Anal. Calcd for C₄H₅N₃OS: C, 33.56; H, 3.52; N, 29.35. Found: C, 33.30; H, 3.55; N, 29.55.

Registry No.—2, 14337-41-8; 5, 37150-52-0; 6, 37150-53-1.

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A Simple Synthesis of the Cis,cis and Trans,trans Isomers of Tetrabenzo[a,c,g,i]cyclododecene (sym-Tetrabenz[12]annulene)¹

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The stereoisomeric tetrabenzo[a,c,g,i]cyclododecenes (sym-tetrabenz[12]annulenes) (2) are interesting compounds, about which there has been some confusion in the literature. In 1955, Wittig, et al.,³ reported that Hofmann degradation of cis-1 leads to two isomers of 2, mp 297.5-298 and 163-164°, to which they ascribed the cis,cis and trans,trans stereochemistry, respectively. Very recently, it has been shown by Irngartinger⁴ and by Wittig and Skipka⁵ that the lower melting isomer in fact has the cis,trans configuration, and we independently came to the same conclusion by repetition of Wittig's synthesis.³ Moreover, Wittig and Skipka⁵ have shown that dehydration of **3a** and **3b** gives rise to



three stereoisomers of 2, mp (corrected) 306-306.5, 253.5, and $301-301.5^{\circ}$; the first of these proved to be the cis, cis compound obtained previously, the second appears to be another cis, cis isomer, while the third is the trans, trans isomer.

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Several years ago we required the tetrabenz[12]annulene 2 as a synthetic intermediate, and we devised a simple synthesis through the Wittig reaction between 2,2'-bis(triphenylphosphoniomethyl)biphenyl dibromide (4)⁶ and 2,2'-biphenyldicarboxaldehyde (5).⁷ This led in low yield to an isomer of 2, mp 296-297°, which we considered⁸ to be Wittig's cis,cis compound³ in view of the correspondence of the melting points, ir spectra, and uv spectra.⁹ The reaction between 4 and 5 has also been investigated by Bergmann, et al.,^{5,10} who apparently obtained Wittig's cis,trans and trans,trans isomers of 2. No details of the reaction between 4 and 5 have been published previously, and Staab, et al.,¹¹ thereby could obtain only traces of 2.

We now report the details of a reinvestigation of the Wittig reaction between 4 and 5. When the reaction was carried out with lithium methoxide in methanol under relatively high dilution conditions, both *cis,cis-2*, mp 296-297° (1.1%), and *trans,trans-2*, mp 302-303° (4.2%), could be isolated by chromatography and fractional crystallization. The structures and stereo-chemistry of these products are based on their spectral



properties, and are confirmed by the correspondence of the spectra and melting points with those reported by Wittig, *et al.*^{3,5} In the case of *cis,cis-2*, direct comparison with a sample obtained from *cis-1* confirmed their identity.

The reaction between 4 and 5 also gave rise to the all-cis tri(biphenyl) derivative 6, mp 181-182° (1.5%), the structure of which is based on the spectral data. The all-cis stereochemistry follows from the absence of a strong trans ethylene band at ~960 cm⁻¹ in the ir spectrum; it is confirmed by the fact that the olefinic protons resonate as a singlet at τ 3.88 in the nmr spectrum, showing both double bonds to have the same

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Notes

stereochemistry and indicating the cis configuration (cis-stilbene, τ 3.45; trans-stilbene, τ 2.90).¹²

The reaction between 4 and 5 was also carried out with lithium ethoxide in dimethylformamide and ethanol (8:1) under more concentrated conditions than used. before. This experiment led to trans, trans-2 in 5.5% yield, although other products were not investigated in this case.

The finding that the reaction between 4 and 5 leads to both cis, cis-2 and trans, trans-2 partly explains the different results reported by Bergmann, et al.,^{5,10} and by us.⁸ However, we have not been able to confirm Bergmann's isolation of cis, trans-2 from this reaction, despite the fact that quite small quantities would have been detected by the typical nmr spectrum.

Experimental Section

Melting points were determined on a Kofler micro hot stage apparatus and are uncorrected. Uv spectra were measured on a Unicam SP 800 and ir spectra on a Unicam SP 200 spectrophotometer. Nmr spectra were determined on a Varian T-60 spectrometer, tetramethylsilane being used as an internal standard. Mass spectra were obtained on an AEI MS-9 spectrometer operating at 70 eV.

Reaction between 2,2'-Bis(triphenylphosphoniomethyl)biphenyl Dibromide (4) and 2,2'-Biphenyldicarboxaldehyde (5). With Lithium Methoxide in Methanol.--A solution of 46 Α. (21.0 g, 24.3 mmol) and 5^7 (5.1 g, 24.3 mmol) in dry methanol (500 ml) was added through one dropping funnel at the same rate as a solution of lithium (700 mg, 100 mmol) in dry methanol (500 ml) was added through a second funnel to dry methanol (4 1.) stirred under nitrogen in a 10-l. three-neck flask, over the course of 12.5 hr. The resulting pale yellow solution was stirred at room temperature under nitrogen for a further 12 hr, and the solvent was then removed under reduced pressure $(<30^\circ)$. Ether (1.5 l.) was added, and the mixture was washed well with dilute hydrochloric acid and then with water. The dried solution was evaporated, and the residue was chromatographed on silica gel (500 g).

Pentane eluted 2,2'-dimethylbiphenyl (650 mg, 15%), the ir spectrum of which was identical with the published one.¹³ Pentane-benzene (95:5) then eluted 2 (\sim 500 mg), the nmr spectrum of which showed that it consisted of the cis,cis and trans,trans isomers in a ratio of \sim 1:4. Further elution with pentanebenzene (95:5 to 90:10) led to 6 (99 mg, 1.5% based on 4), as colorless crystals from petroleum ether (bp 40-60°): mp 181-182°; λ_{max} (cyclohexane) 290 nm (ϵ 22,900); ir (KBr), only weak band (at 955 cm⁻¹) in 950–1000-cm⁻¹ region; nmr (CCl₄) τ 2.4– 3.2 (m, 24 H, benzenoid), 3.88 (s, 4 H, olefinic), 7.88 (s, 6 H, methyl); mass spectrum m/e 538.267 (calcd 538.266).

Anal. Calcd for C₄₂H₃₄: C, 93.63; H, 6.37. Found: C, 93.59; H, 6.45.

Later fractions contained a mixture of stereoisomers of 6 (as determined by the nmr, ir, and mass spectra), but these were not investigated further.

Fractional crystallization of the isomers of 2 from ethyl acetate led to the pure cis, cis isomer (95 mg, 1.1%) and trans, trans isomer (365 mg, 4.2%). cis,cis-2 formed colorless crystals: mp 296–297°; λ_{max} (cyclohexane) 240 nm (ϵ 31,900); ir (KBr) only weak bands (960, 980 cm⁻¹) in 950–1000-cm⁻¹ region; nmr (CCl₄) τ 2.35–3.15 (m, 16 H, benzenoid), 4.18 (s, 4 H, olefinic); mass spectrum m/e 356.155 (calcd 356.156). The melting point was undepressed on admixture with a sample (mp 295-296°) obtained from cis-1, and the uv, ir, and nmr spectra were essentially identical. trans, trans-2 formed colorless crystals: mp 302-303 (depressed on admixture with cis,cis-2); λ_{max} (cyclohexane) 226 nm (ϵ 32,200), 248 sh (24,100), 266 (34,100); ir (KBr) 955 cm⁻¹ (s); nmr (CCl₄) τ 2.6-3.0 (m, 16 H, benzenoid), 3.82 (s, 4 H, olefinic); mass spectrum m/e 356.155 (calcd 356.156).

Anal. Calcd for C28H20: C, 94.34; H, 5.65. Found: C, 94.14; H, 5.55.

B. With Lithium Ethoxide in Dimethylformamide and Ethanol.—A solution of lithium (500 mg, 72 mmol) in dry ethanol (50 ml) was added during 4.5 hr to a stirred solution of 4 (8.65 g. 10 mmol) and 5 (2.1 g, 10 mmol) in dry dimethylformamide (400 ml), at room temperature under nitrogen. The dark brown solution was stirred for 16 hr, and was then poured into ice containing concentrated hydrochloric acid. The organic material was extracted with ether, and the ether extract was washed with water, dried, and evaporated. The residue was chromatographed on a column of silica gel $(75 \times 3.5 \text{ cm})$. Elution with petroleum ether-benzene (80:20) and crystallization from ethyl acetate gave trans, trans-2 (197 mg, 5.5%), mp 303-304°. The melting point was undepressed on admixture with the previously obtained sample, and the uv, ir, and nmr spectra were identical.

Registry No.—cis,cis-2, 37445-16-2; trans,trans-2, 37445-17-3; 4, 37439-54-6; 5, 1210-05-5; 6, 37445-18-4.

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Preparation of 11-Substituted 5.6-Dihydro-11H-6-oxodibenzo[b,e]azepines (Morphanthridines) and Their **N-Dimethylaminoethyl Derivatives**¹

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Enhanced stability of extensively delocalized carbanions, arising from the dispersion interaction³ with dipolar aprotic solvents, favors the formation of Jackson-Meisenheimer complexes⁴ (1) by the conjugate addition to 9-nitroanthracene of various nucleophiles.⁵ Quenching and acidification of the reaction mixtures permit isolation of the adducts (2); the stereochemistry, spectral characteristics, properties, and some chemical transformations of these adducts have been reported.⁵ Addition of benzyl halide to solutions of the Jackson-Meisenheimer complexes prior to work-up results in the formation of oximes $(3)^5$ and benzaldehyde, the products of the Hass-Bender reaction.⁶

Beckmann rearrangement of these oximes provides 11-substituted 5,6-dihydro-11H-6-oxodibenzo[b,e]azepines (5). Many tricyclic compounds of structures similar to 5 with a dialkylaminoalkyl moiety bonded to an atom of the central ring have pharmacological, and in particular, pyschotropic activity.7 Most notable among these are the tricyclic antidepressants imipramine and amitriptylene; the structure of dibenzepin,⁸

(1) Grateful acknowledgment is made to the U.S. Army Research Office for partial support of this work (Grants DA-ARO(D)-G679 and G857).

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