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PYROLYSIS OF 2-METHYLENE-3,4,5,6-DIBENZO-3′,4′-(9,10-PHENANTHRO)SPIROBICYCLOHEXANE TO YIELD TETRABENZANTHRACENE AND ETHYLENE

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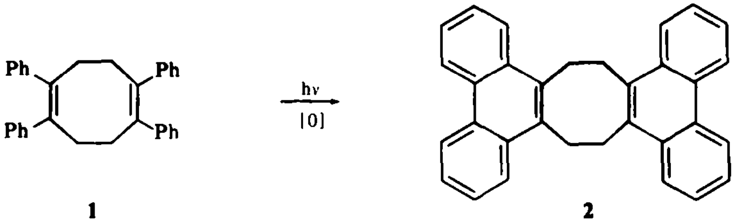
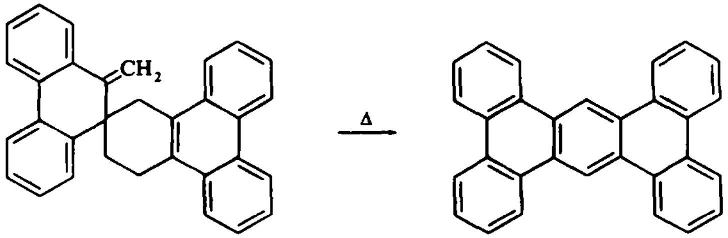
Abstract—The pyrolysis of 2-methylene-3,4,5,6-dibenzo-3′,4′-(9,10-phenanthro)spirobicyclohexane (**3**) does not lead to an isomer, as suggested in the literature, but yields tetrabenz(a,c,h,j) anthracene (**4**). Concerted and two-step reactions, the latter involving an *ene* rearrangement, are considered for the loss of the two-carbon fragment from **3**.

IN A PREVIOUS COMMUNICATION we reported the synthesis of 1,2,5,6-tetraphenylcycloocta(1,5)diene (**1**).[1] We noted that irradiation of **1** in the presence of oxygen led to the apparent formation of 1,2,5,6-*bis*(9, 10-phenanthro)cycloocta(1,5)diene (**2**) with an UV spectrum consistent with the presence of two isolated phenanthrene chromophores.



1 **2**

Likewise, the ultraviolet spectrum of a lower homolog, 1,2,5,6-dibenzocycloocta(1,5)diene (**7**),* is similar to that of *o*-xylene and of twice the molar extinction. *Bis*(9,10-phenanthro)cyclooctadiene (**2**) had been previously reported from the pyrolysis of 2-methylene-3,4,5,6-dibenzo-3′,4′-(9,10-phenanthro)spirobicyclohexane (**3**).[2] The material obtained by Stille and Foster, however, showed a large



3 **4**

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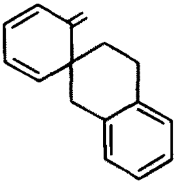
* We thank Professor M. P. Cava for a sample of this compound.

bathochromic shift compared to 9,10-dimethylphenanthrene. This factor suggested that the product obtained from pyrolysis of **3** must have a structure different from **2**. The pyrolysis of **3** in our hands yielded a product which gave IR, UV, and mass spectra identical to the spectra we obtained of the material prepared by Stille and Foster.[*] Analysis of the latter material when purified showed it to be a $C_{30}H_{18}$ hydrocarbon, the mass spectrum of which showed a very intense molecular ion at *m/e* 378. Prominent *m/e* values of 152, 234, and 408 reported[2][†] for the pyrolysis product were not evident either before or after purification. In fact, the mass spectrum is remarkable in its simplicity and in the abundance of doubly charged ions (Experimental Section). The analysis and mass spectrum, suggested a nonsubstituted, annellated aromatic hydrocarbon. Comparison of the UV spectrum ($\lambda_{max}^{CHCl_3}$ 294 mμ, log ε 4·98) with other compounds of this type such as dibenz(a,c)anthracene (λ_{max}^{EtOH} 286 mμ, log ε 5·11)[3] and dibenz(a,h)-anthracene ($\lambda_{max}^{C_6H_6}$ 300 mμ, log ε 5·1),[4] suggested an aromatic system of five rings. The empirical formula suggested a system of seven rings, and thus a cross-conjugated system such as tetrabenz(a,c,h,j)anthracene (**4**) was considered.

This compound had been prepared in an unambiguous manner by Lambert and Martin,[5] and the structure had been confirmed by X-ray analysis.[6] On comparison, the pyrolysis product of **3** was identical in every respect to authentic **4**.[‡]

DISCUSSION

With the structure of the pyrolysis product from **3** elucidated, the mechanism of its formation was examined. In an apparently analogous reaction, the pyrolysis of *o*-xylene gives anthracene.[8] Since compound **3** is a product of the dimerization of 9,10-dimethylene-9,10-dihydrophenanthrene, it might be thought that the anthracene stems from spiro(5,5)-2,3-benz-6-methyleneundeca-7,9-diene (**5**), a dimer of the *o*-xylylene produced in the pyrolysis of *o*-xylene. The reaction, however, proceeds instead through the intermediacy of 1,2-di-*o*-tolylethane (**6**).[7] In the absence of a hydrogen source, the formation of *o*-xylylene under pyrolytic conditions leads to benzocyclobutene, compound **5**, and 1,2,5,6-dibenzocycloocta(1,5)diene (**7**).[8] At room temperature **5** converts rapidly to a polymer (anthracene was not reported as a product[8b]). Similarly, the pyrolysis of 4-vinylcyclohexene to yield benzene has been explained by a mechanism



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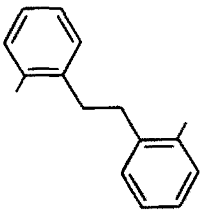

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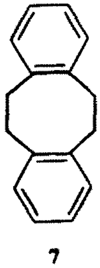

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[*] We thank Professor J. K. Stille for a generous sample of their pyrolysis product.[2]

[†] Professor Stille has informed us that the mass spectrum in their case was actually run on material "A" obtained from the pyrolysis of 3,4-(9,10-phenanthro)-2,5-dihydro-1,1-dioxothiaphene, and that "A" may be different than the tetrabenzanthracene obtained from the pyrolysis of compound 3.

[‡] We wish to thank Professor R. H. Martin for a sample of this hydrocarbon.

which involves loss of a vinyl radical.[9] The transformation of **3** to **4**, therefore, appears to be without good precedent.

The mass spectrum of **3** showed the facile loss of C_2H_4 (M^+-28) and retro-Diels–Alder cleavage to give an abundant ion at *m/e* 204 ($C_{16}H_{12}^+$). Pyrolysis of **3** in degassed solutions of naphthalene at 235° and 285° led to the formation of tetrabenzanthracene (**4**) and gaseous products. The latter consisted primarily of ethane and ethylene in an amount about equal to the amount of **4** formed. Ethane predominated in the mixture with a ratio of 3 : 1 for the pyrolysis at 235° and 6 : 1 for the pyrolysis at 285°. A trace of methane as well as small amounts of propane, butane, and propene were formed at the higher temperature. These C_3 and C_4 hydrocarbons may arise from catalytic cracking of **3** on active sites present in Pyrex glass.*

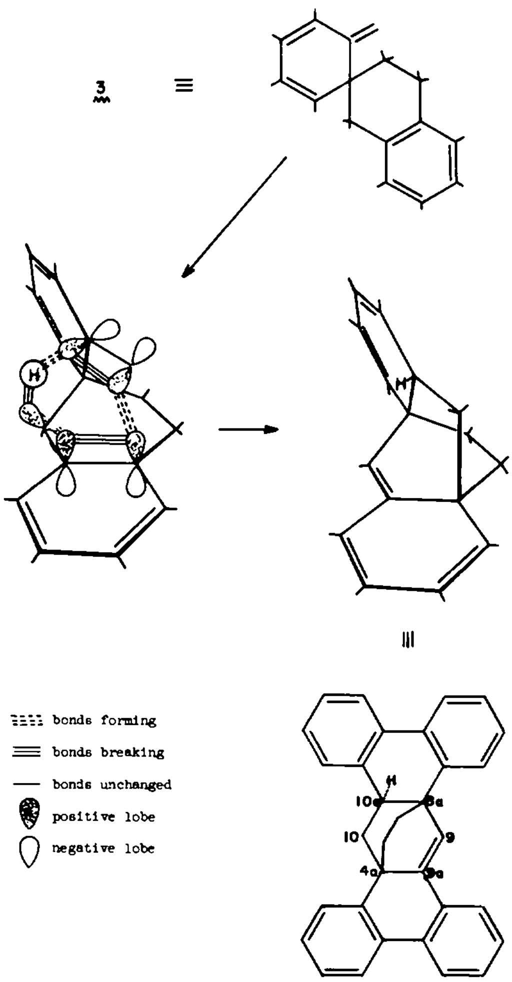

CHART 1. **8**

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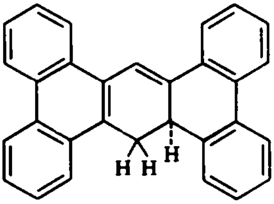
* Personnal communication from Professor Paul H. Emmett, The Johns Hopkins University.

Among the several plausible mechanisms for the formation of **4** in the pyrolysis of **3**, we would like to consider two for which we find some experimental support.

Two-step mechanism. The formation of bicyclo[2,2,2]octene-2 from 4-vinylcyclohexene on an acidic catalyst at 250° has been reported.[10] This is formally an intramolecular *ene* reaction,[11] although in the case cited this mechanism was not proposed. In the pyrolysis of **3**, a similar first step can be drawn (Chart 1) to give 4a, 8a-ethano-10,10a-dihydrotetrabenz(a,c,h,j)anthracene (**8**). Loss of ethylene from **8** would lead to 10,10a-dihydrotetrabenzanthracene (**9**). This compound would be expected to be coloured by analogy to 9-phenyl-9,9a-dihydroanthracene[12] and 9,9,10-triphenyl-9,8a-dihydroanthracene[13] and it could account, in part, for the transient yellow colour observed in the pyrolysis of **3**. Compound **9** would also be expected to convert readily to the fully aromatic **4** in view of the ready conversion of *cis* and *trans*-4a-8a-dihydronaphthalene into naphthalene at moderate temperatures.[14, 15]



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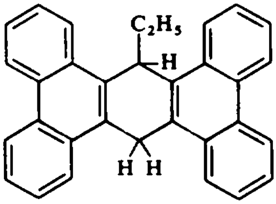

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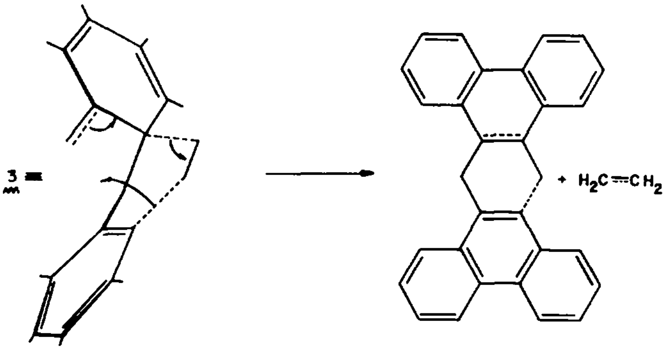
There are several mechanism by which **8** can give ethane. A reasonable intermediate is 9-ethyl-9,10-dihydrotetrabenzanthracene (**10**), which could arise from homolytic cleavage of the ethano bridge followed by abstraction of a hydrogen from C_{10} to give 8a-ethyl-8a,10a-dihydrotetrabenzanthracene. Subsequent [1,5] suprafacial migration of the ethyl group to C_{10} would give 10-ethyl-10,10a-dihydro-tetrabenzanthracene, which would be expected to convert to **10**.[12] The subsequent loss of ethane from **10** has precedent in the reported formation of methane and toluene in the pyrolysis of *trans*-3,6-dimethylcyclohexa-1,4-diene.[16] The pyrolysis of *cis*-3,6-dimethyl-cyclohexa-1,4-diene, in contrast, leads to preferential loss of hydrogen to give *p*-xylene.[16]

In addition to **4**, two other products were recovered by chromatography from the products of the pyrolysis of **3** at 285°. One compound, isolated in 2% yield, gave a UV spectrum consistent with the presence of a phenanthrene chromophore. The mass spectrum showed a molecular ion at *m/e* 408 and ions at *m/e* 379 and 278 (loss of C_2H_5 and C_2H_6). The remainder of the spectrum showed a fragmentation pattern similar to that of tetrabenzanthracene. Pyrolysis of this material for 2 hr at 360° in an evacuated tube without solvent gave pure tetrabenzanthracene, based on the UV spectrum. This unknown material was possibly **10**; unfortunately, too little was available for a rigorous structure determination. A second crystalline product was isolated in 1% yield. This material gave a UV spectrum lacking the finely resolved structure of a nonconjugated phenanthrene chromophore. The mass spectrum showed a molecular ion at *m/e* 408 and an intense peak at *m/e* 231. The lack of a prominent ion at *m/e* 204 ($C_{16}H_{12}^+$) suggests that this compound is not **2**, although the data does not warrant the proposal of other structures.

Concerted formation of ethylene. The photochemical di-π-methane rearrangement of 1,4-pentadienes can be described as a *trans* addition of a σ bond to a π bond.[17] This point of view describes a [$_\sigma 2a + _\pi 2a$] cycloaddition, and is accordingly allowed in the excited state.[18] The present transformation can be viewed as a thermally allowed [$_\pi 2s + _\sigma 2s + _\sigma 2s$] cycloaddition (Chart 2) to give dihydrotetrabenzanthracene (**11**), followed by loss of hydrogen to give **4**. The addition of dienophiles to quadricyclane (**12**) is similar,[19] and only the nonparticipating carbon skeletons differ (eq 1). In the quadricyclane case both termini of each of the reacting σ bonds are joined together and the superstructure of the molecule prevents the elimination of an ethylene molecule, whereas in the rearrangement of **3** one terminus of each of the reacting σ bonds is joined together directly and the other terminus is joined together by a two carbon bridge. Thus a six membered ring is formed, and the loss of ethylene is not constrained by the presence of additional structure.

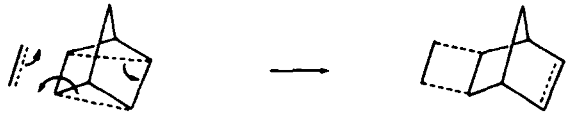


11

— nonparticipating carbon skeleton

---- reacting bonds

CHART 2.



12

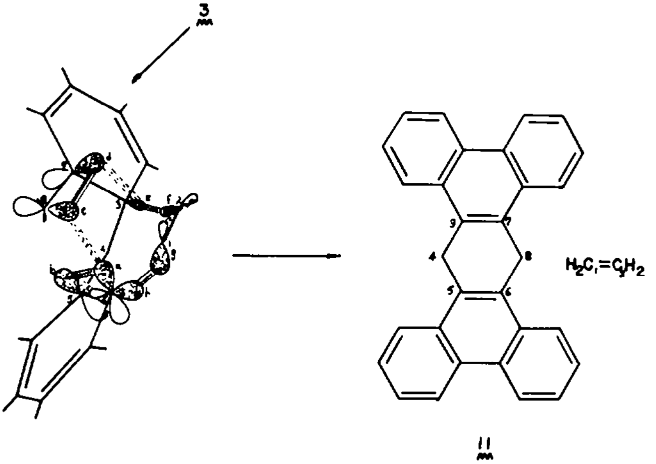
(1)

——— nonparticipating carbon skeleton

- - - - - reacting bonds

The homologous series of ground state cycloadditions beginning with the allowed [2a + 2s] and including the [2s + 2s + 2s] cycloaddition reaction has been thoroughly discussed by Woodward and Hoffman.[18] The rearrangement of **3** to **11** represents a member of this series.

In the Woodward and Hoffman classification of cycloaddition reactions, only one π bond in the di-π-methane rearrangement is explicity considered. Zimmerman has presented an alternative point of view in which both π bonds are considered to be involved in a cyclic transition state.[17, 20] Likewise, the 9–10 π bond of the phenanthrene chromophore in **3** may be considered to participate without important alteration in the stereochemical process. A transition stage in this representation is shown in Chart 3.



ordering in cyclic array

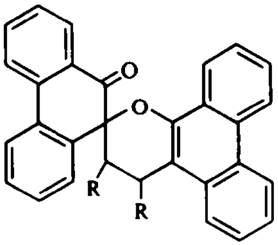
a-b	++	one sign inversion
b-h	+-	
a-c	++	
c-d	++	
d-e	++	
e-f	++	
f-g	++	
g-h	++	

┈ bonds forming
═ bonds breaking
— bonds unchanged
▨ positive lobe
○ negative lobe

CHART 3.

This representation illustrates an 8 π electron cycle with a single inversion (or odd number of inversions) and is therefore a Möbius species, which is favored in the ground state when involving $4n$ electrons.[21]

One functional difference between the concerted and two-step mechanism is that in the two-step mechanism, a group or a hydrogen must migrate from the methylene bridge in **3** to form an isodihydrotetrabenzanthracene, whereas in the concerted process, a dihydrotetrabenzanthracene is formed. Substitution of these hydrogens by groups less prone to migrate, or better, replacement of the methylene bridge with a group without substituents may serve to differentiate the two mechanisms. The exocyclic methylene would also require similar treatment since it can be made equivalent to the methylene bridge by a Cope rearrangement. A compound with the required characteristics has been prepared by Sullivan *et al.*[22] however, to our knowledge compound **13** has not been pyrolysed.



R = Ph

13

EXPERIMENTAL

M.ps, except where noted, were taken with a Thomas–Hoover capillary apparatus and are uncorrected. Elemental analyses were performed by either Mr. Joseph Walters in this department or by Galbraith Laboratories, Inc., Knoxville, Tennessee.

IR spectra were determined on Perkin–Elmer Model 337 or 521 spectrometers, and calibrated against polystyrene. UV spectra were determined on a Cary Model 14 spectrometer. PMR spectra were determined on Varian Associates A-60 or HA-100 spectrometers using TMS as internal standard. Mass spectra were determined on a Hitachie Perkin–Elmer RMU-6 mass spectrometer.

TLC was performed on Eastman Chromatogram sheets containing a fluorescent indicator. Visualization was with 2537 Å light.

*2-Methylene-*3,4,5,6-*dibenzo*-3′,4′-(9,10-*phenanthro*)*spirobicyclohexane* (3). The title compound was prepared in 72% yield (m.p. 237–243°) from 9-chloromethyl-10-bromomethylphenanthrene[23] (300 mg, 0·937 mmole) and NaI (600 mg) in refluxing acetone according to Stille and Foster.[2] Recrystallization twice from C_6H_6-EtOH gave 99·8 mg (0·245 mmole, 52·3%) of colorless fine plates, m.p. (Kofler) 252–253° (lit.[2] 250–251°). Its UV spectrum obtained by us was somewhat different from that which had been reported.[2, 23] We therefore report our data for this product: IR (KBr) 894, 771, 749, and 720 cm^{-1}; UV (EtOH) 215 (log ε 4·72), 225 (4·71), 247 (4·81), 256 (4·81), 268 (4·46), 272 (4·45), 278 (4·39), 287 (4·32), 300 (4·19), 336 (2·83), 342 (2·63), and 351 mμ (2·85); NMR ($CDCl_3$) δ 9·23 (m, 2·1 H), 8·32 (m, 1·2 H), 7·50 (m, 14 H), 5·27 (s, 1·0 H), 5·07 (s, 0·93 H), 3·87 (s, 2·1 H), and an A_2B_2 multiplet appearing as two triplets with centers at δ 2·89 (2·0 H) and 1·98 (2·1 H); mass spectrum (70 eV) *m/e* (rel intensity) 408 (54), 393 (22), 380 (39), 204 (100), 203 (61), and 202 (30). (Calc. for $C_{32}H_{24}$: C, 94·08; H, 5·92. Found: C, 93·81; H, 5·94%).

Structure reassignment for 1,2,5,6-bis (9,10-*phenanthro*)*cyclooctadiene* (2). The product obtained in 33% yield from the pyrolysis of 3 in diethyl phthalate by Stille and Foster,[2] was recrystallized twice from DMF and sublimed at 300° and 5×10^{-3} torr. The IR (KBr), UV ($CHCl_3$), and mass spectra were unchanged by this purification. The purified material was identified as tetrabenz (a,c,h,j) anthracene (4) by comparison with authentic material:[5] m.p. (heated block) 426–428° (lit.[5] 428–429°); IR (KBr) 1425, 1238, 870, 851, 749, and 712 cm^{-1}; UV ($CHCl_3$) 259 (log ε 4·63), 269 (4·70), 294 (4·98), 304 sh (4·85), 333 (4·58), 362 (3·39), 371 (2·87), and 382 mμ (3·33); mass spectrum (70 eV) *m/e* (rel intensity) 378 (100), 377 (8·5), 376 (13), 375 (5·7), 374 (8·6), 189 (23), 188·5 (4·4), 188 (9·7), 187·5 (6·5), 187 (12), 186·5 (2·9), and 186 (5·6). (Calc. for $C_{30}H_{18}$: C, 95·21; H, 4·79. Found: C, 95·22; H, 4·86%). (lit.[2] C, 94·16; H, 5·85%).

Pyrolysis of 2-methylene-3,4,5,6-dibenzo-3′,4′-(9,10-*phenanthro*)*spirobicyclohexane* (3). The pyrolysis apparatus was constructed from a Pyrex 10 mm O.D. break-seal. One end was sealed and then expanded to form a bulb of 5 ml capacity. To the same end of the break-seal, a side arm was attached near the breakable portion for addition of reactants and degassing. To the other end of the break-seal, a side arm of 25 cm × 8 mm was attached. This side arm was bent downward toward the reaction vessel at a right angle and parallel to the longitudinal axis of the break-seal. The distal end of this side arm was drawn to a fine point bent over on itself and could be easily cracked under water. The end of the break-seal to which this side arm was attached was connected to a vacuum system with a Veeco quick coupling.* In a run, this end was sealed off after degassing.

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* Veeco Instruments, Inc., Plainview, New York, 11803.

1. *Naphthalene Blank* (285°). Naphthalene (2·5 g) was placed in the reaction vessel. The vessel was attached to the vacuum system and evacuated to 5×10^{-3} torr. The naphthalene was then cooled in liquid N_2 and pumped for 30 min. Liquid N_2 was removed, and the naphthalene pumped for additional 10 min at room temp. The tube connecting the vessel to the vacuum system was cooled with dry ice. The vessel was submerged in boiling water to melt the naphthalene. After melting the water bath was removed and the naphthalene allowed to solidify. Any naphthalene condensed in the tubing by the dry ice was sublimed back into the reaction vessel. The vessel was evacuated to 5×10^{-3} torr, sealed, then heated for 10 hr at 285°. After cooling to room temp, the vessel was cooled in liquid N_2, then allowed to warm to room temp. The neck of the side arm was cooled with dry ice, the stem immersed in liquid N_2, the break-seal opened, and any gases present allowed to transfer to the liquid N_2 cooled portion for 2 min. The side arm was then sealed off below the area cooled by dry ice. After warming to room temp, the side arm was opened by cracking the finely drawn point under water which had been degassed by boiling, followed by cooling without being disturbed. The same length of 8 mm tubing evacuated, sealed, and opened under water trapped approximately 10 μl of air. GLC of the trapped gas from the naphthalene blank (10 μl) showed only a trace of methane.

2. *Pyrolysis of* 3 *at* 285°. Compound **3** (5·10 mg, 12·49 μmoles) and naphthalene (2·5 g) were placed in the reaction vessel and degassed in the same manner as the blank. During the first 8 hr at 285° the reaction solution turned yellow. On placing in a dark oven at 110° for 20 hr the colour did not change; however, on remaining in the laboratory (exposed to room lighting) for 20 hr, the color faded completely. The reaction vessel was replaced in the oven at 285°. Almost immediately (5 min) the solution turned yellow; however, this time the color was less intense. The reaction was heated an additional 20 hr at 285°, and then allowed to cool at room temp in ambient light until the very light yellow colour faded. The mixture of gases formed were trapped as described above. The composition of this mixture as found by GLC is given in Table I. Based on the loss of one mole of C_2 hydrocarbon for each mole of **3**, the ethane (4·0 μmoles) and ethylene (0·69 μmole) isolated represent yields of 32% and 5·5% respectively. The naphthalene was sublimed from the mixture. The residue was triturated with benzene (three 0·5 ml portions) to give 2·06 mg of benzene soluble material. TLC of this material on alumina (CCl_4) showed only two spots of R_f 0·30 and 0·42. No spot corresponding to **3** (R_f 0·50) was present. Prep TLC of the benzene soluble material on alumina (CCl_4) gave two bands corresponding to the above spots. These were separated and extracted $CHCl_3$. Five other minor bands of material were resolved by this chromatography but were not studied further. From the band of lower R_f, 0·10 mg (0·25 μmole, 2%) of crystalline material was obtained: UV max (cyclohexane) 248 (rel intensity 0·98), 254 (1·00), 270 sh (0·35), 279 (0·26), 288 (0·17), 300 (0·14), 333 (0·01), and 349 mμ (0·01); IR (KBr) 748 and 717 cm^{-1}; mass spectrum (70eV) *m/e* (rel intensity) 408 (9·4), 379 (100), 378 (22), 377 (14), 376 (18), 363 (11), and 189 (13). A sample of this material was heated in an evacuated tube for 2 hr at 360°. On cooling, a crystalline residue was present which gave UV max ($CHCl_3$) 257, 269, 294, 304 sh, 333, 362, and 382 mμ identical in relative intensity and position to tetrabenzanthracene (**4**).

TABLE 1. GLC OF GAS MIXTURES FROM PYROLYSIS OF **3**.[a]

	% Composition[b]					
Temp.	Methane	Ethane	Ethylene	Propane	Butane	Propene
285	1·1	83·0	13·0	2·4	0·18	0·40
235	trace	77·0	23·0	0·8	[c]	[c]

[a] GLC performed on a 6 ft × 0·25 in column packed with 5% squalene on 60/200 mesh silica gel at 80–85° and 60 ml/min He flow measured at room temperature.

[b] Gases are listed in order of elution, methane eluting first. The composition is by weight and is based on relative area only. No adjustment has been made for relative response of the various components, nor for the differing solubilities in water. Adjustment is made for the amount of air present (10 μl).

[c] Not observed.

From the band of higher R_f, 0·05 mg (0·1 μmole, 1%) of crystalline material was obtained: UV max (cyclohexane) 250 sh (rel intensity 0·99), 254 (1·00), 270 sh (0·49), 290 sh (0·23), 302 (0·23), 340 sh (0·04), and 355 mμ (0·02); IR (KBr) 746 and 716 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 408 (76), 393 (50), 379 (41), 378 (48), 231 (100), 216 (56), 215 (56), 205 (59), and 189 (52).

The benzene insoluble material (3·04 mg, 8·0 μmoles, 64%) had m.p. 426–428°. Under precisely the same conditions, the purified material from Stille[2] had m.p. 426–428°. Authentic tetrabenzanthracene (**4**) from Martin[5] had m.p. 425–427°. The IR and UV spectra of the benzene insoluble material were identical to those of tetrabenzanthracene (**4**).

3. *Naphthalene blank* (240°). Naphthalene (2 g) was sublimed directly into the reaction vessel at 5×10^{-3} torr. The vessel was then sealed and heated for 20 hr at 240°. After cooling to room temp, the gases formed were trapped as described above. GLC showed only a trace of methane present.

4. *Pyrolysis of* 3 *at* 235° in naphthalene. The procedure used with the blank was repeated with **3** (3·8 mg, 9·3 μmoles) added to the vessel before addition of naphthalene (4 g). On warming to 100°, the naphthalene melted and dissolved **3**. The reaction was heated for 16 hr at 235°, during which time the solution became yellow. This colour faded on standing overnight in the laboratory. The composition of the gases trapped (20 μl) is given in Table 1. Based on the loss of one mole of C_2 hydrocarbon for each mole of **3**, the yield of ethene (0·34 μmole) is 3·7% and the yield of ethylene (0·11 μmole) is 1·2%. The naphthalene was sublimed from the mixture. TLC on alumina (CCl_4) of the residue showed mainly **3** (R_f 0·39); however, light spots at R_f 0·46 and 0·23 and the origin were present. The residue was triturated with hexane. The UV spectrum of the hexane soluble material showed the same maxima as **3**; however, these maxima were less well resolved. No tetrabenzanthracene (**4**) was evident in this fraction. From the intensity of the maxima at 300 mμ, the amount of **3** was estimated at 3·7 mg (7·8 μmoles, 84%). The hexane insoluble material was triturated with C_6H_6 and then $CHCl_3$. The UV spectrum of the $CHCl_3$ solution had maxima characteristic of tetrabenzanthracene (**4**) at 382, 362, 333, 304 sh, and 294 mμ; however, the presence of other maxima indicated a mixture.

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