Tetrahedron, 1966, Vol. 22, pp. 2957 to 2966. Pergamon Press Ltd. Printed in Northern Ireland

THE INTERMEDIATE FORMATION OF ACENAPHTHYNE

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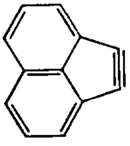
(*Received* 11 *March* 1966; *accepted for publication* 16 *May* 1966)

Abstract—Attempts to detect acenaphthyne (I) in the reactions: (a) dehalogenation of 1,2-dibromoacenaphthylene, (b) pyrolysis of bis-[1-bromoacenaphthylenyl-(2)]mercury and (c) oxidation of acenaphthenequinone-bishydrazone with HgO and MnO_2 are described. It is shown that the products in the presence of 2,5-diphenyl-3,4-benzofurane and tetraphenylcyclopentadienone are unlikely to involve I as an intermediate.

Wittig *et al.*[1–4] generated cycloheptyne, cyclohexyne and cyclopentyne in solution and the decreasing yield of cycloalkyne–diene adducts with decreasing ring size of cycloalkynes was presented as evidence for the degree of strain associated with the intermediate cycloalkynes. Roberts *et al.*[5,6] convincingly established the intermediate character of cyclohexyne and cyclopentyne. Attempts to generate cyclobutyne[6,7] have so far proved unsuccessful.



I

An extension of these investigations to acenaphthyne (I) appeared desirable. The five-membered ring in I, being part of a rigid aromatic system, represents a strained cyclopentyne. It was further expected that the considerable strain associated with structure I might be compensated by a possible conjugation between the triple-bond and the neighbouring double-bonds of the naphthalene moiety. Wittig and Heyn[8] examined 1:2-benzocyclohepten-3-yne and 1:2-benzocyclopenten-3-yne while Huisgen and Sauer[9] suggested earlier that a resonance interaction between the triple-bond and the residual π-electron system might be responsible for the relative stability of the otherwise severely strained benzyne molecule.

Earlier attempts to prepare I include Blumenthal[10] and Dziewoński[11] who by

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[1] G. Wittig and A. Krebs, *Chem, Ber.* **94**, 3260 (1961).

[2] G. Wittig and R. Pohlke, *Chem. Ber.* **94**, 3276 (1961).

[3] G. Wittig and U. Mayer, *Chem. Ber.* **96**, 329 (1963).

[4] G. Wittig, J. Weinlich and E. R. Wilson, *Chem. Ber.* **98**, 458 (1965).

[5] F. Scardiglia and J. D. Roberts, *Tetrahedron* **1**, 343 (1957).

[6] L. K. Montgomery and J. D. Roberts, *J. Amer. Chem. Soc.* **82**, 4750 (1960).

[7] G. Wittig and E. R. Wilson, *Chem. Ber.* **98**, 451 (1965).

[8] G. Wittig and H. Heyn, *Chem. Ber.* **97**, 1609 (1964).

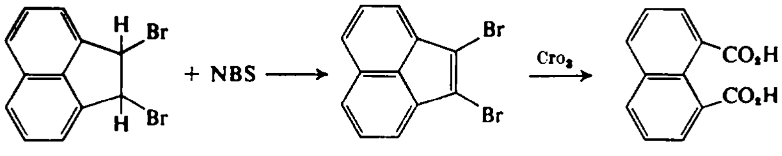
[9] R. Huisgen and J. Sauer, *Angew Chem.* **72**, 107 (1960).

[10] M. Blumenthal, *Ber. Dtsch. Chem. Ges.* **7**, 1092 (1874).

[11] K. Dziewoński, *Ber. Dtsch. Chem. Ges.* **36**, 962 (1903).

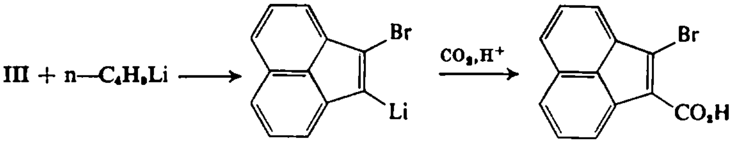
oxidizing acenaphthene obtained decacycline and dinaphthylen-thiophene but the former was considered to be a trimer of I.

The dehalogenation of the hitherto unknown 1,2-dibromoacenaphthylene (III) was envisaged as a suitable pathway to I. Refluxing II with N-bromosuccinimide (NBS) in CCl_4 produced a dibromoacenaphthylene in 23% yield. Chromic acid oxidation of this product gave naphthalic acid, showing the product to have the desired 1,2-dibromoacenaphthylene (III) structure.



II III

Attempts to dehalogenate III with Mg in refluxing tetrahydrofurane (THF) led to a brown amorphous material which did not melt till 300°. Whereas an excess of Mg in 3 hr produced 77% bromide, the use of an equivalent of Mg after 70 hr gave only 64% bromide. The reaction of III with n-butyl-lithium was studied. At −60°, 1-*bromoacenaphthylenyl-2-lithium* (IV) was obtained which on carboxylation yielded 1-*bromoacenaphthylenyl-2-carboxylic acid* (V) in 59% yield. Allowing IV to stand at room temperature for 2 hr followed by carboxylation gave the acid V in 50% yield.



IV V

Heating a suspension of IV in light petroleum only gave polymeric material. The unusual stability of IV and the reported stability of the related 1-bromo-2-lithium-cyclopentene-1[4] is ascribed to resistance offered to the formation of the strained triple-bond that would result from an intramolecular elimination of LiBr from IV. In this connection, 1-fluoro-2-lithium-cyclohexene-1 loses LiF intramolecularly even at −120° to form cyclohexyne.[3]

The reaction of III with Li–Hg in the presence of furane or with Mg in the presence of anthracene gave polymeric material. A Diels-Alder adduct of I with furane or anthracene could not be isolated. However, refluxing a solution of III in THF with Mg in the presence of 2,5-diphenyl-3:4-benzofurane (VI) gave rise to 10,13-*diphenyl*-11:12-*benzofluoranthene* (VII) and 10,13-*diphenyl*-10,13-*endoxy*-11:12-*benzo*-9,10,13,14-*tetrahydrofluoranthene* (VIII) in 4% and 2% yield respectively. The reaction mixture was carefully screened for the desired *acenaphthyne–diene adduct* (IX), but none was detected.

Bergmann[12] has reported the preparation of VIII, m.p. 210°, from acenaphthylene and VI. Dehydration of VIII with HBr–AcOH yielded VII, m.p. 270–271°. The VIII obtained in this work had a m.p. 194–195°. Reinvestigation of Bergmann's work revealed their product to be a mixture of two substances (TLC) which were separated

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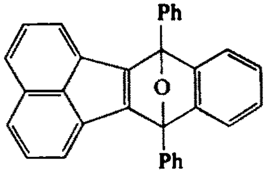
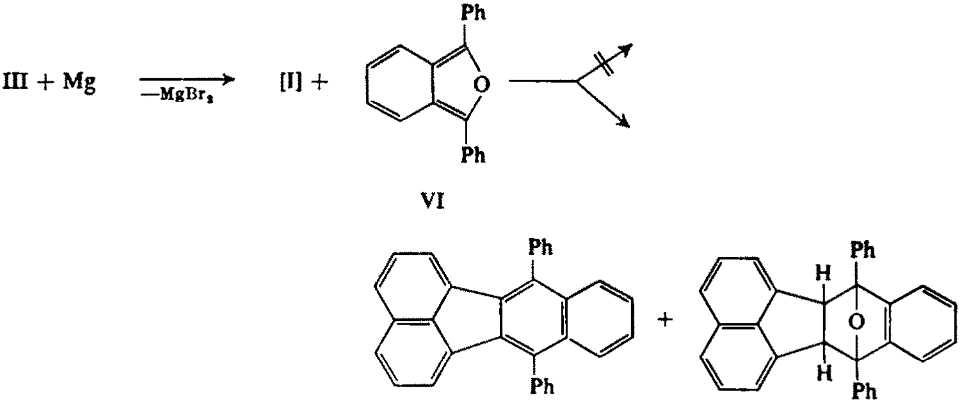
[12] E. Bergmann, *J. Amer. Chem. Soc.* **74**, 1075 (1952).

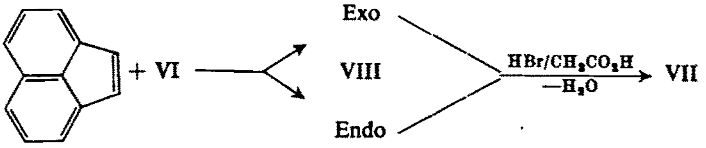


IX

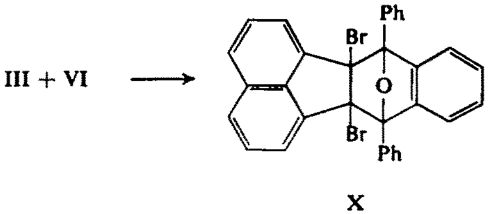


VII VIII

by column chromatography. Recrystallization of the two products gave: (a) light-green rods, m.p. 209° (74%) and (b) white flakes, m.p. 194–195° (26%) which proved to be identical with VIII isolated in this work. Microanalytical data and mol. wt. determination for both (a) and (b) agreed with formula VIII, and treatment with HBr–AcOH in each case gave VII establishing them to be exo–endo isomers. No attempt was made to make any stereochemical assignments.



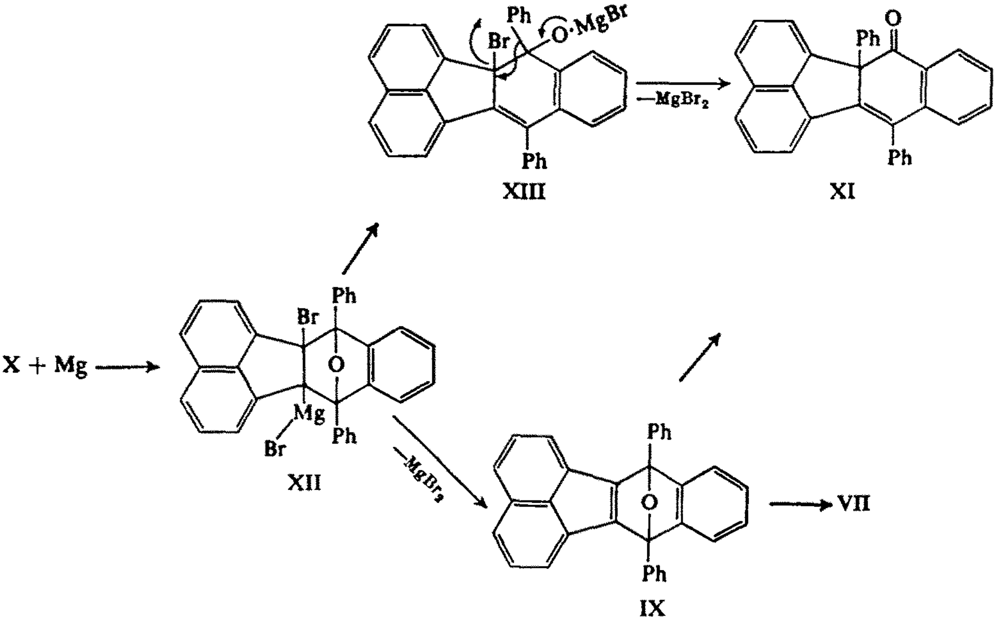
Although the formation of VII and VIII could be explained via I, the alternative possibility of a primary addition of diene VI to III was next examined. Refluxing a mixture of III and VI in THF gave a 45% yield of the Diels-Alder adduct X. In contrast to acenaphthylene, III adds to VI stereospecifically to give a single product.



X

If the yield of adduct is a quantitative measure of strain in the parent olefin, the five-membered ring in III falls between 1,2-dibromocyclopentene and 1,2-dibromocyclobutene, which under comparable conditions add to the diene VI to give the corresponding Diels-Alder adducts in 1% and 90% yields respectively.[4,7]

The reaction of X with Mg in THF, using excess of Mg yielded only VII (55%). With an equivalent of Mg VII was obtained in 44% yield together with 45% unreacted X. In addition a new substance was isolated whose IR spectrum showed a strong absorption at 1690 cm^{-1} diagnostic of an α,β-unsaturated ketone. On the basis of analytical data and in analogy with the work of Wittig and Mayer,[3] XI is considered a likely structure for the ketone. The formation of VII and XI is rationalized as follows:



The Grignard reagent (XII) can either form IX by direct elimination of $MgBr_2$ or cleave the endoxide function to produce the alkoxide XIII. The transition from XIII to XI involves elimination of a bromide anion by the migrating phenyl group. A similar case of phenyl migration has been reported[13] in the conversion of 2-chloro-1-hydroxy-1-phenyl-1,2,3,4-tetrahydronaphthalene to 2-phenyltetralone by PhMgBr. An alternative is the isomerization of IX to XI. Reduction of IX might also be responsible for the formation of VII, the reducing species being either the $MgBr_2$–Mg functioning as a Lewis acid, or the Grignard reagent itself. In view of the unavailability of IX, the precise nature of these transformations must remain speculative.

In order to determine whether the dehalogenation of X with Mg involves IX as an intermediate, the reaction was repeated in the presence of diene VI. In addition to VII isolated in 40% yield, a second product having a strong IR absorption at 1007 cm^{-1}, indicative of an endoxide group, was isolated in 17% yield. The analytical data are in

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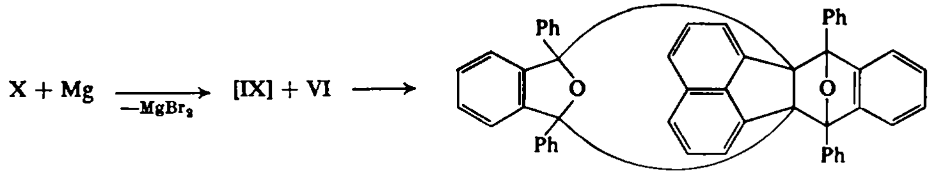
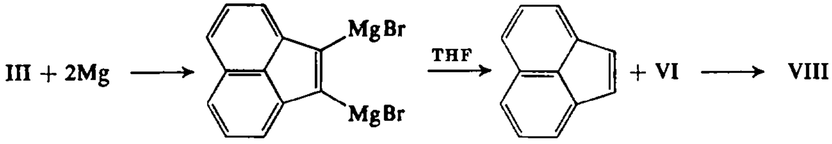
[13] M. Tiffeneau and A. Orekhoff, *C. R. Acad. Sci. Paris* **170**, 465 (1920); see also J. K. Sille and R. A. Newsom, *J. Org. Chem.* **26**, 1375 (1961).

agreement with its formulation as *bis*-[1,3-*diphenylphthalanylene*-(1 : 3)]*acenaphthene* (XIV). Heating XIV with Se at 300° gave VII. The isolation of XIV clearly establishes IX as an intermediate in the reaction of X with Mg.



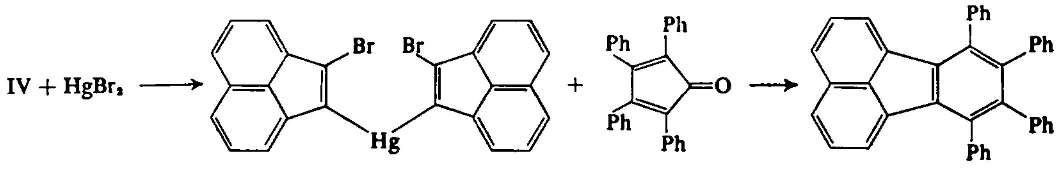
XIV

In retrospect therefore, the mode of formation of VII and VIII in the reaction of III with Mg in the presence of diene VI remains open. The observation that an initial addition of III to VI, followed by dehalogenation with Mg yields VII does not rule out, and indeed obscures, a possible competing reaction leading to I as the intermediate. The genesis of VIII is likewise uncertain. It probably arises from the bis-Grignard compound (XV) which is protonated by THF to acenaphthylene, addition of which to VI would give VIII.



XV

Bis[1-*bromo-acenaphthylenyl*-2]*mercury* (XVI) was next investigated as a possible source of I. Heating XVI at 240° in the presence of tetraphenylcyclopentadienone (XVII) gave a 76% yield of 10,11,12,13-*tetraphenylfluoranthene* (XVIII). On heating a suspension of XVI in decaline at 240° however, 65% of XVI was recovered; the remainder being decomposed material. The contrasting behaviour of XVI with and without XVII suggests that XVIII is formed via a direct addition of XVII to XVI, with subsequent elimination of $HgBr_2$ and CO. A free-radical pathway involving elimination of Hg as a first step is unlikely in view of the fact that elementary Hg could not be detected in the decomposition of XVI in the absence of XVII. Wittig and Ebel[14] have argued that a direct addition of diene to a double bond substituted with Hg, bromine and particularly iodine would on account of their large steric requirements be severely hindered. Previous work[15] however has shown that the carbon-mercury-carbon array.



XVI XVII XVIII

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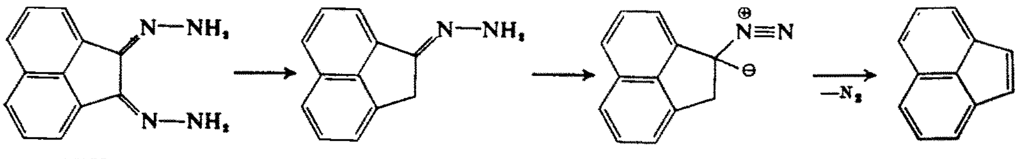
[14] G. Wittig and H. F. Ebel, *Liebigs Ann.* **650**, 24 (1961).

[15] G. C. Hampson, *Trans. Faraday Soc.* **30**, 877 (1934); de Laszlo, *Ibid.*, **30**, 884 (1934).

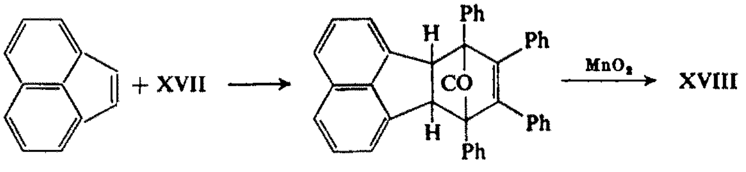
although normally linear, can be distorted by almost 30° about its normal position. At 240° XVI could therefore be forced into a suitable conformation for an addition of XVII to be facilitated.

As a last attempt at generating I, the oxidation of the known *acenaphthenequinone-bishydrazone* (XIX)[16] was studied. Refluxing a solution of XIX with HgO gave mostly dark unidentifiable products. A small amount of acenaphthylene, formed by way of a Wolf-Kishner reaction, was isolated. Oxidation of XIX with Hgo in the presence of diene VI gave the exo–endo isomers VIII as the only isolated products (3%). Compound VIII clearly derives from an addition of acenaphthylene to VI.



XIX

Wittig and Heyn[8] have successfully used active MnO_2 to generate 1:2-benzocyclopenten-3-yne from indanedione(1,2)bishydrazone, having failed to realise a reaction with HgO. Oxidation of XIX with MnO_2 in the presence of XVII gave a small amount of XVIII. The possibility of acenaphthylene being the precursor of XVIII needed clarification. Refluxing a mixture of acenaphthylene and XVII in benzene yielded the Diels-Alder adduct 10,11,12,13-*tetraphenyl*-10,13-*endocarbonyl*-9,10,13,14-*tetrahydrofluoranthene* (XX) in 60% yield. The IR spectrum of XX showed absorption due to the endocarbonyl group at 1780 cm^{-1}. The similarly constituted 7-benzonorbornenone absorbs at 1792 cm^{-1}.[17] Further reaction of XX with MnO_2 in refluxing benzene gave XVIII in 56% yield.



XX

Although the results can not be brought to bear on the initially posed problem relating to the intermediate formation of I, they do show that the isolation of cycloalkyne–diene adducts as a criterion of cycloalkyne formation should be used with considerable care.

EXPERIMENTAL

All m.ps determined on an apparatus designed by Dr. Tottoli of W. Büchi, Flawil/Switzerland are corrected. IR spectra (Perkin–Elmer 21 spectrometer); mol. wts (osmometer Model 30 I A of Mechrolab Inc., Mountain View/California) in the solvents indicated. Work with organo-metallic compounds was carried out using dry solvents in an inert atmosphere of dry and O_2-free N_2. Al_2O_3 used for chromatography was of Merck grade. Microanalyses were carried out by Dr. A. Schoeller, Kronach/Oberfranken, W. Germany.

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[16] L. Berend and J. Herms, *J. Prakt. Chem.* **60**, 16 (1899).

[17] P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.* **82**, 1244 (1960).

1,2-*Dibromoacenaphthene* (II). Bromine (60 ml; 1·18 moles) was added dropwise to a stirred soln of acenaphthylene (180 g; 1·18 moles) in 350 ml ether at room temp. The reaction mixture was stirred under ice-cooling for another 2 hr. The crystalline II was filtered off and washed with ice-cold ether and dried *in vacuo* at 40°, yield 150 g (41%) m.p. 120–122°. An analytical sample, m.p. 124–125° was recrystallized from EtOH. (Found: C, 46·32; H, 2·76. Calc. for $C_{12}H_8Br_2$: C, 46·19; H, 2·58%.)

1,2-*Dibromoacenaphthylene* (III). A soln of II (56 g; 179 mmoles) in CCl_4 (500 ml) was refluxed with NBS (32 g; 179 mmoles) and dibenzoyl peroxide (1 g) for 2 hr. The succinimide formed was filtered off and the brown CCl_4 soln was washed with two 60 ml portions of 1N NaOH. After washing with water and drying, the solvent was removed and the residue chromatographed on 450 g basic Al_2O_3. Elution with light petroleum (b.p. 40–60°)–cyclohexane gave a product which after two recrystallizations from EtOH gave III (13·3 g; 23%) as orange-yellow crystals m.p. 114–115°. (Found: C, 46·61; H, 2·05; Br, 51·32; mol.wt. 305·1 in benzene. $C_{12}H_6Br_2$ mol.wt. 310·0 requires: C, 46·49; H, 1·95; Br, 51·55%.)

Chromic acid oxidation of III. CrO_3 (5·5 g; 56 mmoles) was added in small portions to a soln of III (2·17 g; 7 mmoles) in hot glacial AcOH (45 ml) and the mixture refluxed for 6 hr. It was then poured into 1 l. water and the solid dissolved in 50 ml 1N NaOH and the soln filtered and acidified with conc. HCl. The ppted acid was filtered off, washed with water and dried over P_2O_5 *in vacuo*. The naphthalic acid (430 mg; 28·5%) was converted to the anhydride by dissolving in hot conc. HNO_3 (10 ml) and allowing to crystallize. Recrystallization from 10 ml glacial AcOH gave the anhydride, m.p. 274°. A mixed m.p. with an authentic sample of naphthalic acid anhydride gave no depression and IR spectra of the two samples were superimposable.

1-*Bromoacenaphthylenyl-2-lithium* (IV). To a stirred suspension of III 0·93 g; 3 mmoles) in abs ether (20 ml) at −60°, 1·2N n-butyl-lithium (2·5 ml; 3 mmoles) was added. Compound III dissolved to give a yellow soln which soon deposited IV and the mixture was poured into a stirred and saturated soln of CO_2 in ether at −60°. After hydrolysis, the ethereal soln was shaken with 1N NaOH (10 ml) and the alkaline extract acidified with conc. HCl under ice-cooling. The ppted acid was filtered off, washed with water and dried over P_2O_5 yielding 0·49 g (59%) of 1-*bromoacenaphthylenyl-2-carboxylic acid* (V) m.p. 260–262° (dec). Recrystallization from benzene–acetone gave pure V, m.p. 262–263°. (Found: C, 56·65; H, 2·60; Br, 29·30; mol. wt. 285·5 in acetone. $C_{13}H_7BrO_2$ mol. wt. 275·1 requires: C, 56·75; H, 2·56; Br, 29·05%.)

Bis[1-*bromoacenaphthylenyl*-2-]*mercury* (XVI). To a stirred supsension of IV (prepared from III; 10 g; 32 mmoles) in ether at −60°, solid $HgCl_2$ (3 g; 11 mmoles) was added. The mixture was allowed to warm to room temp and stirred overnight. The yellow solid was filtered off, extracted with hot MeOH (300 ml) and the dried product recrystallized from 1 l. hot dimethylformamide yielding XVI (5·8 g; 55%) as yellow felty needles, m.p. 314° (dec.) (Found: C, 43·44; H, 1·82; Hg, 30·63.[18] $C_{24}H_{12}HgBr_2$ requires; C, 43·62; H, 1·83; Hg, 30·36%.)

Acenaphthenequinone-bishydrazone (XIX). Acenaphthenequinone m.p. 265–268° (16 g; 88 mmoles), hydrazine hydrate (8·8 g; 176 mmoles) and EtOH (30 ml) were heated to 100° in a sealed tube for 16 hr. The resulting solid was refluxed with 800 ml of chf–EtOH (1:1) and animal charcoal. The filtrate, after another treatment with charcoal, on cooling deposited XIX (7·4 g; 40%) m.p. 191–192° (dec). Recrystallization from chf–EtOH gave yellow needles m.p. 194° (dec). (Found: C, 68·68; H, 5·02; N, 25·75. Calc. for $C_{12}H_{10}N_4$: C, 68·57; H, 4·76; N, 26·67%.)

Reaction of acenaphthylene with 2,5-*diphenyl*-3,4-*benzofurane* (VI). Acenaphthylene (0·6 g; 4 mmoles) and VI (1·1 g; 4 mmoles) were heated under reflux in 10 ml xylene for 7 hr. The product, on diluting the cooled xylene soln with light petroleum (50 ml b.p. 40–60°) was recrystallized from 40 ml isoamyl alcohol. The product m.p. 175–200° (0·9 g; 53%) was chromatographed on 160 g basic Al_2O_3. Elution with light petroleum (b.p. 60–70°)–benzene using continous chromatography gave two products: (a) 550 mg (76%) which on recrystallization from AcOEt–EtOH gave 450 mg of VIII m.p. 208–209°. (Found: C, 90·65; H, 5·15; mol.wt. 416·8 in benzene. $C_{32}H_{22}O$ mol.wt. 422·5 requires: C, 90·96; H, 5·25%.) (b) 190 mg (24%), recrystallization from AcOEt–EtOH gave 160 mg of VIII, m.p. 194–195°. (Found: C, 91·13; H, 5·25; mol.wt. 421·9 in benzene $C_{32}H_{22}O$ mol.wt. 422·5 requires: C, 90·96; H, 5·25%.)

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[18] Determination of Hg was carried out following the method of Sandin and Margolis in R. Fresenius and G. Jander, *Handbuch der Analytischen Chemie* p. 517, Springer-Verlag, Berlin (1945).

Removal of the elements of water from (a) and (b) was carried out as described by Bergmann,[11] yielding 10,13-*diphenyl*-11:12-*benzofluoranthene* (VII) in 70% and 52% yields respectively.

Reactions of 1,2-*dibromoacenaphthylene* (III)

With Mg *in the presence of* 2,5-*diphenyl*-3:4-*benzofurane* (VI). A soln of III (3·1 g; 10 mmoles) and VI (9·4 g; 35 mmoles) in abs THF (45 ml) was refluxed with Mg (0·5 g; 21 mmoles) under N_2 for 6 hr. The THF was removed *in vacuo* and the residue extracted with 150 ml benzene and 50 ml chf. Air was bubbled through the fluorescent soln till no more fluorescence was observed (1 week). The residue after removal of solvents was chromatographed on 400 g basic Al_2O_3. Cyclohexane–CCl_4 eluted 200 mg of a strongly fluorescent product which on recrystallization from 25 ml glacial AcOH gave 150 mg (3·7%) 10,13-*diphenyl*-11:12-*benzofluoranthene* (VII) m.p. 271–272°, identified by its mixed m.p. with an authentic sample. Elution with benzene gave 100 mg of a product m.p. 180–185°, which on recrystallization from cyclohexane yielded VIII (70 mg; 1·7 %), m.p. 194–195°. A mixed m.p. with an authentic sample gave no depression.

With 2,5-*diphenyl*-3:4-*benzofurane* (VI). A soln of III (2·95 g; 9·5 mmoles) and VI (8·95 g; 33 mmoles) in abs THF (45 ml) was refluxed for 6 hr. After diluting with 50 ml benzene air was bubbled through the soln for 96 hr. The residue on removing the solvents from the dried soln was chromatographed on 400 g basic Al_2O_3. Cyclohexane–CCl_4 eluted III (1·45 g; 50%) m.p. 114–115° (mixed m.p.); CCl_4–benzene eluted 2·48 g (45%). 10,13-*diphenyl*-10,13-*endoxy*-9,14-*dibromo*-11:12-*benzo*-9,10,13,14-*tetrahydrofluoranthene* (X) m.p. 217–218°. Recrystallization from AcOEt–EtOH gave X m.p. 222–223°. (Found: C, 66·02; H, 3·79; Br, 27·07. $C_{32}H_{20}Br_2O$ requires; C, 66·22; H, 3·47; Br, 27·54%.)

Reactions of 10,13-*diphenyl*-10,13-*endoxy*-9,14-*dibromo*-11:12-*benzo*-9,10,13,14-*tetrahydrofluoranthene* (X)

With an excess of Mg. A soln of X (2 g; 3·4 mmoles) in abs THF (35 ml) were refluxed with Mg (0·4 g; 16·4 mmoles) under N_2 for 6 hr. Chf (100 ml) was added and the organic phase was washed with water and dried. The residue on removal of solvents was chromatographed on 400 g basic Al_2O_3. Compound VI (760 mg), m.p. 265–259°, was eluted with CCl_4. Recrystallization from AcOEt–EtOH gave VII (520 mg; 37%), m.p. 272–273°. (Found: C, 94·88; H, 4·96; mol.wt. 397·0 in benzene. Calc. for $C_{32}H_{20}$ mol.wt. 404·5; C, 95·01; H, 4·98%.)

With an equivalent of Mg. A soln of X (1·16 g; 2 mmoles) in abs THF (20 ml) was refluxed with Mg (50 mg; 2 mmoles) under N_2. The Mg was completely consumed in 3 hr and the clear soln was refluxed another 3 hr; then ether (70 ml) was added and the organic phase washed thrice with water. A Volhardt titration of the aqueous extract gave 57% bromide. The organic phase was dried and the residue after removal of solvents was chromatographed on 200 g neutral Al_2O_3. Cyclohexane–CCl_4 (7:3) eluted VII (354 mg; 44%), m.p. 272–273° (mixed m.p,). Elution with CCl_4 gave X (517 mg; 45%) m.p. 215–217°. Recrystallization from AcOEt–EtOH gave pure X m.p. 219–220°. Benzene finally eluted 46 mg of a yellow product which on recrystallization from EtOH (10 ml) gave XI (30 mg; 3·5%) as yellow flakes m.p. 228–230° in accordance with the IR spectrum at 1690 cm^{-1}. (Found: C, 91·36; H, 4·32. $C_{32}H_{20}O$ requires: C, 91·40; H, 4·79%.)

With Mg *in the presence of diene* VI. Compound X (2·5 g; 4·3 mmoles) and VI (9·4 g; 35 mmoles) were dissolved in THF (45 ml) and refluxed with Mg (0·5 g; 20·5 mmoles). The reaction was started by adding a few drops of ethylene bromide. After 6 hr MeOH was added and the mixture extracted with three 50 ml portions of benzene and once with 50 ml chf. Air was bubbled through the chf–benzene extract for 4 days to oxidize unreacted VI. The residue on removal of solvent was chromatographed on 400 g basic Al_2O_3. Cyclohexane–CCl_4 eluted VII (40%). Benzene eluted a product which on recrystallization from benzene–cyclohexane gave 500 mg (17%) *bis*-[1,3-*diphenylphthalanylene*-1,3] *acenaphthene*-1,2 (XIV) m.p. 267–269° (dec). A second recrystallization from benzene gave XIV m.p. 272°. (Found: C, 90·56; H, 5·28, $C_{52}H_{34}O_2$ requires: C, 90·40; H, 4·96%.)

Pyrolysis of XIV *with selenium.* A mixture of XIV (80 mg) and Se powder (500 mg) were heated to 300° for 7 hr. The resulting mass was extracted with 10 ml hot benzene, filtered free from Se and the benzene extract chromatographed on 30 g basic Al_2O_3. Cyclohexane–CCl_4 eluted VII (5 mg; 10·6%), m.p. 269–270°. A mixed m.p. with an authentic sample of VII gave no depression.

Pyrolysis of bis[1-*bromoacenaphthylenyl*-2]*mercury* (XVI)

In the presence of tetraphenylcyclopentadienone (XVII). Compound XVI (2·46 g; 4 mmoles) and XVII (3·8 g; 10 mmoles) were well mixed and heated at 240–250° for 4 hr. The dark powder was chromatographed on 250 g neutral Al_2O_3. Benzene–light petroleum (b.p. 60–70°) eluted 3·1 g (76%) of a product m.p. 300° which on recrystallization from benzene gave a product m.p. 312–314°, identical with an authentic sample of 10,11,12,13-*tetraphenylfluoranthene* (XVIII) prepared according to Dilthey *et al.*[19] (Found: C, 94·96; H, 5·12. Calc. for $C_{40}H_{26}$: C, 94·82; H, 5·17%.)

In decalin. A suspension of XVI (1·3 g; 2 mmoles) in decalin was heated at 245–250° in a sealed tube for 4 hr. The insoluble substance was filtered off and recrystallized from dimethylformamide (100 ml) yielding XVI (0·85 g; 65%) m.p. 312–313° (mixed m.p.). The decalin solution on distillation *in vacuo* gave a dark unidentifiable residue.

Oxidation of acenaphthenequinone-bishydrazone (XIX)

With HgO. Compound XIX (2·1 g; 10 mmoles) was dropped into a vigorously stirred suspension of HgO (8·66 g; 40 mmoles) and powdered KOH (0·5 g) in abs benzene (280 ml). Compound XIX, which is only slightly soluble in benzene, was placed in a soxhlet and was slowly dissolved by the refluxing benzene in 3 hr. The oxidation was started by the addition of a few drops of hydrazine hydrate and the reaction was stopped 3 hr after addition of XIX was complete. Unreacted HgO and the metallic Hg formed were separated and the dark brown benzene soln stripped of solvent and the residue chromatographed on 400 g basic Al_2O_3. CCl_4–benzene (1:1) eluted 200 mg of a yellow viscous oil which did not crystallize. Sublimation at 80°/14 mm gave 20 mg of a yellow solid which on resublimation gave a small amount of acenaphthylene m.p. 86–90° (mixed m.p.). AcOEt eluted 1·5 g of a brown intractable material which could not be purified.

With HgO *in the presence of diene* VI. The preceding oxidation was repeated using HgO (8·66 g; 40 mmoles) powdered KOH (0·5 g) and XIX (2·1 g; 10 mmoles) in abs benzene (250 ml) in the presence of VI (2·97 g; 11 mmoles). After 6 hr, 360 ml N_2 (corrected to NTP) were collected in an attached gas-burette. The inorganic residue was filtered off, air was bubbled through the benzene soln for 4 days and the benzene residue chromatographed on basic Al_2O_3. CCl_4 eluted 520 mg of a yellowish oil which yielded a product, m.p. 140–160° which was rechromatographed on 150 g basic Al_2O_3. Cyclohexane–benzene (1:1) eluted 374 mg of product which after two recrystallizations from AcOEt-EtOH gave 100 mg (2·4 %) light yellow rods m.p. 208–209° which proved to be identical with the higher melting isomer of adduct VIII. (Found: C, 90·75; H, 5·43. Calc. for $C_{31}H_{22}O$: C, 90·96; H, 5·25%). Benzene eluted 43 mg of product which on recrystallization from cyclohexane gave 32 mg (0·76%) of substance m.p. 190–192°, identical (mixed m.p. and TLC) with the lower melting isomer of VIII. AcOEt and MeOH eluted only dark unidentifiable products.

With MnO_2 *in the presence of diene* XVII. As already described, XIX (2·1 g; 10 mmoles), active MnO_2[20] (43 g) and powdered KOH (0·5 g) were refluxed in abs benzene (280 ml) in the presence of XVII (4·23 g; 11 mmoles). After complete extraction of XIX, the reaction mixture was refluxed for 3 hr. The hot benzene soln was filtered free from MnO_2, which was further extracted in a soxhlet with benzene. The combined benzene extracts were stripped of solvent and the dark residue was chromatographed on 400 g basic Al_2O_3. Light petroleum (b.p. 60–70°)–benzene (7:3) eluted 33 mg orange crystals which on recrystallization from EtOH gave 10 mg of product, m.p. 162–164°, which was not investigated. Further elution gave 17 mg impure crystals which were washed with cold cyclohexane to give 5 mg product m.p. 295°. TLC showed the material to be identical with XVIII. Benzene eluted XVII (2·13 g; 50%) and elution with AcOEt gave 2·48 g of dark tarry material. TLC of this material showed it to be a very complex mixture.

10,11,12,13-*Tetraphenyl*-10,13-*endocarbonyl*-9,10,13,14-*tetrahydrofluoranthene* (XX). Acenaphthylene (0·92 g; 6 mmoles) and XVII (1·92 g; 5 mmoles) were refluxed in 25 ml benzene. The reaction was incomplete even after 1 week. On allowing the benzene soln to stand at room temp overnight, a crystalline product was obtained which on recrystallization from cyclohexane–benzene yielded XX (1·59 g; 60%), m.p. 216–217° (dec) with IR absorption at 1780 cm^{-1}. (Found: C, 91·70; H, 5·26. $C_{41}H_{28}O$ requires: C, 91·77; H, 5·27%.)

Reaction of XX *with* MnO_2. Compound XX (1·14 g; 2·1 mmoles) in benzene (200 ml) was refluxed

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[19] W. Dilthey, S. Henkels and A. Schäfer, *Ber. Dtsch. Chem. Ges.* **71**, 979 (1938).

[20] J. Attenburrow, *J. chem. Soc.* 1094 (1952).

with MnO_2 (6 g) and powdered KOH (200 mg) for 20 hr, with vigorous stirring. The MnO_2 was filtered off and the residue after removal of solvent was chromatographed on 150 g basic Al_2O_3. Elution with benzene–light petroleum (b.p. 60–70°) (3:7) gave 788 mg of a fluorescent substance which on recrystallization from 15 ml benzene gave XVIII (606 mg; 56%), m.p. 312–314° (mixed m.p.).

Acknowledgement—The work was carried out in the laboratory of Prof. Dr. h. c. G. Wittig, Director, Institut für Organische Chemie der Universität Heidelberg, W. Germany. The author wishes to thank Prof. Wittig for his advice and encouragement. The award of a Deutsche Akademische Austauschdienst scholarship is gratefully acknowledged.