-isomers could be assigned unambiguously.

(*E*)-2-Ethyl-4′-methylstilbene (12a): vide supra.

(*Z*)-2-Ethyl-4′-methylstilbene (12b): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.24–7.05 (m, 4 H), 6.99 (AB system, (A) 7.00, (B) 6.97, J(AB) = 8.5 Hz, 4 H), 6.62 (AB system, (A) 6.67, (B) 6.58, J(AB) = 12.2 Hz, 2 H), 2.67 (q, ^3J(HH) = 7.6 Hz, 2 H), 2.28 (s, 3 H), 1.21 (t, ^3J(HH) = 7.6 Hz, 2 H); MS m/e (rel intensity) 222 (**12b**$^{\bullet+}$, 100), 207 (56), 192 (31), 178 (24), 130 (19), 115 (23), 105 (34); HRMS calcd for $C_{17}H_{18}$ 222.1408, found 222.1402.

(*E*)-4-Ethyl-2′-methylstilbene (25a): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.61 (d, 6.7 Hz, 1 H), 7.37 (AB system, (A) 7.48, (B) 7.26, J(AB) = 8.0 Hz, 4 H), 7.15 (AB system, (A) 7.30, (B) 7.00, J(AB) = 16.5 Hz, 2 H), 7.19 (br s, 3 H), 2.68 (q, ^3J(HH) = 7.6 Hz, 2 H), 2.44 (s, 3 H), 1.27 (t, ^3J(HH) = 7.6 Hz, 3 H); MS, m/e (rel intensity) 222 (**25a**$^{\bullet+}$, 100), 207 (28), 193 (31), 178 (22), 119 (32); HRMS calcd for $C_{17}H_{18}$ 222.1408, found 222.1408.

(*Z*)-4-Ethyl-2′-methylstilbene (25b): ^{1}H NMR ($CDCl_3$ 250 MHz) δ 7.20–7.17 (m, 4 H), 7.02 (AB system, (A) 7.04, (B) 7.00, J(AB) = 8.6 Hz, 4 H), 6.60 (s, 2 H), 2.58 (q, ^3J(HH) = 7.6 Hz, 2 H), 2.28 (s, 3 H), 1.19 (t, ^3J(HH) = 7.6 Hz, 3 H); MS, m/e (rel intensity) 222 (**25b**$^{\bullet+}$, 100), 207 (40), 193 (35), 178 (26), 115 (14); HRMS calcd for $C_{17}H_{18}$ 222.1408, found 222.1411.

Catalytic Hydrogenation. A solution of 0.2 g (0.9 mmol) of **12** or **25**, respectively (1:1 mixture of *E*- and *Z*-isomers), and 0.1 g of 5% Pd/C in ethanol (10 mL) was hydrogenated at atmospheric pressure and room temperature for 1 h. After filtration, the filtrate was evaporated at reduced pressure, yielding a residue of **22** or **26**, respectively (0.85 mmol, 94%). An analytically pure sample was obtained by preparative GLC (5% Carbowax, 180 °C).

2-Ethyl-4′-methyldibenzyl (22): ^{1}H NMR ($CDCl_3$, 250 MHz), δ 7.26–7.16 (m, 8 H), 3.00–2.88 (m, 4 H), 2.74 (^3J(HH) = 7.5 Hz, 2 H), 2.40 (s, 3 H), 1.29 (t, ^3J(HH) = 7.5 Hz, 3 H); MS, m/e (rel intensity) 224 (**22**$^{\bullet+}$, 39), 119 (50), 105 (100); HRMS calcd for $C_{17}H_{20}$ 224.1565, found 224.1572.

4-Ethyl-2′-methyldibenzyl (26): ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.23–7.15 (m, 8 H), 2.91–2.82 (m, 4 H), 2.65 (q, ^3J(HH) = 7.6 Hz, 2 H), 2.33 (s, 3 H), 1.25 (t, ^3J(HH) = 7.6 Hz, 3 H); MS, m/e (rel intensity) 224 (**26**$^{\bullet+}$, 40), 119 (100), 105 (43); HRMS calcd for $C_{17}H_{20}$ 224.1565, found 224.1560.

Independent Synthesis of 2,2′-Dimethyldibenzyl (17). To a solution of 2-(methylbenzyl)magnesium chloride, prepared from 2-methylbenzyl chloride (ca. 10 mmol) and magnesium (ca. 20 mmol) in diethyl ether (20 mL), a solution of 2-methylbenzyl chloride (ca. 10 mmol) in tetrahydrofuran (5 mL) was added under reflux. The reaction mixture was heated under reflux for 1 h. After having been cooled to room temperature, excess magnesium was destroyed by slowly adding 1 M HCl (10 mL). The aqueous phase was extracted with diethyl ether twice (20 mL). The combined organic layers were washed with water and brine, dried ($MgSO_4$), and concentrated under reduced pressure, yielding a residue of crude **17** in ca. 60% yield (ca. 6 mmol). An analytically pure sample was obtained by preparative GLC (5% Carbowax, 160 °C). Its spectral data were in agreement with those described above.

Acknowledgment. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid (L.W.J.) from the Netherlands Organization for the Advancement of Pure Research

(ZWO). We gratefully acknowledge valuable comments by the referees.

Registry No. **2a**, 101954-98-7; **2b**, 101954-99-8; **4a**, 101955-00-4; **4b**, 101955-01-5; **5a**, 101955-02-6; **5b**, 101955-03-7; **6a**, 101955-04-8; **6b**, 101955-05-9; **7a**, 37949-03-4; **7b**, 826-73-3; **8**, 97232-13-8; **9**, 54949-01-8; **10**, 101955-06-0; **12a**, 101955-07-1; **12b**, 101955-08-2; **17**, 952-80-7; **19**, 101955-09-3; **20**, 39110-21-9; **21**, 22927-13-5; **22**, 101955-10-6; **23**, 59659-68-6; **24**, 4748-78-1; **25a**, 101955-11-7; **25b**, 101955-12-8; **26**, 101955-13-9; **30**, 2628-17-3; **31**, 101979-24-2; (methoxymethylene)triphenylphosphorane, 20763-19-3; 6,7,8,9-tetrahydro-7-(methoxymethylene)-5*H*-benzocycloheptene, 101955-14-0; methylenetriphenylphosphorane, 3487-44-3; 2-methylbenzyl chloride, 552-45-4.

The Philicity of Fluorophenoxycarbene

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Received November 30, 1985

Fluorophenoxycarbene (FCOPh) was generated by thermolysis (50 °C) of 3-fluoro-3-phenoxydiazirine and added to six alkenes, affording the corresponding cyclopropanes. The substrates and relative reactivities were the following: tetramethylethylene (7.14), trimethylethylene (17.9), isobutene (14.3), 1-hexene (1.00), methyl acrylate (18.7), and acrylonitrile (33.6). The ambiphilic reactivity pattern of FCOPh resembles those of ClCOPh and ClCOMe. An ab initio study of FCOPh afforded geometries and frontier orbital energies for the cis and trans conformers of the carbene. Both conformers are predicted to be ambiphiles in alkene addition reactions, on the basis of simple frontier molecular orbital considerations.

One operational distinction between electrophilic, ambiphilic, and nucleophilic carbenes is based upon their differing selectivities toward olefinic substrates in the carbene/olefin cyclopropanation reaction.[1] *Electrophilic* carbenes add with increasing rate to alkenes of increasing π-electron richness (decreasing π-ionization potential); *nucleopilic* carbenes add with increasing rate to alkenes of decreasing π-electron availability (increasing π-ionization potential); *ambiphilic* carbenes exhibit a parabolic dependence on alkene π-electron availability that is characterized by high reactivity toward both electron-rich and electron-poor alkenes but low reactivity toward alkenes of intermediate electronic character.

This spectrum of carbenic reactivity can be understood in terms of frontier molecular orbital (FMO) interactions[1,2] and can be anticipated by estimation of the "carbene selectivity index," m_{CXY}.[1,3] Experimentally, m_{CXY} is defined (and measurable for electrophilic carbenes) as the least-squares slope of the correlation between log $(k_i/k_o)_{CXY}$ vs. log $(k_i/k_o)_{CCl_2}$, where the relative reactivities refer to the additions of the carbenes to a "standard" set of alkenes at 25 °C.[3] The observed dependence of m_{CXY} on the X and Y substituents of 9 carbenes, CXY, is correlated by eq 1, where $\sum_{X,Y}$ represents the sum of the appropriate substituent constants for X and Y, and m_{CCl_2} is set equal to unity.[1,3]

$$m_{CXY} = -1.10\sum_{X,Y}\sigma^+_R + 0.53\sum_{X,Y}\sigma_I - 0.31 \quad (1)$$

Using measured and calculated (from eq 1) values of m_{CXY}, we constructed a "carbene selectivity spectrum", locating carbenes according to the magnitude of m_{CXY}.[1,4] The resulting "spectrum" showed that experimentally nucleophilic carbenes, such as $(MeO)_2C$[5] and $MeOCNMe_2$,[6] had $m_{CXY} \gtrsim 2.2$, whereas typical electrophilic carbenes, such as CF_2,[7] had $m \lesssim 1.5$.[1,4] Thus, ambiphilic carbenes were expected to reside in the "intermediate" region of the selectivity spectrum; i.e., $1.5 \lesssim m_{CXY} \lesssim 2.2$.

Experiments subsequently demonstrated that both chloromethoxycarbene,[8-10] $m_{CXY}^{calcd} = 1.59$, and chlorophenoxycarbene,[11,12] $m_{CXY}^{calcd} = 1.49$,[11] did indeed behave as ambiphiles toward C=C-substituted alkenes and ring-substituted styrenes.

The known electrophilic carbene of highest m_{CXY}, CF_2[7] ($m_{CF_2}^{calcd} = 1.47$; $m_{CF_2}^{obsd} = 1.48$)[1] has a carbene selectivity index that is nearly identical with that of ClCOPh, so that the "border" between electrophilic and ambiphilic carbenes appears to lie a bit below 1.50. Where is the border between ambiphilic and nucleophilic carbenes? It must lie between 2.22, m_{CXY}^{calcd} for the nucleophilic dimethoxycarbene, and 1.59, m_{CXY}^{calcd} for the ambiphilic chloromethoxycarbene.

Recently, fluorophenoxydiazirine, a precursor for fluorophenoxycarbene (FCOPh), became available.[13] Using σ^+_R (PhO) = −0.87, σ^+_R(F) = −0.57, σ_I(PhO) = 0.38, and σ_I (F) = 0.50,[14] we can calculate from eq 1 that m_{CXY} = 1.74

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0022-3263/86/1951-2168$01.50/0