(4.54), 241 (4.73), 284 (4.83), 293 (4.91), 303 (5.27), 321 (4.17), 331 (4.07), 351 (3.77), 371 (3.71), 389 (3.77), 406 (3.78), 412 (3.77); ^{1}H NMR (see Table I); ^{13}C NMR δ 155.4, 150.8, 131.9, 129.1, 128.8, 128.0, 127.6, 127.2, 123.3, 117.1, 112.8, 95.4, 94.1; mass spectrum, m/e 324.0939, calcd 324.0939 for $C_{26}H_{12}$.

Benzo[7,8]cyclodeca[1,2,3,4-*def*]biphenylene (10). Hydrocarbon **10** was prepared from *o*-phthaldehyde (0.41 g, 3.06 mmol; recrystallized from hexanes), in a manner analogous to that of **11**, and isolated as a yellow solid (0.0661 g, 21% yield based on the 1,8-bis(phosphonium) salt): ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.23-6.91 (complex multiplet, 4 H), δ 6.74-6.28 (complex multiplet, 10 H); mass spectrum, m/e (relative intensity) 280 (2.3), 279 (21.9), 278 (100.0, M^+), 277 (92.6), 276 (68.3), 274 (19.6), 138 (59.6), 137 (18.0), 125 (16.2).

5,6,9,10-Tetrabromo-5,6,9,10-tetrahydrobenzo[7,8]cyclodeca[1,2,3,4-*def*]biphenylene (12). The tetrabromide **12** was prepared from **10**, by the addition of 0.708 M Br_2/CCl_4 (0.58 mL, 0.41 mmol) solution, in a manner analogous to that of **13**, and isolated as a thick yellow oil (0.0742 g, 56%): ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.23-6.20 (complex multiplet, 11.14 H; including δ 6.48 (d, J = 8 Hz, 1.14 H)), δ 5.93 (d, J = 12 Hz, 0.86 H), o 5.53 (d, J = 8 Hz, 1.14 H), δ 5.00 (d, J = 12 Hz, 0.86 H).[42]

5,6,9,10-Tetradehydrobenzo[7,8]cyclodeca[1,2,3,4-*def*]biphenylene (2). Hydrocarbon **2** was prepared by dehydrohalogenation of **12** with KO-*t*-Bu (0.1023, 0.912 mmol), in a manner analogous to that of **3**, and isolated as amber radial crystalline patches of **2** (0.0299 g, 88%): slowly dec[5] >160 °C; UV λ_{max} (log ϵ_o) 235 (4.17), 263 (4.75), 268 (4.76), 278 (4.88), 292 (4.51), 301 (4.31), 309 (4.42), 353 (3.48), 372 (3.66), 392 (3.79); ^{1}H NMR (see Table I); ^{13}C NMR δ 155.0, 150.8, 129.0, 128.9, 127.7, 127.4, 127.0, 116.7, 112.5, 96.0, 95.2; mass spectrum, m/e 274.0778, calcd 274.0782 for $C_{22}H_{10}$.

Registry No. **2**, 100229-92-3; **3**, 100229-93-4; **4**, 53397-65-2; **6**, 36230-18-9; **7**, 100229-97-8; **8**, 643-79-8; **9**, 7149-49-7; **10**, 100230-00-0; **11**, 100229-98-9; **12**, 100230-01-1; **13**, 100229-99-0; **14**, 2169-87-1; **15**, 31554-15-1; **16**, 38998-33-3; **17**, 100229-94-5; **18**, 100229-95-6; **19**, 501-65-5; **20**, 58150-58-6; **21**, 53397-66-3; **22**, 7203-21-6; **23**, 6555-54-0; **24**, 27559-98-4; **25**, 5385-26-2; **26**, 100229-96-7.

Diels-Alder Reactions of Protoporphyrin IX Dimethyl Ester with Electron-Deficient Alkynes

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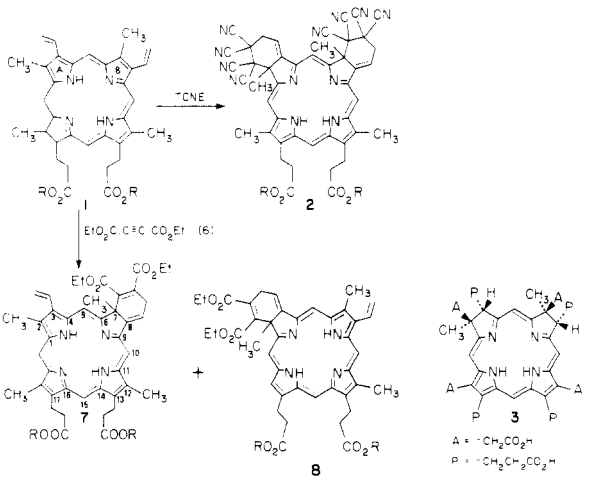
The vinyl and cross-conjugated porphyrin β,β' double bonds of either ring A or B of protoporphyrin IX dimethyl ester react in a [4 + 2] cycloaddition with electron-deficient acetylenes. The methyl and ethyl esters of acetylenedicarboxylic acid and β-(phenylsulfonyl)propiolic acid react to give the corresponding chlorins with the ring A and B isomers being readily separable by chromatography. The initial products are rearranged by treatment with base. Reaction with triethylamine or 1,5-diazabicyclo[5.4.0]undec-5-ene gave, in every case, two diastereomers, where the former rearrangement led to the kinetically controlled and the latter the thermodynamically controlled products. The Diels-Alder reaction with the unsymmetric acetylenes is both regio- and stereospecific.

We have shown that tetracyanoethylene (TCNE) reacts with protoporphyrin IX dimethyl ester (**1**) in both [2 + 2] and [2 + 4] cycloaddition reactions.[1] One of the products from the Diels-Alder reaction at both rings A and B (**2**) had a chromophore similar to that of sirohydrochlorin[2] (**3**). The iron complex of **3**, siroheme[3] (**4**), is the prosthetic group for sulfite[4] and nitrite[5] reductases; and **3**, or a reduction product, is a biosynthetic precursor of vitamin B_{12}.[6]

Numerous isobacteriochlorin models for sirohydrochlorin have been prepared.[7-9] However, we[10] and others[11] have suggested that an internal electron transfer might account for part of the reduction processes mediated by these macrocycles. Such a process would require the specific substitution pattern found in both rings A and B of siroheme. To this end we are planning to use the Diels-Alder

Scheme I



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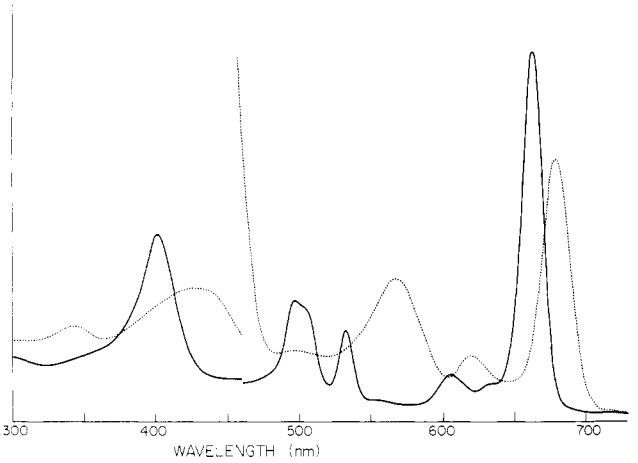


Figure 1. Optical spectra (CH_2Cl_2) of **7** (—) and its rearranged isomer **9** (...). The corresponding ring A isomers (**8** and **10**) have spectra identical with the ring B partners.

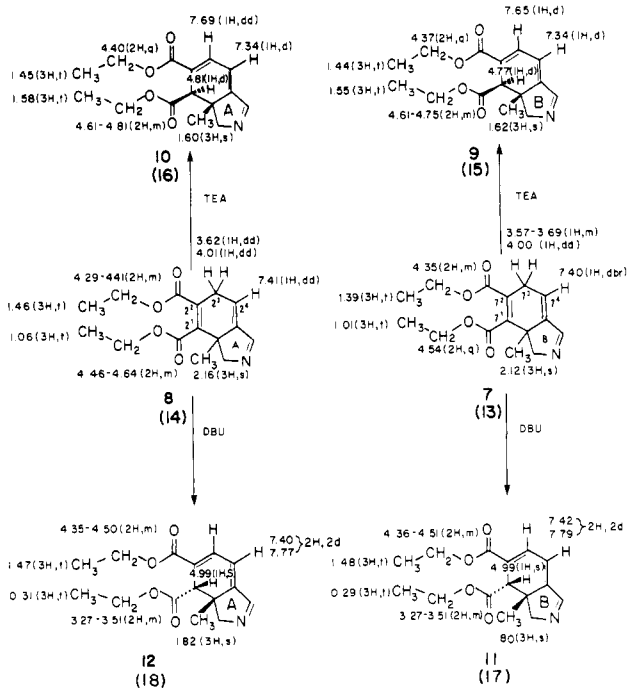
chemistry, previously described,[12] to prepare **3** from a preformed porphyrin.

Results and Discussion

Johnson and co-workers[13] had suggested that both TCNE and dimethyl acetylenedicarboxylate (**5**, DMAD) reacted with **1** to give only the corresponding isobacteriochlorins. Rather than giving one compound, the former reaction gave eight characterizable products,[1] and, as outlined below, the latter reaction gives chlorins rather than isobacteriochlorins. Refluxing **1** with a 20-fold molar excess of diethyl acetylenedicarboxylate (**6**, DEAD) in toluene gave, after 6 days, a mixture with a strong absorption at 666 nm (characteristic of chlorins)[14] (Figure 1). The isomeric chlorins (**7** and **8**, Scheme I) were separated on silica by using CH_2Cl_2/CH_3OH. The faster, less polar compound was the ring B (**7**) and the more polar ring A (**8**) isomer as shown by their ^1H NMR spectra (discussed below).

During chromatography a small amount of material absorbing at 686 nm was formed. The same products **9** and **10** (Scheme II) could be quantitatively obtained, from **7** and **8**, respectively, by treatment with triethylamine (TEA) in CH_2Cl_2 after 2-h reflux or upon standing at room temperature overnight. The bathochromic shift upon base treatment (Figure 1) was suggestive of the rearrangement **7** → **9** (and **8** → **10**) and this was confirmed by NMR spectroscopy. Scheme II shows the chemical shifts of the ring A and ring B substituents before and after rearrangement with TEA. The most significant changes are the appearance of a new signal at ~4.8 ppm for the new sp^3 carbons at C-2^1 and C-7^1 in **9** and **10** and the change from two protons to one at the newly generated (C-2^3 and C-7^3) sp^2 carbon atoms of **9** and **10**. Significant changes are also observed with the signals of the ethyl esters. In every case the protons of the methylene groups are diasterotopic and usually show up as multiplets. The methyl protons of the ethyl groups, after rearrangement, show only a small upfield shift, suggesting that they cannot readily approach the porphyrin ring. A surprising observation, considering the ethoxycarbonyl group becomes attached to a tetrahedral carbon (2^1 or 7^1) upon rearrangement, unless the angular methyl group (at C-2 or C-7) can block its approach. This is in fact the case since treatment of **7** and **8** (or **9** and **10**) with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) gives two additional rearranged isomers **11** and **12** (Scheme II). These two new compounds have optical spectra identical with those of **9** and **10**, and they differ only in the geometric arrangement of the ethoxycarbonyl groups, at C-2^1 and C-7^1 with respect to the angular methyl at C-2 and C-7. Treatment of **11** or **12** with TEA does not cause any further isomerization, and we conclude that **11** and **12** represent the thermodynamically stable pair of isomers while **9** and **10** are the kinetically controlled products. The more stable, less strained, trans configuration (with respect to the methyl (at C-2 and C-7) and ethoxycarbonyl groups (at C-2^1 and C-7^1)) for **11** and **12** was confirmed by a positive NOE effect between the C-2 methyl and C-2^1 proton of the Ring A isomer and the C-7 methyl and C-7^1 proton of the ring B isomer for **12** and **11**, respectively. No such NOE effect was observed for **9** and **10**.

Scheme II. Relevant ^1H NMR Chemical Shifts ($CHCl_3$, δ) for the Ring A and B Diels-Alder Products 8 and 7 and Their "Cis" (10, 9) and "Trans" (12, 11) Rearranged Isomers[a]



[a] For compounds **13**–**18**, $-CO_2CH_3$ instead of $-CO_2CH_2CH_3$.

Further evidence of the assigned conformations for the pairs of rearranged isomers was indicated by the small allylic coupling between the protons on C-2^1 and C-2^3 of **10** and C-7^1 and C-7^3 of **9**. The degree of allylic coupling is dependent upon the dihedral angle between the π-system and the C–H bond of the allylic proton.[15] Examination of a model shows that in **9** and **10** the allylic proton is parallel to the plane of the π-cloud, consistent with the observed 3-Hz coupling. In the case of **11** and **12** the model shows that the allylic protons are perpendicular to the π-plane accounting for the lack, as observed, of allylic coupling.

Finally, since the ethoxycarbonyl groups at C-2^1 and C-7^1 of **11** and **12** are trans to the angular methyl group (occupying a pseudoaxial position), they are free to rotate over

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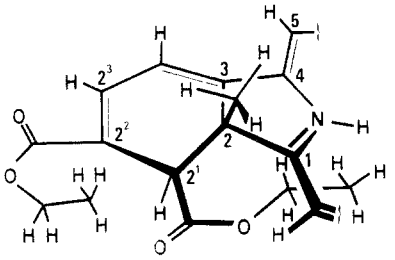

Figure 2. Three-dimensional representation of the rearranged isomer **11** showing the pseudoaxial ethoxycarbonyl group at C-2′ extending into the deshielding region of the "chlorin" π-system.

the porphyrin ring (Figure 2). This is shown by the upfield shift of the methyl groups of the C-2[1] and C-7[1] ethoxycarbonyl groups which appear at 0.31 and 0.29 ppm due to the shielding effect of the aromatic porphyrin system.

Reaction of protoporphyrin IX dimethyl ester (**1**) with dimethyl acetylenedicarboxylate (**5**) proceeds more rapidly than with DEAD but gives the same overall yield of the two, readily separable, isomers **13** and **14** analogous to **7** and **8**. The faster reaction rate presumably reflects less steric hindrance for the methoxycarbonyl as opposed to the ethoxycarbonyl group in the region of the angular methyl group. Otherwise the products, **13** and **14**, behave in a manner similar to **7** and **8**. Thus when treated with TEA the cis isomers **15** and **16** are formed; reaction of **13** or **15** with DBU gives the trans isomer **17**, while **14** and **16** give **18** with DBU. Once again a single methoxycarbonyl group of **17** and **18** shows an upfield shift (at δ 2.95) while the remaining methoxycarbonyl groups of **17** and **18** and those of **13**–**16** appear between 3.93 and 4.25 ppm.

While the reactions between **1** and the esters of acetylenedicarboxylic acid give an indication of the Diels–Alder chemistry and the facile rearrangements of the products, the compounds thus derived do not readily lend themselves to manipulation toward sirohydrochlorin (**3**). Toward this end we have examined the reaction of **1** with the unsymmetric ethyl β-(phenylsulfonyl)propiolate[16] (**19**). The Diels–Alder reaction is both faster (20 h, refluxing CH_2Cl_2) and gives a higher yield, 68%, of ring B (**20**) and A (**21**) isomers which were separable on silica gel. Both isomers showed a strong absorption at 662 nm consistent with their chlorin-like structures.

The NMR spectra of **20** and **21** show some pecularities but allow for the definitive assignment of the ring A and B isomers. In the 400-MHz room-temperature NMR spectra of both **20** and **21**, only three sharp signals for the meso protons are seen, the fourth meso proton occurring as a broad signal. In both cases the ethyl group of the ester is also very broad with the methyl protons appearing at ~1 ppm and spread over 1 ppm while the methylene protons are even more diffuse in the region of 4.5 ppm. When the spectrum is measured at 100 MHz, all of these signals sharpen up. At 50°, in the 400-MHz spectrum, the meso proton becomes sharper while the whole ethyl group becomes more diffuse. In addition, the phenyl and vinyl protons (see below) are also broader than usual.

Inspection of a model shows that the ethoxycarbonyl and phenylsulfonyl groups flanking the C-20 meso proton of **21** and the same substituents with the vinyl group flanking the C-5 meso proton of **20** are sterically constrained, and hindered rotation of these groups can be expected (Figure 3). Since the majority of signals in the NMR spectra of **20** and **21** are not broadened, it is unlikely that the

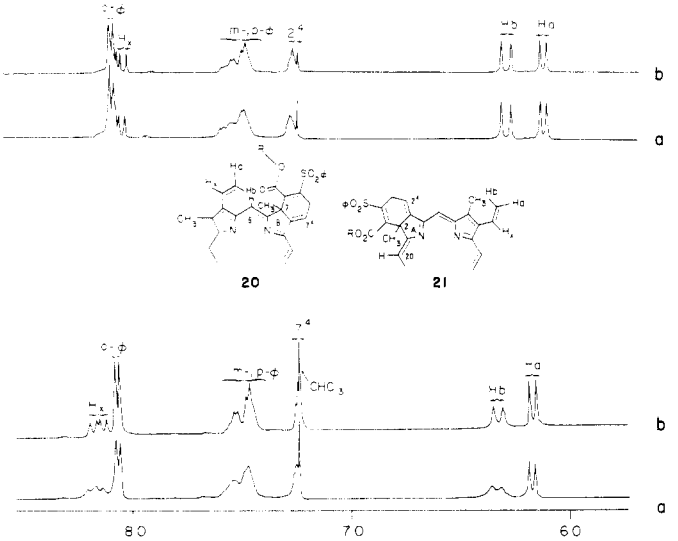

Figure 3. ^{1}H NMR of the ring B (lower) and ring A (upper) isomers **20** and **21** showing the effect of hindered rotation on the vinyl group in **20** which is absent in **21**. The lower traces (a) were measured at room temperature; the upper traces (b) at 50 °C.

anomalies result from a large increase or decrease in spin–lattice relaxation times. Rather, the hindered rotation of the peripheral groups will give rise to a number of "slowly" interconverting conformations. The considerable magnetic anisotropies of the aromatic benzene and porphyrin rings, along with those of the vinyl and ethoxycarbonyl groups, will result in each conformation exhibiting distinct chemical shift differences such that the signals from each proton may be spread over many hertz. The changes observed with decreasing field strength and increasing temperature are consistent with the above explanation which is but one example of the classical observations in this area made by Anet.[17]

While the hindered rotations do not aid in defining the total structure of the isomers **20** and **21**, they do allow us to determine which is derived from reactions at rings A and B. Thus the more polar isomer **21** exhibits, at room temperature, sharp signals from the proton NMR of the vinyl group (Figure 3) which do not change at higher temperature. On the other hand, **20** exhibits, at room temperature, broad signals for the vinyl protons which become sharper at 50° (Figure 3). It is clear that the vinyl group of **20** is more sterically hindered than that of **21**, and on this basis we assign the ring A and B isomers as shown in Figure 3.

Reaction of **1** with methyl β-(phenylsulfonyl)propiolate (**22**) affords ring B (**23**) and ring A (**24**) isomers analogous to **21** and **20**. Hindered rotation of the same peripheral groups is once again observed. In this case, the methyl esters on rings A and B are too broad to be seen though they can be integrated, for three protons, in the region of 3.6 ppm. The fact that reaction of **1** with any of the acetylenes **5**, **6**, **19**, and **22** gives only one ring A and one ring B isomer means that the Diels–Alder reaction is both stereo- and regiospecific. We have so far assumed, with the unsymmetric acetylenes **19** and **22**, that the regiospecificity is that shown in Figure 3. The reactions of **20**, **21**, **23**, and **24** with both TEA and DBU confirm this assignment. In every case each original Diels–Alder reaction gives a kinetically controlled cis isomer with TEA (**20** → **25**, **21** → **26**, **23** → **27**, and **24** → **28**) and the thermodynamic "trans" isomer with DBU (**20** → **29**, **21** → **30**, **23** → **31**, and **24** → **32**). Some relevant NMR chemical shifts for

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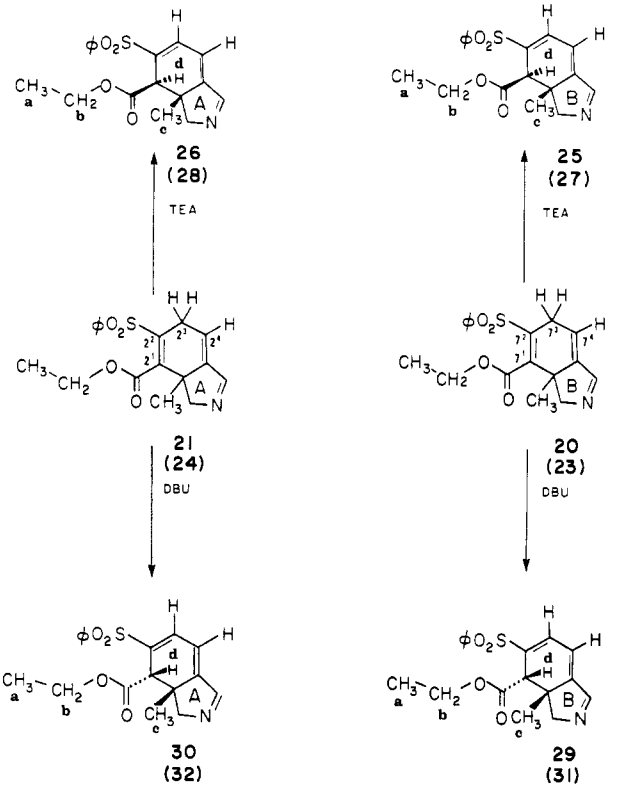
Scheme III. Relevant Chemical Shifts ($CHCl_3$, δ) of the "Trans" Isomers 26, 28, 30, and 32 and the Cis Isomers 25, 27, 29, and 31



	H_a[a]	H_b	H_c	H_d
25	1.54 (3 H, t)	4.62–4.86 (2 H, m)	1.71 (3 H, s)	4.82 (1 H, d)
26	1.57 (3 H, t)	4.62–4.93 (2 H, m)	1.71 (3 H, s)	4.85 (1 H, d)
27	4.22 (3 H, s)		1.66 (3 H, s)	4.79 (1 H, d)
28	4.25 (3 H, s)		1.60 (3 H, s)	4.79 (1 H, d)
29	0.15 (3 H, t)	2.93–3.01 (2 H, q)	1.74 (3 H, s)	4.77 (1 H, s)
30	0.15 (3 H, t)	2.86–3.01 (2 H, m)	1.78 (3 H, s)	4.79 (1 H, s)
31	2.57 (3 H, s)		1.71 (3 H, s)	4.80 (1 H, s)
32	2.58 (3 H, s)		1.75 (3 H, s)	4.82 (1 H, s)

[a] In every case Ha is the methyl group of the ester. For compounds in parenthesis $-CO_2CH_3$ instead of $-CO_2CH_2CH_3$.

these compounds are shown in Scheme III. The cis products (**25** and **26**), from the reaction with TEA, exhibit resonances for the methyl of the ethoxycarbonyl group at somewhat lower field from those of the parent compounds **20** and **21** and similar to the ethoxycarbonyl groups of **7–10**. As with **9** and **10**, however, the C-2^1 and C-7^1 protons appear as doublets due to allylic coupling consistent with their assigned cis structures. The methyl ester analogues **27** and **28** behave similarly. On the other hand, the DBU products of **29–32** show dramatic upfield shifts of the methyl groups of their esters. This can only occur when the ester functions are on the pseudoaxial position at C-2^1 and C-7^1, confirming the assigned regiospecificity of the reactions.

Conclusion

Powerful dienophiles such as TCNE can react with the dienes of both rings A and B of protoporphyrin IX (**1**) to generate an isobacteriochlorin. However, with the weaker dienophiles described here the reaction stops after a single Diels–Alder reaction. After this first cyclization, the resultant exocyclic double bond leaves the clorin chromophore, with which it is conjugated, electron deficient thus inhibiting further reaction. Reduction of this exocyclic double bond is possible,[12] and further manipulations to generate an isobacteriochlorin chromophore should be possible. The ultimate objective is the synthesis of sirohydrochlorin (**3**). To this end the Diels–Alder adducts from the reaction with β-(phenylsulfonyl)propiolate esters have (in one of the pyrrolic rings) all the carbon skeleton of sirohydrochlorin. Appropriate cleavage of the tetrasubstituted double bond could generate acetic and propionic side chains and provide a convenient route from a readily synthesized vinyl-substituted porphyrin to factor I[6] and then sirohydrochlorin.

Experimental Section

^1H NMR spectra were measured on a Bruker WH-400 or a U.B.C. NMR center modified Nicolet-Oxford H-270 spectrometer by using $CDCl_3$ with Me_4Si as internal standard. Mass spectra were obtained at 70 eV with a Kratos MS 50 spectrometer.

A Cary recording spectrometer (Model 1756) was used to record UV and visible spectra. Flash chromatography[18] was performed by using silica gel (Merck, Korngrösse 0.040–0.063 nm, 230–400 mesh ASTM) or silica gel 60 GF 254. For preparative thin-layer chromatography, precoated plates were used from Analtech (silica gel GF, 1500 microns).

Dienophiles. Dimethyl acetylenedicarboxylate (DMAD, **5**) and diethyl acetylenecarboxylate (DEAD, **6**) were purchased from Aldrich. Ethyl β-(phenylsulfonyl)propiolate (**19**) and methyl β-(phenylsulfonyl)propiolate (**22**) were prepared as described previously.[16]

Diels–Alder Reactions of Protoporphyrin IX Dimethyl Ester (1). (i) With Diethyl Acetylenedicarboxylate (6). Protoporphyrin IX dimethyl ester (**1**, 500 mg, 0.85 mmol) was dissolved in dry toluene (50 mL), and DEAD (0.5 mL, 3.15 mmol) was added. The reaction mixture was refluxed in the dark for 6 days after which time only traces of **1** were present. The solvent was removed in vacuo, and the residue was chromatographed on SiO_2 with dichloromethane/2% diethyl ether. Besides some recovered **1**, the ring isomers **7** and **8** were obtained in 20% and 19% yield (based on reacted **1**).

Compound 7: ^1H NMR δ–2.47 (s br, 2 NH), 1.01 (t, J = 7 Hz, 3 H, $CH_3CH_2O_2C$-7^1), 1.39 (t, J = 7 Hz, 3 H, $CH_3CH_2O_2C$-7^2), 2.12 (s, 3 H, Me-7), 3.15 and 3.19 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.40, 3.46, 3.66 (3 s, 9 H) and 3.64 (s, 6 H) (Me-2, -12, and -18 and methyl ester-13 and -17), 3.57–3.69 (m, 1 H-7^3), 4.00 (dd, J = ~20, J = 7 Hz, 1 H-7^3), 4.16 and 4.29 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.35 (m, 2 H, $CH_3CH_2O_2C$-7^2), 4.54 (q, J = 7 Hz, 2 H, $CH_3CH_2O_2C$-7^1), 6.15 (d, J = 12 Hz, 1 vinyl H-3), 6.33 (d, J = 18 Hz, 1 vinyl H-3), 7.40 (d, br, J = 7 Hz, H-7^4), 8.17 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 9.25, 9.29, 9.64, and 9.77 (4 s, 4 meso H) [The ^1H NMR spectrum at 50 °C shows the following changes: the methylene groups of the ethyl ester at C-7^1 and C-7^2 become more complex; H-7^4 appears as dd, J = 3, J = 7 Hz.]; MS, m/e 760 (M^+), 744, 729, 687, 672, 599. Anal. Calcd for $C_{44}H_{48}N_4O_8 \cdot {}^1/_2H_2O$: C, 68.66; H, 6.37; N, 7.28. Found: C, 68.31; H, 6.34; N, 7.21.

Compound 8: Vis (CH_2Cl_2) λ_{max} (nm) (ε) 663 (17 700), 635 (1900), 606 (1800), 534 (6300), 505 (5500), 498 (5600), 403 (86 600); ^1H NMR δ –2.57 (s br, 2 NH), 1.06 (t, J = 7 Hz, 3 H, $CH_3CH_2O_2C$-2^1), 1.46 (t, J = 7 Hz, 3 H, $CH_3CH_2O_2C$-2^2), 2.16 (s, 3 H, Me-2), 3.16 and 3.21 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.38, 3.49, 3.54, 3.65, and 3.66 (5 s, 15 H, Me-7, -12, and -18 and methyl ester-13 and -17), 3.62 (dd, J = 2, J = 21 Hz, 1 H-2^3), 4.01 (dd, J = 7, J = 21 Hz, 1 H-2^3), 4.17 (t, J = 8 Hz, 2 H, 1 β-propionyl-CH_2), 4.29–4.41 (m, 4 H, 1 β-propionyl-CH_2 and $CH_3CH_2O_2C$-2^2), 4.46–4.64 (m, 2 H, $CH_3CH_2O_2C$-2^1), 6.15 (dd, J = 2, J = 12 Hz, 1 vinyl H-8), 6.34 (dd, J = 2, J = 18 Hz, 1 vinyl H-8), 7.41 (dd, J = 2, J = 7 Hz, H-2^4), 8.13 (dd, J = 12, J = 18 Hz, 1 vinyl H-8), 1 vinyl H-8), 9.15, 9.36, 9.74, 9.80 (4 s, 4 meso H) [The ^1H NMR at 50 °C does not show any changes.]; MS, m/e 760 (M^+), 745, 687, 672, 599, and 169.

(ii) With Dimethyl Acetylenedicarboxylate (5). Protoporphyrin IX dimethyl ester (**1**) (50 mg, 0.085 mmol) was dissolved in dichloroethane (25 mL), and DMAD (5 mL, 50.95 mmol) was added. After having been refluxed in the dark for 3 days, the reaction was complete. Evaporation of the solvent and chro-

(18) Still, W. C.; Kuhn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

matography of the residue on SiO_2 in dichloromethane/2% methanol gave the isomers **13** and **14** each in 20% yield.

Compound 13: ^1H NMR δ −2.47 (s br, 2 NH), 2.10 (s, 3 H, Me-7), 3.15 and 3.19 (2 t, superimposed, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.40, 3.46, 3.63, 3.64, and 3.65 (5 s, 15 H, Me-2, -12, and -18 and methyl ester-13 and -17), 3.56–3.70 (m, 1 H-7^3), 3.90–4.04 (m, 1 H-7^3), 3.89 and 3.98 (2 s, 6 H, methyl ester-7^1 and -7^2), 4.15 and 4.29 (2 t, J = 8, 4 H, β-propionyl-CH_2-13 and -17), 6.16 (dd, J = 1.5, J = 12 Hz, 1 vinyl H-3), 6.33 (dd, J = 1.5, J = 18 Hz, 1 vinyl H-3), 7.37 (dd, J = 2, J = 6 Hz, H-7^4), 8.16 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 9.20, 9.28, 9.65, 9.78 (4 s, 4 meso H); MS, m/e 732 (M^+), 716, 673, 658, 643. Anal. Calcd for $C_{42}H_{44}N_4O_8 \cdot {}^1/_2H_2O$: C, 68.02; H, 6.07; N, 7.56. Found: C, 68.08; H, 5.96; N, 7.54.

Compound 14: ^1H NMR δ −2.60 (s br, 2NH), 2.09 (s, 3 H, Me-2), 3.15 and 3.21 (2 t, superimposed, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.39, 3.51, 3.55, 3.66, and 3.67 (5 s, 15 H, Me-7, -12, and -18 and methyl ester-13 and -17), 3.45–4.05 (m, 2 H, 2 H-2^3), 3.91 and 4.03 (2 s, 6 H, methyl ester-2^1 and -2^2), 4.17 and 4.34 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 6.16 (d, J = 12 Hz, 1 vinyl H-8), 6.34 (d, J = 18 Hz, 1 vinyl H-8), 7.40 (d, J = 6 Hz, H-2^4), 8.16 (dd, J = 12, J v 18 Hz, 1 vinyl H-8), 9.09, 9.36, 9.73, and 9.82 (4 s, 4 meso H); MS, m/e 732 (M^+, $C_{42}H_{44}N_4O_8$), 716, 673, 658, and 643.

(iii) With Ethyl β-(Phenylsulfonyl)propiolate[16] (19). Protoporphyrin IX dimethyl ester (1) (361 mg, 0.61 mmol) and **19** (426 mg, 1.79 mmol) were dissolved in dichloromethane (25 mL) and refluxed in the dark for 20 h. The solvent was removed in vacuo, and the residue was chromatographed on SiO_2 with dichloromethane/2% diethyl ether. Besides 57 mg of recovered 1, the isomers **20** and **21** were obtained each in 34% yield (based on reacted 1).

Compound 20: Vis (CH_2Cl_2) λ_{max} (nm) 662, 631, 604, 535, 505 sh, 499, and 403; ^1H NMR δ −2.55 (s br, 2 NH), 0.93 (m br, line width at half peak height ($\Delta\omega_{1/2}$) ~50 Hz, $CH_3CH_2O_2C$-7^1), 2.13 (s, 3 H, Me-7), 3.15 and 3.17 (2 t, J = 8 Hz, 4 H, 2 α-propionyl-CH_2-13 and -17), 3.40, 3.42, 3.63 (3 s, 9 H), and 3.65 (s, 6 H) (Me-2, -12, and -18 and methyl ester-13 and -17), 3.3–3.8 (2 H, $CH_3CH_2O_2C$-7^1), 4.15 and 4.25 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.48 and 4.61 (2 m, very br, 2 H, H-7^3), 6.18 (d, J = 12 Hz, 1 vinyl H-3), 6.34 (d br, J = 18 Hz, 1 vinyl H-3), 7.23–7.31 (m, H-7^4), 7.41–7.61 (m, 3 Ar H), 8.04–8.12 (m, 2 Ar H), 8.09–8.25 (m br, 3 main signals, 1 vinyl H-3), 9.23, 9.66, 9.79 (3 s, 3 meso H), and 9.30 (s br, $\Delta\omega_{1/2}$ ~40 Hz, 1 meso H) [The ^1H NMR at 50 °C shows the following changes: the signals for $CH_3CH_2O_2C$-7 and 2 H-7^3 become even broader. The vinyl H at 6.34 (d) becomes sharper and a dd is observed at 8.16, J = 12, J = 18 Hz. The m at 7.22–7.26 for H-7^4 and the Ar H at 7.41–7.61 have more fine structure. The broad m at 9.30 sharpens up; $\Delta\omega_{1/2}$ ~20 Hz.]; MS, m/e 828 (M^+, $C_{47}H_{48}N_4O_8S$), 812, 755, 740, 702, 688, 672, 600, 100, and 77. Anal. Calcd for $C_{47}H_{48}N_4O_8S \cdot {}^1/_2H_2O$: C, 67.38; H, 5.97; N, 6.69. Found: C, 67.28; H, 6.14; N, 6.55.

Compound 21: Vis (CH_2Cl_2) λ_{max} (nm) 662, 631, 603, 534, 505 sh, 497, and 402; ^1H NMR δ −2.66 (s br, 2 NH), 0.99 (m br, $\Delta\omega_{1/2}$ 50 Hz, $CH_3CH_2O_2C$-2^1), 2.13 (s, 3 H, Me-2), 3.16 and 3.23 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.36, 3.45, 3.52 (3 s, 9 H), and 3.66 (2 s, 6 H) (Me-7, -12, and -18 and methyl ester-13 and -17), 3.3–3.8 (2 H, $CH_3CH_2O_2C$-2^1), 4.16 t, J = 8 Hz, 2 H) and 4.35 (t br, J = 8 Hz, 2 H) (β-propionyl-CH_2-13 and -17) [Region between 4.0 and 5.0 integrates for 2 H, 2 H-2^3), 6.10 (dd, J = 2, J = 12 Hz, 1 vinyl H-8), 6.28 (dd, J = 2, J = 18 Hz, 1 vinyl H-8), 7.23–7.28 (m, H-2^4), 7.41–7.61 (m, 3 Ar H), 8.05–8.15 (m, 2 Ar H) overlapping 8.05 (dd, J = 12, J = 18 Hz, 1 vinyl H-8), 9.27 (s, 1 meso H), 9.76 (s, 2 meso H), and 9.10–9.35 (s, very br, 1 meso H). The ^1H NMR at 50 °C shows the following changes: signals for $CH_3CH_2O_2C$-2^1 and 2 H-7^3 become very broad. The m at 7.21–7.27 (H-2^4) and m at 7.41–7.61 (3 Ar H) have more fine structure. The broad s 9.10–9.35 (1 meso H) becomes sharper.]; MS, m/e 828 (M^+, $C_{47}H_{48}N_4O_8S$), 110, and 77. Anal. Calcd for $C_{47}H_{48}N_4O_8S \cdot {}^1/_2H_2O$: C, 67.38; H, 5.97; N, 6.69. Found: C, 67.91; H, 6.02; N, 6.70.

(iv) With Methyl β-(Phenylsulfonyl)propiolate[16] (22). Protoporphyrin IX dimethylester (1) (289 mg, 0.489 mmol) and **22** (279 mg, 1.246 mmol) were dissolved in dichloromethane (25 mL) and refluxed in the dark for 19 h. The solvent was removed in vacuo, and the residue was chromatographed on SiO_2 with dichloromethane/2% diethylether. The isomers **23** and **24** were obtained in a 1:1 ratio in 41% yield.

Compound 23: Vis (CH_2Cl_2) λ_{max} (nm) (ϵ) 662 (36 700), 605 (4100), 534 (9000), 506 sh (11 400), 488 (12 300), 402 (163 300); ^1H NMR δ −2.57 (s br, 2 NH), 2.16 (s, 3 H, Me-7), 3.15 and 3.17 (2 t, J = 8 Hz, α-propionyl-CH_2-13 and -17), 3.39, 3.41, 3.63, 3.64 (4 s, 12 H), and 3.66 (s, 6 H) (Me-2, -12, and 18 and methyl ester-7, -13, and -17), 3.89–4.08 (m br, 2 H-7^3), 4.14 and 4.26 (2 t, J = 8 Hz, 4 H), β-propionyl-CH_2-13 and -17), 6.20 (d, J = 12 Hz, 1 vinyl H-3), 6.35 (d br, J = 18 Hz, 1 vinyl H-3), 7.22–7.28 (m, H-7^4), 7.42–7.62 (m, 3 Ar H), 8.01–8.10 (m, 2 Ar H), 8.11–8.24 (m, 3 main signals, 1 vinyl H-3), 9.22, 9.64, 9.77 (3 s, 3 meso H), 9.25 (s br, $\Delta\omega_{1/2}$ = 40 Hz, 1 meso H) [The ^1H NMR at 50 °C shows the following changes: the signal for 2H-7^3 becomes broader and integrates in the region 4.0–4.4. The following signals become sharper and show more fine structure: 6.35 (d, 1 vinyl H-3), 7.22–7.28 (m, H-7^4), 7.42–7.62 (m, 3 Ar H), 8.17 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 9.25 (s br, $\omega_{1/2}$ = 10 Hz, 1 meso H).]; MS, m/e 814 (M^+, $C_{46}H_{46}N_4O_8S$): 218, 142, 110, and 77.

Compound 24: Vis (CH_2Cl_2) λ_{max}(nm) (ϵ) 662 (38 000), 632 s (3400), 605 (4500), 536 (9800), 507 sh (12 300), 500 (12 400), 404 (171 400); ^1H NMR δ −2.67 (s br, 2 NH), 2.12 (s, 3 H, Me-2), 3.16 and 3.23 (2 t, J = 8 Hz, 4 H), α-propionyl-17), 3.36, 3.47 and 3.53 (3 s, 9 H), and 3.66 and 3.67 (2 s, 9 H) (Me-7, -12, and -18 and methyl ester -2^1, -13, and -17), 3.90–4.15 (m br, 2 H-2^3), 4.16 (t, J = 8 Hz, 2 H) and 4.35 (t br, J = 8 Hz, 2 H), (β-propionyl-CH_2-13 and -17), 6.12 (dd, J = 2, J = 12 Hz, 1 vinyl H-8), 6.29 (dd, J = 2, J = 18 Hz, 1 vinyl H-8), 7.22–7.29 (m, H-2), 7.42–7.61 (m, 3 Ar H), 8.08 (dd, J = 12, J = 18 Hz, 1 vinyl H-8) overlapped by 8.02–8.14 (m, 2 Ar H), 9.12 (s br, $\Delta\omega_{1/2}$ ~40 Hz, 1 meso H), 9.28, 9.76, 9.78 (3 s, 3 meso H) [The ^1H NMR at 50 °C shows the following changes: the broad m for 2 H-2^3 becomes even broader and integrates between 4.0–4.4 ppm. The following signals become sharper and show more fine structure: 7.21–7.27 (m, H-2^4), 7.42–7.60 (m, 3 Ar H), 9.12 (s, $\Delta\omega_{1/2}$) = 10 Hz, 1 meso H).]; MS, m/e 814 (M^+, $C_{46}H_{46}N_4O_8S$), 218, 142, 110, and 77.

Rearrangements of 7, 8, 13, 14, 20, 21, 23, and 24 with Triethylamine (TEA). General Procedure. The Diels–Alder adduct was dissolved in CH_2Cl_2, and a few drops of TEA were added. The solution was then refluxed for 2 h or allowed to stand at room temperature overnight. The solvent and excess TEA were removed in vacuo, and the crude product was purified by chromatography. The rearranged product was obtained almost quantitatively.

Compound 9: ^1H NMR δ −2.50 (s br, 2 NH), 1.44 (t, J = 7 Hz, 3 H, $CH_3CH_2O_2C$-7^2), 1.55 (t, J = 7 Hz, 3 H, $CH_3CH_2O_2C$-7^1), 1.62 (s, 3 H, Me-7), 3.15 and 3.18 (2 t, J = 8 Hz, 4 H, α-priopionyl-CH_2-13 and -17), 3.39, 3.45, 3.62, 3.63, and 3.65 (5 s, 15 H, Me-2, -12, and -18 and methyl ester -13 and -17), 4.14 and 4.28 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.37 (q, J = 7 Hz, $CH_3CH_2O_2C$-7^2), 4.61–4.75 (m, 2 H, $CH_3CH_2O_2C$-7^1), 4.77 (d, J = 3 Hz, H-7^1), 6.12 (d, J = 12 Hz, 1 vinyl H-3), 6.33 (d, J = 18 Hz, 1 vinyl H-3), 7.34 (d, J = 6 Hz, H-7^4); 7.65 (dd, J = 3, J = 6 Hz, H-7^3), 8.13 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 9.26, 9.40, 9.61, and 9.71 (4 s, 4 meso H); MS, m/e 760 (M^+, $C_{44}H_{48}N_4O_8$), 744, 687, 672, 643, 615, 599, 571, 541, and 527.

Compound 10: Vis ($CH_2Cl)_2$ λ_{max} (nm) (ϵ) 688 (13 400), 625 (2800); 576 (7500), 508 (3600), 435 (43 600), 424 (45 400), 359 (18 400); ^1H NMR δ −2.59 (s br, 2 NH), 1.45 (t, J = 7 Hz, 3 H, $CH_3CH_2O_2C$-2^2), 1.58 (t, J = 7 Hz, 3 H, $CH_3CH_2O_2C$-2^1), 1.60 (s, 3 H, Me-2), 3.17 and 3.21 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.39, 3.51, 3.52 (3 s, 9 H), and 3.67 (s, 6 H) (Me-7, -12, and -18 and methyl ester-13 and -17), 4.17 and 4.34 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.40 (q, J = 7 Hz, $CH_3CH_2O_2C$-2^2), 4.61–4.81 (m, 2 H, $CH_3CH_2O_2C$-2^1), 4.81 (d, J = 3 Hz, H-2^1), 6.12 (dd, J = 2, J = 12 Hz, 1 vinyl H-8), 6.34 (dd, J = 2, J = 18 Hz, 1 vinyl H-8), 7.34 (d, J = 8 Hz, H-2^4), 7.69 (dd, J = 3, J = 6 Hz, H-2^3), 8.13 (dd, J = 12, J = 18 Hz, 1 vinyl H-8), 9.32, 9.39, 9.72, and 9.81 (4s, 4 meso H); MS, m/e 760 (M^+, $C_{44}H_{48}N_4O_8$), 744, 687, 672, 636, 599, 563, and 535.

Compound 15: ^1H NMR δ −2.54 (s br, 2 NH), 1.62 (s, 3 H, Me-7), 3.16 and 3.20 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.41, 3.46, 3.63, 3.65, and 3.67 (5 s, 15 H, Me-2, -12, and -18 and methyl ester-13 and -17), 3.93 and 4.23 (2 s, 6 H, methyl ester-2^1 and -2^2), 4.16 (t, J = 8 Hz, 2 H) and 4.30 (m, 2 H) (β-propionyl-CH_2-13 and -17), 4.75 (d, J = 3 Hz, H-2^1), 6.16 (d,

J = 12 Hz, 1 vinyl H-3), 6.34 (d, J = 18 Hz, 1 vinyl H-3), 7.31 (d, J = 6 Hz, H-7^4), 7.68 (dd, J = 3, J = 6 Hz, H-7^3), 8.11 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 9.27, 9.32, 9.68, and 9.77 (4s, 4 meso H); MS, m/e 732 (M^+), 716, 673, 658, 643, and 585.

Compound 16: ^{1}H NMR δ −2.57 (s br, 2 NH), 1.62 (s, 3 H, Me-2), 3.16 and 3.21 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.40, 3.50, 3.54 (3 s, 9 H), and 3.66 (s, 6 H) (Me-7, -12, and -18 and methyl ester-13 and -17), 3.93 and 4.25 (2 s, 6 H, methyl ester-2^1 and -2^2), 4.17 and 4.33 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.79 (m, $\Delta\omega_{1/2}$ = 7 Hz, H-2^1), 6.17 (d, J = 12 Hz, 1 vinyl H-8), 6.36 (d, J = 18 Hz, 1 vinyl H-8), 7.34 (d, J = 6 Hz, H-2^4), 7.74 (m, $\Delta\omega_{1/2}$ = 12 Hz, H-2^3), 8.16 (dd, J = 12, J = 18 Hz, 1 vinyl H-8), 9.25, 9.35, 9.74, and 9.85 (4 s, 4 meso H).

Compound 25: Vis (CH_2Cl_2) λ_{max} (nm) (ϵ) 684 (26 300), 625 (7200), 579 (14 400), 551 sh (9800), 420 br (71 400), 397 sh (61 900), 350 (46 600); ^{1}H NMR δ −2.52 (s br, 2 NH), 1.54 (t, J = 7 Hz, 3 H, CH_3CH_2O$_2$C-7^1), 1.71 (s, 3 H, Me-7), 3.15 and 3.19 (2 t, J = 8 Hz, 4 H α-propionyl-CH_2-13 and -17), 3.39, 3.47, 3.60, 3.64, and 3.66 (5 s, 15 H, Me-2, -12, and -18 and methyl ester-13 and -17), 4.15 and 4.30 (2 t, J = 8 Hz, 4 H β-propionyl-CH_2-13 and -17), 4.62–4.86 (m, 2 H, CH_3CH_2O$_2$C-7^1), 4.82 (d, J = 3 Hz, H-7^1), 6.10 (dd, J = 2, J = 12 Hz, 1 vinyl H-3), 6.27 (dd, J = 2, J = 18 Hz, 1 vinyl H-3), 7.41 (d, J = 6 Hz, H-7^4), 7.54–7.64 (m, 3 Ar H), 7.89 (dd, J = 3, J = 6 Hz, H-7^3), 8.03 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 8.07–8.11 (m, 2 Ar H), 9.04, 9.31, 9.70, 9.75 (4 s, 4 meso H); MS, m/e 828 (M^+), 755, 740, 687, 667, 614, 600, 541, 527, 218, 142, 110, and 77.

Compound 26: ^{1}H NMR δ −2.55 (s br, 2 NH), 1.57 (t, J = 7, CH_3CH_2O$_2$C-2^1), 1.71 (s, 3 H, Me-2), 3.17 and 3.21 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.40, 3.43, 3.56 (3 s, 9 H), and 3.66 (s, 6 H) (Me-7, -12, and -18 and methyl ester-13 and -17), 4.17 and 4.32 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.62–4.93 (m, 2 H, CH_3CH_2O$_2$C-2^1), 4.85 (d, J = 3 Hz, H-2^1), 6.19 (dd, J = 2, J = 12 Hz, 1 vinyl H-8), 6.35 (dd, J = 2, J = 18 Hz, 1 vinyl H-8), 7.42 (d, J = 6 Hz, H-2^4), 7.55–7.65 (m, 3 Ar H), 7.89 (dd, J = 6, J = 3 Hz, H-2^3), 8.05–8.12 (m, 2 Ar H), 8.15 (dd, J = 12, J = 18 Hz, 1 vinyl H-8), 8.95, 9.38, 9.73, and 9.85 (4 s, 4 meso H); MS, m/e 814 (M^+), 755, 740, 686, 667, 614, 600, 110, and 77. Anal. Calcd for $C_{47}H_{48}N_4O_8S\cdot H_2O$: C, 66.66; H, 5.91; N, 6.61. Found: C, 66.75; H, 5.96; N, 6.62.

Compound 27: Vis (CH_2Cl_2) λ_{max} (nm) (ϵ) 683 (29 500), 623 (8000), 579 (15 100), 552 sh (10 200), 432 br (74 500), 348 (48 200); ^{1}H NMR δ −2.60 (s br, 2 NH), 1.66 (s, 3 H, Me-7), 3.15 and 3.18 (2 t, J = 6 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.28, 3.35, 3.49, 3.64, 3.66 (5 s, 15 H, Me-2, -12, and -18 and methyl ester-13 and -17), 4.14 (t, J = 6 Hz, 2 H) and 4.29 (t br, J ~ 6 Hz, 2 H) (β-propionyl-CH_2-13 and -17), 4.22 (s, 3 H, methyl ester-7^1), 4.79 (d, J = 3 Hz, H-7^1), 6.16 (d, J = 12 Hz, 1 vinyl H-3), 6.25 (d, J = 18 Hz, 1 vinyl H-3), 7.35 (d, J = 6 Hz, H-7^4), 7.54–7.62 (m, 3 Ar H), 7.89 (dd, J = 3, J = 6 Hz, H-7^3), 7.99 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 8.03–8.10 (m, 2 Ar H), 8.94, 9.24, 9.67, 9.71 (4 s, 4 meso H); MS, m/e 814 (M^+), 798, 672, 658, 600, 110, and 77.

Compound 28: Vis (CH_2Cl_2) λ_{max} (nm) (ϵ) 682 (31 500), 622 (8400), 579 (16 500), 422 br (73 800), 353 (45 800); ^{1}H NMR δ −2.71 (s br, 2 NH), 1.60 (s, 3 H, Me-2); 3.14 and 3.19 2 t, J = 6 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.34, 3.40, 3.45, 3.65, and 3.66 (5 s, 15 H, Me-7, -12, and -18 and methyl ester-13 and -17), 4.13 and 4.29 (2 t, J = 6 Hz, 4 H, β-propionyl-13 and -17), 4.25 (s, 3 H, methyl ester-2^1), 4.79 (d, J = 3 Hz, H-2^1), 6.14 (d, J = 12 Hz, 1 vinyl H-8), 6.30 (d, J = 18 Hz, 1 vinyl H-8), 7.20–7.26 (m, H-2^4), 7.54–7.62 (m, 3 Ar H), 7.85 (dd, J = 3, J = 6 Hz, H-2^3), 8.04–8.11 (m, 2 Ar H and 1 vinyl H-8), 8.81, 9.14, 9.67, 9.75 (4 s, 4 meso H); MS, m/e 814 (M^+), 798, 740, 658, 600, and 277.

Rearrangements with 1,5-Diazabicyclo[5.4.0]undec-5-ene (DBU). General Procedure. The Diels–Alder adducts or the TEA-rearranged products were dissolved in dichloromethane, and a few drops of DBU were added. Reaction occurred immediately. The reaction mixture was poured into 2 N HCl and extracted with dichloromethane. The organic layer was washed with water and brine and dried over $MgSO_4$. After removal of the solvent, the crude product was purified by chromatography on SiO_2 with dichloromethane/1% methanol. The products **11**, **12**, **17**, **18**, and **29–32** were obtained in almost quantitative yield.

Compound 11: ^{1}H NMR δ −2.26 (s br, 2 NH), 0.29 (t, J = 7 Hz, H, CH_3CH_2O$_2$C-7^1), 1.48 (t, J = 7 Hz, 3 H, CH_3CH_2O$_2$C-7^2), 1.80 (s, 3 H, Me-7), 3.16 and 3.19 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.27–3.51 (m, 2 H, CH_3CH_2O$_2$C-7^1), 3.41, 3.46, 3.62, 3.65, 3.66 (5 s, 15 H, Me-2, -12, and -18 and methyl ester-13 and -17), 4.16 and 4.29 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.36–4.51 (m, 2 H, CH_3CH_2O$_2$C-7^2), 4.99 (s, H-7^1), 6.13 (dd, J = 1.5, J = 12 Hz, 1 vinyl H-3), 6.35 (dd, J = 1.5, J = 18 Hz, 1 vinyl H-3), 7.42 and 7.79 (2 d, each J = 8 Hz, H-7^3, H-7^4), 8.11 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 9.12, 9.31, 9.63, 9.71 (4 s, 4 meso H); MS, m/e 760 (M^+), 687, 672, and 599. Anal. Calcd for $C_{44}H_{48}N_4O_8\cdot{}^1/_2H_2O$: C, 68.66; H, 6.50; N, 7.28. Found: C, 68.72; H, 6.27; N, 7.25.

Compound 12: Vis (CH_2Cl_2) λ_{max} (nm) (ϵ) 688 (15 800), 625 (3400), 577 (17 500), 552 (5000), 500 (3200), 432 (37 000), 417 (373 000), 354 (20 000); ^{1}H NMR δ −2.28 (s br, 2 NH), 0.31 (t, J = 7 Hz, 3 H, CH_3CH_2O$_2$C-2^1), 1.47 (t, J = 7 Hz, 3 H, CH_3CH_2O$_2$C-2^2), 1.82 (s, 3 H, Me-2), 3.15 and 3.20 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.27–3.51 (m, 2 H, CH_3CH_2O$_2$C-2^1), 3.38, 3.48, 3.54, 3.65, 3.66 (5 s, 15 H, Me-7, -12, and -18 and methyl ester-13 and -17), 4.15 and 4.30 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.35–4.50 (m, 2 H, CH_3CH_2O$_2$C-2^2), 4.99 (s, H-2^1), 6.13 (dd, J = 1.5, J = 12 Hz, 1 vinyl H-8), 6.31 (dd, J = 1.5, J = 18 Hz, 1 vinyl H-8), 7.40 and 7.77 (2 d, J = 6 Hz, H-2^3, H-2^4), 8.16 (dd, J = 12, J = 18 Hz, 1 vinyl H-8), 8.97, 9.36, 9.63, 9.78 (4 s, 4 meso H); MS, m/e 760 (M^+), 687, 672, and 599.

Compound 17: ^{1}H NMR δ −2.29 (s br, 2 NH), 1.79 (s, 3 H, Me-7), 2.95 (s, 3 H, methyl ester-7^1), 3.17 and 3.21 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.42, 3.49, 3.63, 3.65, and 3.67 (5 s, 15 H, Me-2, -12, and -18 and methyl ester-13 and -17), 3.99 (s, 3 H, methyl ester-7^2), 4.18 and 4.32 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 5.06 (s, H-7^1), 6.17 (d, J = 12 Hz, 1 vinyl H-3), 6.38 (d, J = 18 Hz, 1 vinyl H-3), 7.45 and 7.83 (2 d, J = 8 Hz, H-7^3, H-7^4), 8.13 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 9.15, 9.37, 9.70, and 9.78 (4 s, 4 meso H); MS, m/e 732 (M^+, $C_{42}H_{44}N_4O_8$), 701, 673, 658, 657, 614, and 585.

Compound 18: ^{1}H NMR δ −2.28 (s br, 2 NH), 1.81 (s, 3 H, Me-2), 2.95 (s, 3 H, methyl ester-2^1), 3.16 and 3.21 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.40, 3.49, 3.57, 3.66, 3.67 (5 s, 15 H, Me-7, -12, and -18 and methyl ester-13 and -17), 3.990 (s, 3 H, methyl ester-2^2), 4.17 and 4.32 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 5.06 (s, H-2^1), 6.17 (d, J = 12 Hz, 1 vinyl H-8), 6.36 (d, J = 18 Hz, 1 vinyl H-8), 7.45 and 7.82 (2 d, J = 6 Hz, H-2^3, H-2^4), 8.17 (dd, J = 12, J = 18 Hz, 1 vinyl H-8), 8.99, 9.42, 9.70, 9.84 (4 s, 4 meso H); MS, m/e 732 (M^+, $C_{42}H_{44}N_4O_8$), 701, 673, 658, and 585.

Compound 29: Vis (CH_2Cl_2) λ_{max} (nm) (ϵ) 686 (33 500), 626 (8100), 583 (14 200), 554 sh (9800), 466 sh (40 400), 435 br (64 200), 396 s (50 000), 352 (47 100); ^{1}H NMR δ −2.41 (s br, 2 NH), 0.15 (t, J = 7 Hz, 3 H, CH_3CH_2O$_2$C-7^1), 3.15 and 3.19 (2 t, J = 8, 4 H, α-propionyl-CH_2-13 and -17); 3.40, 3.45, 3.62, 3.64, 3.65 (5 s, 15 H, Me-2, -12, and -18 and methyl ester -13 and -17), 4.16 and 4.29 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.77 (s, H-7^1), 6.17 (dd, J = 2, J = 12 Hz, 1 vinyl H-3), 6.35 (dd, J = 2, J = 18 Hz, 1 vinyl H-3), 7.48 and 7.891 (2 d, J = 6 Hz, H-7^3, H-7^4), 7.54–7.64 (m, 3 Ar H), 8.05–8.17 (m, 3 H, 2 Ar H and 1 vinyl H-3), 9.04, 9.34, 9.70, 9.75 (4 s, 4 meso H); MS, m/e 828 (M^+), 740, 667, and 600. Anal. Calcd for $C_{47}H_{48}N_4O_8S\cdot{}^1/_2H_2O$: C, 67.38; H, 5.97; N, 6.69. Found: C, 67.10; H, 6.08; N, 6.46.

Compound 30: Vis (CH_2Cl_2) λ_{max} (nm) (ϵ) 686 (35 800), 625 (7700), 583 (13 600), 555 sh (9000), 471 sh (26 600), 431 (61 200), 417 (59 300), 396 (43 300), 354 (40 800); ^{1}H NMR δ −2.51 to −2.34 (m br, 2 NH), 0.15 (t, J = 7 Hz, 3 H, CH_3CH_2O$_2$C-2^1), 1.78 (s, 3 H, Me-2), 2.86–3.01 (m, CH_3CH_2O$_2$C-2^1), 3.16 and 3.21 (2 t, 4 H, α-propionyl CH_2-13 and -17), 3.39, 3.48, 3.54, 3.65, and 3.66 (5 s, 15 H, Me-7, -12, and -18 and methyl ester-13 and -17), 4.17 and 4.31 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.79 (s, H-2^1), 6.17 (dd, J = 2, J = 12 Hz, and 1 vinyl H-8), 6.34 (dd, J = 2, J = 18 Hz, 1 vinyl H-8), 7.48 and 7.91 (2 d, J = 6 Hz, H-2^3, H-2^4), 7.56–7.63 (m, 3 Ar He; 8.08–8.19 (m, 3 H, 2 Ar H and 1 viinyl H-8), 8.90, 9.40, 9.71, and 9.83 (4 s, 4 meso H); MS, m/e 828 (M^+), 740, 667, and 600. Anal. Cacd for $C_{47}H_{48}N_4O_8S\cdot H_2O$: C, 66.66; H, 5.91; N, 6.62. Found: C, 66.90; H, 5.80; N, 6.63.

Compound 31: Vis (CH_2Cl_2) λ_{max} (nm) (ϵ) 687 (33 000), 626 (8300), 583 (14 100); 557 sh (10 000), 470 sh (38 600), 436 br (67 000), 395 sh (77 300), 353 (51 500); ^{1}H NMR δ −2.43 (s br, 2 NH), 1.71 (s, 3 H, Me-7), 2.57 (s, 3 H, methyl ester-7^1), 3.15 and 3.19 (2 t, J = 7 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.41, 3.46, 3.61, 3.64,

and 3.65 (5 s, 15 H, Me-2, -12, and -18 and methyl ester-13 and -17), 4.17 and 4.29 (2 t, J = 6 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.80 (s, H-7[1]), 6.17 (dd, J = 2, J = 12 Hz, 1 vinyl H-3), 6.33 (dd, J = 2, J = 18 Hz, 1 vinyl H-3), 7.48 and 7.90 (2 d, J = 6, H-7[3]), H-7[4]), 7.55–7.63 (m, 3 Ar H), 8.07 (dd, J = 12, J = 18 Hz, 1 vinyl H-3), 8.10–8.16 (m, 2 Ar H), 9.01, 9.34, 9.70, and 9.75 (4 s, 4 meso H); MS, m/e 814 (M^+), 755, 740, 672, 666, 599, and 526. Anal. Calcd for $C_{46}H_{46}N_4O_8S\cdot H_2O$: C, 66.34; H, 5.76; N, 6.73. Found: C, 66.57; H, 5.85; N, 6.56.

Compound 32: Vis (CH_2Cl_2) λ (nm) (ϵ) 687 (27 200), 627 (6800), 583 (11 600), 557 s (8300), 468 s (33 000), 436 br (52 700), 396 s (42 800), 350 (39 400); ^1H NMR δ −2.5 (s br, 2 NH), 1.75 (s, 3 H, Me-2), 2.58 (s, 3 H, methyl ester-2[1]), 3.14 and 3.20 (2 t, J = 8 Hz, 4 H, α-propionyl-CH_2-13 and -17), 3.37, 3.47, 3.50, 3.65, and 3.66 (5 s, 15 H, Me-7, -12, and -18 and methyl ester-13 and -17), 4.15 and 4.31 (2 t, J = 8 Hz, 4 H, β-propionyl-CH_2-13 and -17), 4.82 (s, H-2[1]), 6.14 (dd, J = 2, J = 12 Hz, 1 vinyl H-8), 6.31 (dd, J = 2, J = 18 Hz, 1 vinyl H-8), 7.48 and 7.92 (2 d, J = 6 Hz, H-2[3], H-2[4]), 7.56–7.64 (m, 3 Ar H), 8.09 (dd, J = 12, J = 18 Hz, 1 vinyl H-8), 8.10–8.17 (m, 2 Ar H), 8.87, 9.38, 9.70 and 9.81 (4 s, 4 meso H); MS, m/e 814 (M^+), 755, 740, 674, 672, 500, and 599.

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Registry No. **1**, 5522-66-7; **5**, 762-42-5; **6**, 762-21-0; **7**, 100205-63-8; **8**, 100205-64-9; **9**, 100205-66-1; **10**, 100205-67-2; **11**, 100295-94-1; **12**, 100295-95-2; **13**, 94238-43-4; **14**, 94238-24-1; **15**, 94238-35-4; **16**, 94238-25-2; **17**, 94293-60-4; **18**, 94293-59-1; **19**, 80404-53-1; **20**, 100228-57-7; **21**, 100205-65-0; **22**, 94238-23-0; **23**, 94269-75-7; **24**, 94238-27-4; **25**, 100205-68-3; **26**, 100205-69-4; **27**, 94346-19-7; **28**, 94238-29-6; **29**, 100295-96-3; **30**, 100295-97-4; **31**, 94269-76-8; **32**, 94293-61-5.

A New Synthesis, Chemical Behavior, and Spectra of Perchlorodiphenylacetylene

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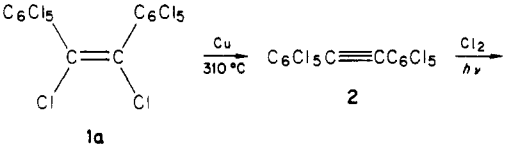
A new, high-yield synthesis of perchlorodiphenylacetylene (**2**) by dechlorination of *cis*-perchlorostilbene (**1a**) with Cu at 310 °C is described. The photochemical reaction of tolane **2** with Cl_2 or tetrachloroethylene affords *trans*-perchlorostilbene (**1b**) or mixtures of perchloro-1,2-diphenylcyclobutene (**3**) and perchloro-1,2-dihydrocyclobuta[*l*]phenanthrene (**4**), respectively. The thermal dimerization of tolane **2** at 350 °C gives a mixture of perchloro-1,2,3-triphenylnaphthalene (**5**), perchloro-2,3,8-triphenylbenzofulvene (**6**), and perchloro-5,10-diphenylideno[2,1-*a*]indene (perchloro-5,10-diphenyldibenzo[*a*,*e*]pentalene (**7**)). Fulvene **6** dechlorinates to indenoindene **7** under stronger reaction conditions. Naphthalene **5** photochlorinates with Cl_2 to perchloro-1,2,3-triphenyl-3,4-dihydronaphthalene (**8**), which reverts to naphthalene **5** at 190 °C. The reaction of tolane **2** with oleum gives perchloro-α,α'-dihydroxystilbene cyclic sulfate (**12**), which decomposes thermically (220 °C) yielding perchlorodiphenylethanedione (**14**). The hydrolysis of dihydronaphthalene **8** affords perchloro-4,5,6-triphenylindenone (**18**). The mechanisms of some unusual reactions, as well as the IR and UV–vis spectra of the new compounds, are presented and discussed.

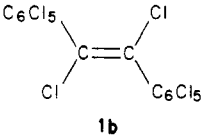
It has been emphasized earlier[1] that the perchlorophenylethylenes, such as perchlorostyrene,[2,3] the perchlorostilbenes,[4] and the perchloropolyarylethylenes,[5] are passive toward addition reactions. In contrast, perchlorophenylacetylene displays a remarkable reactivity.[1] The main reason for such a difference of behavior is of steric nature: While the adducts of perchlorophenylethylenes are, or should be, sterically strained, distorted molecules,[6,7] the ethylenes resulting from perchlorophenylacetylenes would be essentially strain-free molecules.

If perchlorophenylacetylene displays any steric effect at all, it is some shielding of the acetylene carbon bonded to the benzene ring. In fact, some of its reactions have been explained in terms of such a shielding, which, however, appears ineffectual in intramolecular processes.[1]

Scheme I



1a



1b

Therefore, it was regarded as significant to undertake a study on the synthesis and behavior of perchlorotolane (perchlorodiphenylacetylene) where *both* acetylene carbons are shielded by the neighbouring (ortho) chlorines.[8]

Results and Discussion

Perchlorotolane (2) (Scheme I). Perchlorotolane (**2**) has been synthesized in an excellent yield by dechlorination of *cis*-perchlorostilbene (**1a**)[4] with copper, at 310 °C. Tolane **2** had been obtained before[4,10] in ways other than

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