and 0.5 g of palladium-on-charcoal (10%) catalyst was added. Reduction was carried out in a Parr hydrogenator at room temperature during 24 hr. The catalyst was removed by filtration and the filtrate was concentrated to give 0.75 g of solid residue, which was washed with chloroform and crystallized from ethanol. The resulting material, melting range 223–240° dec, showed traces of inorganic impurity but could not be readily purified further. This material gave a strong positive ninhydrin reaction. Its infrared spectrum was essentially identical with that of the dl-pentafluorophenylalanine prepared via the acetamidomalonic ester route. The azide band was absent.

Reaction of 4 with Ammonia.—In a 100-ml Pyrex tube sealed at one end was placed 3.75 g of bromo acid dissolved in 10 ml of ethanol. The solution was cooled to −70° and 35 ml of liquid ammonia was added. The tube was sealed and shaken at room temperature for 4 days. The tube was opened and the excess ammonia was driven off by air blowing. Ethanol was removed by heating on a steam bath to give a solid residue. After crystallization from 66% ethanol, 2.5 g of white needles, mp 192°, was obtained. This material failed to give a ninhydrin reaction, was soluble in aqueous Na_2CO_3 and NaOH, but was insoluble in dilute HCl. This product reacted slowly with bromine in CCl_4, but decolorized an aqueous solution of $KMnO_4$; spectral data: ir, 3520 and 3415 (NH_2), 3100–2500 (CO_2H), 1690 (conjugated CO_2H) cm^{-1}; ultraviolet, λ 325 mμ (ϵ 17,600) and 230 mμ (ϵ 8800); pmr, δ 8.09 (doublet, $J_{H,H}$ = 15 Hz), 6.96 (doublet, $J_{H,H}$ = 15 Hz.). *Anal.* Calcd for $C_9H_5O_2NF_4$: C, 45.96; H, 2.13; N, 5.96; F, 32.34; mol wt, 235. Found: C, 46.29; H, 2.14; N, 6.67; F, 32.46; mol wt (neut equiv), 232. The yield of 4-amino-2,3,5,6-tetrafluoro-*trans*-cinnamic acid was 91%.

2-Phenyl-4-pentafluorobenzylidene-5(4H)-oxazolone. Method A.—Pentafluorobenzaldehyde reacted with hippuric acid in the presence of sodium acetate and acetic anhydride according to a known procedure.[25] The yield of light yellow needles, mp 169.5–170.2°, was 54%; spectral data: ir, 3080, 1804 (vs) (lactone C=O), 1666, 1645, 1600, 1560, 1450, 1330, 1068, 992, 700 cm^{-1}; ultraviolet, $\lambda_{max}^{Et_2O}$ 310 mμ (ϵ 28,550), 254 (ϵ 14,800), 237 (ϵ 15,240),

(25) H. B. Gillespie and H. R. Snyder, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp 490, 491.

$\lambda_{max}^{CHCl_3}$ 320 mμ. In 95% ethanol solution,[16] diminution of the band at 310 mμ occurs after less than 30 min with a corresponding development and increase in intensity of a new band at 230 mμ. *Anal.* Calcd for $C_{16}H_6O_2NF_5$: C, 56.64; H, 1.78. Found: C, 56.25; H, 1.84.

Method B.—Pentafluorobromobenzene (3.1 g) in 15 ml of anhydrous ether was added to 0.313 g of magnesium turnings in a three-neck flask, fitted with a mechanical stirrer, reflux condenser, and dropping funnel. After the Grignard reagent had formed, an additional 15 ml of ether was added, the contents of the flask were cooled, 1.15 g of cadmium chloride was added in two portions, and the mixture was stirred and warmed slightly for 30 min. Ether was removed under diminished pressure and replaced by 15 ml of thiophene-free benzene. A solution of 2.5 g of 2-phenyl-4-chloromethylene-5(4H)-oxazolone[15] in 20 ml of benzene was added with continuous stirring during 10–15 min. The yellow reaction mixture was warmed on a water bath for 1.5 hr (50–60°), cooled, and acidified with dilute acetic acid. The benzene layer was separated and dried over anhydrous magnesium sulfate, and the benzene was removed to leave about 100 mg (*ca* 2%) of azlactone, mp 170–172°. This material was identical with that obtained by method A.

dl-Pentafluorophenylalanine.—When a mixture of the aforementioned oxazolone and red phosphorus in acetic anhydride was gently refluxed with 50% hydriodic acid for 3–4 hr,[25] a 60% yield of amino acid, mp 251–254° dec, was obtained. This material was identical with that obtained by the acetamidomalonate method (*vide supra*).

Condensed Cyclobutane Aromatic Compounds. XXX. The Synthesis of Some Unusual 2,3-Naphthoquinonoid Heterocycles. A Synthetic Route to Derivatives of Naphtho[2, 3-*b*]biphenylene and Anthra[*b*]cyclobutene[1]

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The isolable, but highly reactive, 1,3-diphenylnaphtho[2,3-*c*]furan (9) has been prepared by a simple reaction sequence starting with 2,3-dimethylnaphthalene. Compound 9, which represents the first known stable 2,3-naphthoquinonoid substance, is an extremely reactive diene component in the Diels–Alder reaction: its reactivity exceeds that of its much studied lower benzolog, 1,3-diphenylbenzo[*c*]furan (7). A number of Diels–Alder adducts of 9 have been prepared, some of which have been aromatized; in this way, the synthesis of derivatives (36 and 47) of the naphtho[2,3-*b*]biphenylene and anthra[*b*]cyclobutene systems has been achieved. Reaction of 9 with phosphorus pentasulfide gives 1,3-diphenylnaphtho[2,3-*c*]thiophene (10), the first derivative of a new aromatic heterocyclic system. Thiophene 10 is a much less reactive diene in Diels–Alder additions than is furan 9, suggesting considerable resonance stabilization for the naphtho[2,3-*c*]thiophene system.

In the course of studies concerned with synthetic routes to benzocyclobutene (1) and naphtho[*b*]cyclobutene (2), our attention became drawn to differences in reactivity between their ring-opened *o*-quinonoid hydrocarbon precursors 3 and 4. Although both 3 and 4 are extremely reactive and nonisolable species, the 2,3-naphthoquinonoid compound 4 shows evidence of

being the more reactive of the two. This difference in behavior is not unexpected if 3 and 4 are viewed as carbon analogs of *o*-benzoquinone (5) and the as yet unknown 2,3-naphthoquinone (6), respectively.[3] The *o*-quinonoid system of 3 can achieve a fair degree of stabilization if the methylene groups form part of a heterocyclic ring, and especially if they also bear conjugating substituents. Thus, 1,3-diphenylbenzo[*c*]furan (7) and 1,3-diphenylbenzo[*c*]thiophene (8)

(1) A portion of this work was reported as a preliminary communication: M. P. Cava and J. P. VanMeter, *J. Am. Chem. Soc.*, 84, 2008 (1962).

(2) To whom all inquiries should be addressed: Department of Chemistry, Wayne State University, Detroit, Mich. 48202.

(3) M. P. Cava and R. L. Shirley, *J. Am. Chem. Soc.*, 82, 654 (1960).

are stable crystalline compounds which have been known for many years.

1   2   3   4

5   6   7   8
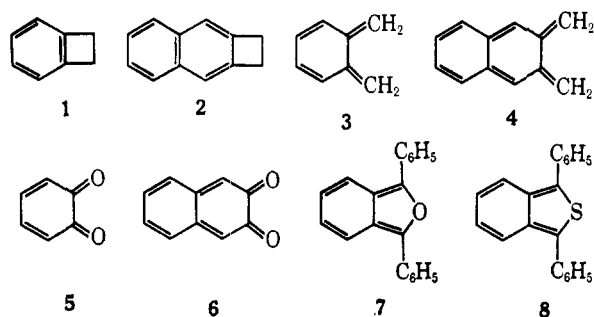
Some time ago, we reported briefly upon the synthesis and properties of the first heterocycles which incorporate the o-quinonoid system of 4, namely 1,3-dipenylnaphtho[2,3-c]furan (9) and 1,3-diphenylnaphtho[2,3-c]thiophene (10).[1,4] A detailed account of this work and the use of compound 9 in the synthesis of some new aromatic systems containing a condensed cyclobutane ring form the subject of the present paper.


9   10
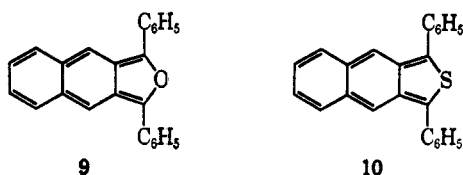
Results

Synthesis of 1,3-Diphenylnaphtho[2,3-c]furan.—3-Benzoyl-2-naphthoic acid (11) was prepared in excellent over-all yield from 2,3-dimethylnaphthalene (12) by the following synthetic sequence: sodium dichromate oxidation of 12 to naphthalene-2,3-dicarboxylic acid (13),[5] conversion of 13 to its anhydride (14),[6] and Friedel-Crafts condensation of 14 with benzene to give 11[7,8] (Scheme I). Sodium borohydride reduction of 11 gave, after acidification, lactone 15. Reaction of 15 with phenylmagnesium bromide afforded, after careful work-up with ammonium chloride, the crystalline lactol 16.

Treatment of the above-mentioned Grignard reaction mixture from 15 with dilute hydrochloric acid gave rise to a bright red, orange fluorescent, nonpolar amorphous product; the same material could be obtained from pure lactol 16 and mineral acid. It was not possible to crystallize this red compound either before or after chromatography, and the material invariably underwent decomposition in the course of prolonged laboratory manipulation. The red compound, which proved to be the quinonoid furan 9, was finally obtained in crystalline form by heating a suspension of lactol 16 in a small amount of acetic acid for a few minutes on the steam bath. The deep red glistening plates of 9 thus

obtained were directly pure and analyzed fairly well for $C_{24}H_{16}O$. The dried crystals could be stored for several months in the absence of light and air. On the other hand, solutions of 9 in organic solvents decolorized slowly on standing; recrystallization of crystalline 9 was never achieved. Oxidation of either furan 9 or lactol 16 with chromium trioxide in pyridine gave the same product, namely 2,3-dibenzoylnaphthalene (17).

SCHEME I

12   13

14   11

15   16

9 →

17
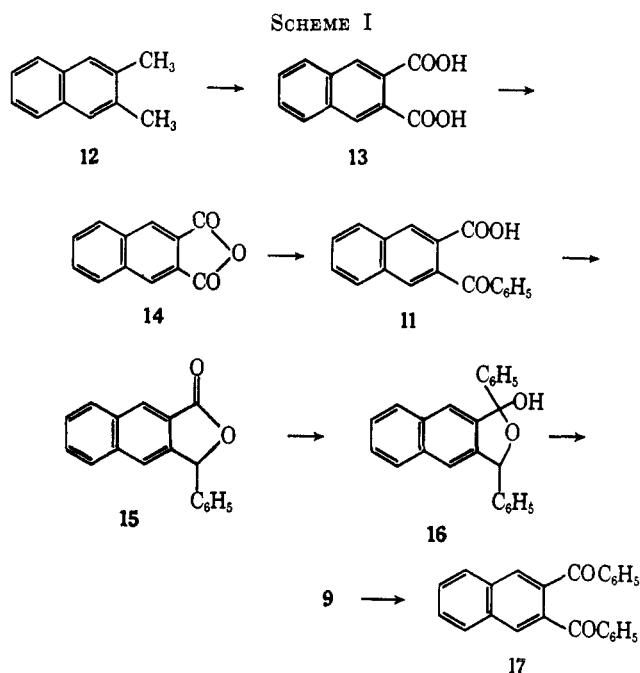
Diels-Alder Additions of 1,3-Diphenylnaphtho[2,3-c]furan.—Furan 9 proved to be an extremely reactive diene component in Diels-Alder additions. Thus, it reacted practically instantaneously at room temperature with N-phenylmaleimide, maleic anhydride, and tetracyanoethylene to give, respectively, adducts 18, 19, and 20. Dimethyl acetylenedicarboxylate, ω-nitrostyrene, 1,4-naphthoquinone, and 1,4-benzoquinone added to 9 within a few minutes at room temperature to give the corresponding adducts 21, 22, 23, and 24. The less reactive dienophiles acenaphthylene and hexafluoro-2-butyne added to 9 within 10 min in refluxing benzene to give adducts 25 and 26. Adducts 25 and 23 were aromatized by hydrogen bromide in acetic acid to yield the naphthofluoranthene derivative 27 and 6,13-diphenylpentacene-5,14-quinone (28), respectively. Several attempts to aromatize adducts 18, 19, 22, and 24 under similar conditions led to no characterizable products.[9]

Synthesis of a Naphtho[b]biphenylene Derivative.—In addition to the Diels-Alder reactions described in the preceding section, several other additions to 9 were investigated; these will be described separately in this and in the following section, since their primary objective was the synthesis of new types of condensed cyclobutane aromatic systems.

1,3-Dipenylbenzo[c]furan (7) has been employed previously as a trapping agent for the detection of the

(4) Recently, the related nitrogen heterocycle benz[f]isoindole and its 1-phenyl derivative have been generated, but they proved to be too unstable to permit their isolation: J. E. Shields and J. Bornstein, *Chem. Ind.* (London), 1404 (1967).

(5) L. Friedman, *Org. Syn.*, **43**, 60 (1963).

(6) M. Freund and K. Fleischer, *Ann.*, **399**, 215 (1913); **402**, 68 (1914).

(7) H. Waldmann and H. Mathiowetz, *Ber.*, **64**, 1713 (1931).

(8) E. de B. Barnett and R. A. Lowry, *ibid.*, **65**, 1649 (1932).

(9) Since our preliminary communication, an additional Diels-Alder reaction of 9 has been described, namely, its very slow addition to 2,2-dimethylthiete 1,1-dioxide, as well as aromatization of the resulting adduct to an anthrathiete derivative: L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965).

18, X = NC₆H₅
19, X = O

20

21, R = COOCH₃
26, R = CF₃

22

23

24

25

27

28
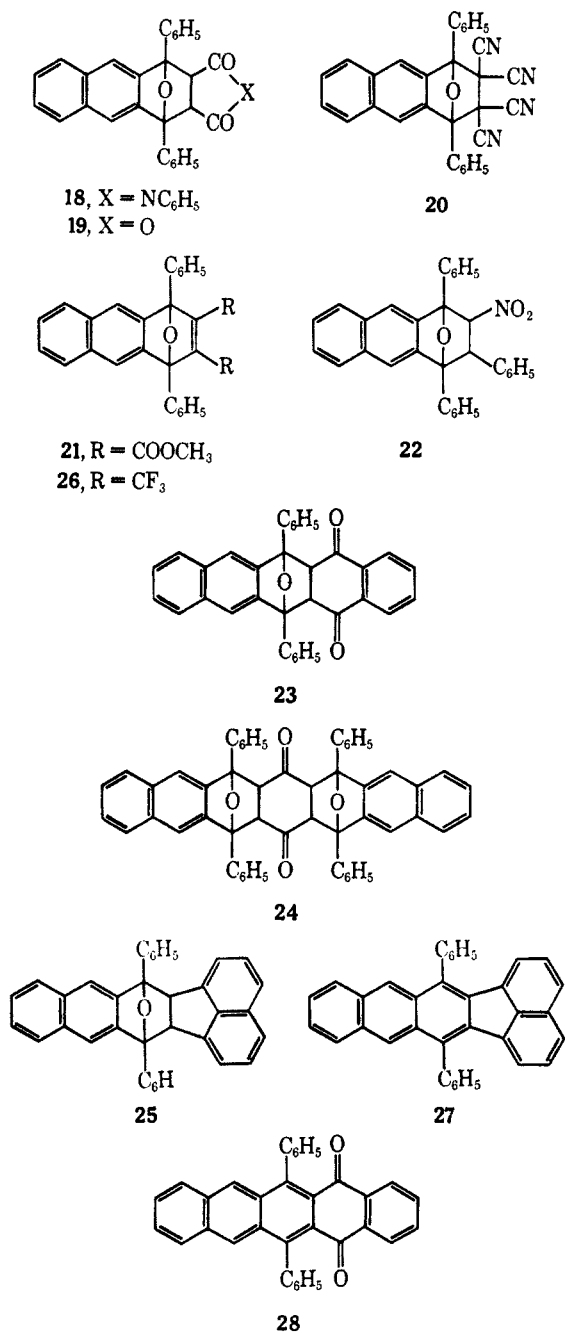
transient intermediates benzocyclobutadiene (29) and 1-bromobenzocyclobutadiene (30). The crystalline adducts 31 and 32 were isolated, and adduct 31 was aromatized by hydrochloric acid to 5,10-diphenyl-benzo[b]biphenylene (33).[10] When similar experiments were attempted using furan 9, no crystalline adduct (34) of 9 and 29 could be isolated, although a crystalline bromo adduct (35) was easily obtained by trapping 30 with 9. Hydrogenolysis of the bromo substituent of 35 was effected using palladium and hydrazine, and afforded the crystalline compound 34. The fact that the hydrogenolysis of 35 had indeed given structure 34 was confirmed by the observation that a similar hydrogenolysis of the analogous bromo adduct 32 gave the previously characterized, crystalline direct adduct 31 of benzocyclobutadiene with furan 7.

(10) M. P. Cava and R. Pohlke, *J. Org. Chem.*, **27**, 1564 (1962).

Aromatization of compound 34 was carried out with polyphosphoric acid at 130–170° and yielded dark brown needles, mp 228–231°, which analyzed for C₃₂H₂₀ and were at first assumed to be the desired 5,12-diphenylnaphtho[2,3-b]biphenylene (36). Thin layer chromatography of this material, however, showed it to be a mixture of two components having almost identical R_f values. These two components were assumed to be the naphthobiphenylene 36 and the isomeric 3,6-diphenyl-1,2-benzo-4,5-naphthopentalene 37. The formation of 37 is easily rationalized by assuming a skeletal rearrangement of carbonium ion 38 during the aromatization of 34. The hydrocarbon mixture could not be separated by column chromatography, but the pure pentalene 37 was isolated by way of its crystalline 2,4,7-trinitrofluorenone complex. Its visible absorption spectrum showed bands at 441 and 470 mμ, corresponding to those at 423 and 447 mμ in the spectrum of its known lower benzolog 3,6-diphenyl-1,2,4,5-dibenzo-pentalene (39).[11]

A similar polyphosphoric acid aromatization of adduct 31 yielded an inseparable mixture of the benzo-biphenylene 33 and the benzopentalene 39. Spectral analysis indicated the presence of 21% of 39 in the mixture. That the rearrangement of 39 does not take place by way of the benzobiphenylene 33 was shown by heating the latter compound with polyphosphoric acid, when the unrearranged hydrocarbon was recovered.
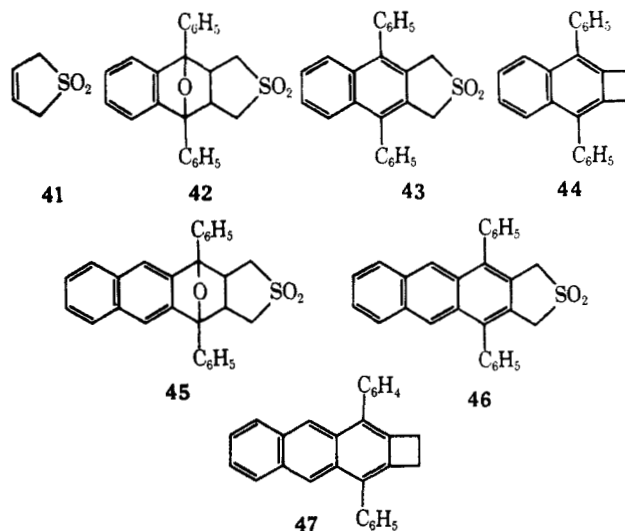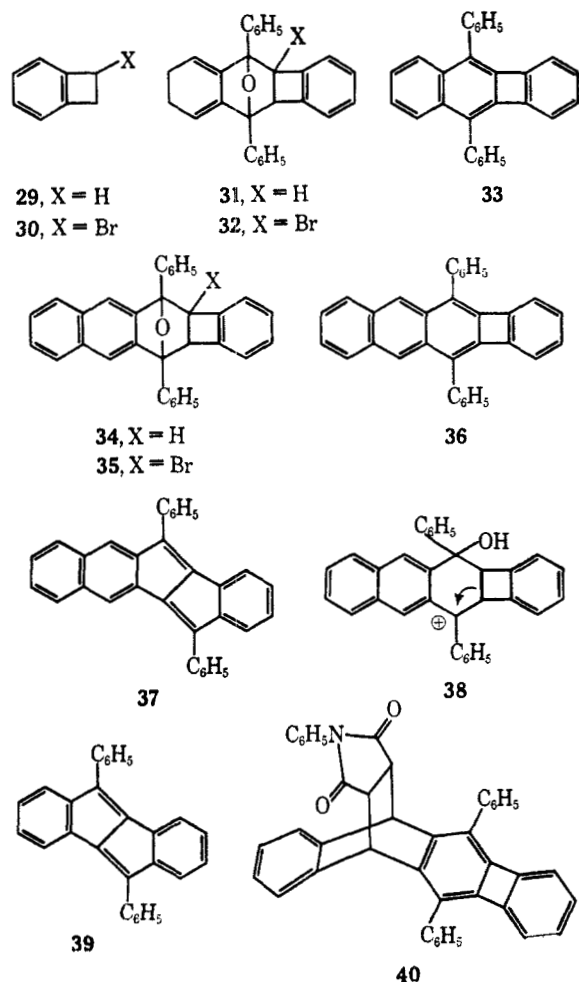
The reaction of adduct 31 with phosphorus penta-sulfide in carbon disulfide gave the pure benzobi-phenylene 33.[12] A similar reaction of 34 with phosphorus pentasulfide afforded the pure naphthobi-phenylene 36 as orange-yellow needles, mp 228–229°. Compound 36 proved to be quite stable to dienophiles, but it reacted very slowly with N-phenylmaleimide in boiling toluene to give the biphenylene derivative 40. The stereochemistry of adduct 40 was not investigated, but it is probably the isomer formed, as written, by addition of the dienophile over the portion of the anthracene ring of 36 which does not bear the bulky phenyl substituents.

Synthesis of an Anthra[b]cyclobutene Derivative.— The literature records no examples of the use of the commercially available unconjugated sulfone 3-sulfolene (41) as the dienophile in a Diels–Alder reaction. We have now found that 3-sulfolene will add to the o-quinonoid furans 7 and 9, and that the resulting adducts are readily converted to naphtho[b]cyclobutene and anthra[b]cyclobutene derivatives.

Furan 7 adds very slowly to sulfone 41 in refluxing benzene. By using an excess of the thermally unstable 41 and a prolonged heating period, however, the desired Diels–Alder adduct 42 was obtained in 97% yield. Treatment of adduct 42 with hydrogen bromide in acetic acid gave the aromatized sulfone, 4,9-diphenyl-1,3-dihydronaphtho[2,3-c]thiophene 2,2-dioxide (43). Pyrolysis of sulfone 43 in refluxing diethyl phthalate for more than 5 hr resulted in the formation of 3,8-diphenyl-naphtho[b]cyclobutene (44); some of the starting sulfone (26%) was recovered unchanged. The syn-

(11) K. Brand, *Ber.*, **45**, 3071 (1912).

(12) For the advantageous use of this reagent in the dehydration of other adducts of furan 7, see M. P. Cava and F. M. Scheel, *J. Org. Chem.*, **32**, 1304 (1967).

29, X = H
30, X = Br

31, X = H
32, X = Br

33

34, X = H
35, X = Br

36

37

38

39

40

41

42

43

44

45

46

47

thiophene **10** as red crystals, which appear to be stable indefinitely.

Thiophene **10** reacted easily at room temperature with the very reactive dienophile tetracyanoethylene to yield the crystalline adduct **48**. On the other hand, the less reactive dienophile N-phenylmaleimide did not add to **10** on prolonged standing at room temperature.

48
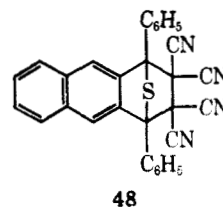
Discussion

The greater reactivity of furan **9** compared to furan **7** is apparent from several aspects of its behavior. Whereas **9** is too reactive to be successfully recrystallized and decomposes slowly even in the solid state, **7** is easily recrystallized and may be stored in the crystalline state indefinitely. Furan **9** must certainly be one of the most reactive isolable diene components in Diels–Alder additions. Although we have made no quantitative comparison of the addition rates of **9** and **7** to dienophiles, we have observed that **9** is immediately decolorized in solution at room temperature by maleic anhydride, whereas **7** is decolorized only after some time under similar conditions. Other rough comparisons can be made by reference to the literature. For example, we have found that **9** is decolorized by dimethyl acetylenedicarboxylate within 3 min at room temperature, whereas the addition of this reagent to **7** was reported as carried out in refluxing benzene for 105 min.[15] In another example, we have found that the addition of **9** to acenaphthylene is complete within 5 min in refluxing benzene, whereas the addition of **7** to the same dienophile was reported as carried out in refluxing xylene for 7 hr.[16] It seems likely that **9** will prove to be a trapping reagent of value for the interception of particularly reactive transient dienophiles.

thesis of hydrocarbon **44** described above uses readily available starting materials and is definitely more practical than the previously described synthesis of **44** which employs the difficulty accessible hydrocarbon cyclobutene as a starting material.[13] Compound **44** has been of interest to us as a precursor of an insolable naphtho[b]cyclobutadiene derivative.[14]

In a similar manner, furan **9** was found to add to 3-sulfolene (**41**); adduct **45** was obtained in quantitative yield after 25 min in refluxing benzene. Aromatization of **45** to 4,11-diphenyl-1,3-dihydroanthra[2,3-c]thiophene 2,2-dioxide (**46**) was effected by hydrogen bromide in acetic acid. Pyrolysis of sulfone **46** in refluxing diethyl phthalate for 11 hr resulted in the recovery of 71% of the starting sulfone. The sulfur dioxide extrusion product, 3,10-diphenylanthra[b]cyclobutene (**47**), was isolated in 43% yield based upon unrecovered sulfone. Some experiments designed to transform **47** into a derivative of anthra[b]cyclobutadiene will be described in a subsequent publication.

Synthesis of 1,3-Diphenylnaphtho[2,3-c]thiophene.—Furan **9** reacted with phosphorus pentasulfide in carbon disulfide solution to give 1,3-diphenylnaphtho-[2,3-c]thiophene (**10**), which was isolated by way of its crystalline 2,4,7-trinitrofluorenone derivative. Decomposition of the complex on alumina yielded the pure

(13) C. D. Nenitzescu, M. Avram, I. G. Dinulescu, and G. Mateescu, *Ann.*, **653**, 79 (1962).
(14) M. P. Cava and B. Hwang, *Tetrahedron Letters*, 2297 (1965).
(15) J. A. Berson, *J. Am. Chem. Soc.*, **75**, 1240 (1953).
(16) E. Bergmann, *ibid.*, **74**, 1075 (1952).

It is interesting to note the very considerable difference in the thermal stabilities of sulfones **43** and **46**. In the experiments performed, the combined yield of recovered sulfone and condensed cyclobutane aromatic hydrocarbon (**44** or **47**) was the same (83%); both experiments were carried out in boiling diethyl phthalate (*ca.* 300°). After a reaction period of almost 5.5 hr, 26% of the naphthalene sulfone **43** was unchanged; in contrast, after 11 hr, 71% of the anthracene sulfone **46** was unchanged. The much greater thermal stability of **46** compared to **43** reflects the expectation that the energy difference between the 2,3-anthraquinodimethane intermediate **49** and its anthracene-derived precursor should be greater than the corresponding energy difference between the 2,3-naphthoquinodimethane intermediate **50** and its naphthalene-derived precursor. The remarkable stability of both hydrocarbon products **44** and **47** to prolonged heating at *ca.* 300° is also worthy of note. Since the unsubstituted naphtho[*b*]-cyclobutene (**2**) is largely cleaved to the unstable *o*-quinonoid isomer **3** within 1 hr at 250°,[17] we believe that the bulky phenyl substituents of both **44** and **47** produce a very appreciable buttressing effect which opposes the tendency to thermal cleavage.

49   50
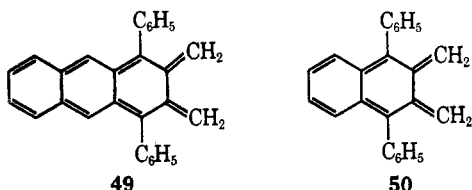
The greatly decreased reactivity of the benzothiophene **8** compared to the corresponding furan **7** is well illustrated by the fact that when mixtures of **7** and **8** are treated with maleic anhydride, only furan **7** reacts to form an adduct.[18] The much greater stability to storage and to dienophiles of naphthothiophene **10** compared to naphthofuran **9** is, therefore, to be expected. The degree of stability of **10** is, indeed, sufficiently large that we have initiated studies aimed at the synthesis of the parent heterocycle naphtho[2,3-*c*]-thiophene.

Experimental Section[19]

2,3-Naphthalic Anhydride (14).—The sodium dichromate oxidation of 2,3-dimethylnaphthalene (**12**) to naphthalene-2,3-dicarboxylic acid (**13**) was carried out in 82% yield as reported in the literature.[5] Diacid **13** (227 g) was heated with a refluxing mixture of acetic anhydride (600 ml) and acetic acid (3000 ml). On standing overnight at room temperature, the solution deposited anhydride **14** (157 g, 79%) as plates, mp 250–251° (lit.[6] mp 246°).

3-Benzoyl-2-naphthoic Acid (11).—The following variant of the previously reported procedure[7,8] was employed. Aluminum chloride (36 g) was added to a mixture of powdered anhydride **14** (26 g) and benzene (250 ml). The mixture was heated for 15 hr on the steam bath, the suspension being swirled occasionally during the first 20 min of the heating period. The reaction

product was stirred with a mixture of aqueous hydrochloric acid and chloroform until all of the solid disappeared. The organic extract was washed with water and then extracted thoroughly with aqueous sodium bicarbonate. Acidification of the basic extract with hydrochloric acid gave a precipitate which, after drying, was crystallized from chloroform–petroleum ether (Skelly B) to give acid **11** (30.7 g, 89%), mp 212–214° (lit.[7] 209.5°).

1,3-Dihydro-3-phenylnaphtho[2,3-*c*]furan-1-one (Lactone 15.)—The procedure used was a modification of the published preparation of 3-phenylphthalide.[20] The powdered keto acid **11** (37.7 g) was dissolved in water by the addition of enough aqueous sodium hydroxide to effect solution. Sodium borohydride (25 g) was added and the solution was stirred for 70 hr at room temperature. After making the solution almost neutral with hydrochloric acid, additional sodium borohydride (5 g) was added and the solution was stirred for an additional 46 hr. The solution was acidified with hydrochloric acid and the lactone was extracted into methylene chloride. The organic phase was washed successively with hydrochloric acid, water, and sodium bicarbonate solution. Evaporation of the dried (sodium sulfate) solution and crystallization of the residue from benzene afforded lactone **15** (29.0 g, 80%), mp 153–155°.

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.59; H, 5.03.

1,3-Dihydro-1,3-diphenylnaphtho[2,3-*c*]furan-1-ol (Lactol 16). —A solution of phenylmagnesium bromide (0.12 mole) in ether (90 ml) was added over a period of 20 min to a stirred suspension of lactone **15** (15.6 g, 0.06 mole) in dry tetrahydrofuran (200 ml) at 0°. After stirring for an additional 10 min, the reaction mixture was poured into an excess of saturated aqueous ammonium chloride. The organic layer was separated, and the aqueous layer was extracted twice with ether. The combined organic extracts were dried (sodium sulfate) and concentrated to a volume of 30–40 ml. The precipitated lactol **16** (18.5 g, 91%) was filtered and washed with petroleum ether (Skelly F); it had mp 149–157° dec.

Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.02; H, 5.50.

1,3-Diphenylnaphtho[2,3-*c*]furan (9).—A mixture of lactol **16** (2.351 g) and glacial acetic acid (25 ml) was heated on the steam bath and stirred with a glass rod until all of the white lactol was converted into the deep red furan. After cooling, furan **9** (1.958 g, 89%) was removed by filtration, washed with petroleum ether (Skelly B), and dried *in vacuo*. It had mp 148–154° and the following absorption spectrum in benzene: λ_{max} 367 mμ (ϵ 5700), 383 (5700), 524 (7900), and 546 (7900).

Anal. Calcd for $C_{24}H_{16}O$: C, 89.97; H, 5.03. Found: C, 89.43; H, 5.29.

2,3-Dibenzoylnaphthalene (17).—Chromium trioxide (9.5 g) was added slowly in small portions with stirring to pyridine (150 ml) at 0°. Lactol **16** (9.01 g) was then added slowly, and stirring was continued at room temperature for 4.5 days. The reaction mixture was poured into water and extracted with 1:1 benzene–ethyl acetate. After washing with dilute hydrochloric acid and water, the dried (MgSO₄) organic phase was evaporated and the resulting oil was crystallized from ether to give diketone **17** (7.82 g, 87%), mp 143–145°.

Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.82; H, 4.69.

A similar oxidation of furan **9** (0.485 g) afforded the same diketone **17** in 63% yield.

Adduct of 9 with N-Phenylmaleimide. N-Phenyl-1,4-diphenyl-1,4-oxido-1,2,3,4-tetrahydroanthracene-2,3-dicarboximide (18).—Furan **9** (0.219 g) was added in small portions to a stirred solution of N-phenylmaleimide (0.123 g) in ether (15 ml) at room temperature. Adduct **18** (0.293 g, 87%) separated from the solution as needles, mp 287–290° dec. The analytical sample was recrystallized from benzene–ethanol.

Anal. Calcd for $C_{34}H_{23}NO_3$: C, 82.74; H, 4.70; N, 2.84. Found: C, 82.54; H, 4.94; N, 2.82.

Adduct of 9 with Maleic Anhydride. 1,4-Diphenyl-1,4-oxido-1,2,3,4-tetrahydroanthracene-2,3-dicarboxylic Anhydride (19).—Solid maleic anhydride was added to a solution of furan **9** (0.566 g) in 1:1 methylene chloride–benzene (50 ml) until the red color of the furan disappeared. Evaporation of the solution and crystallization of the residue from methylene chloride–

(17) M. P. Cava, R. L. Shirley, and B. W. Erickson, *J. Org. Chem.*, **27**, 755 (1962).

(18) C. Dufraisse and D. Daniel, *Bull. Soc. Chim. France*, [5] **4**, 2063 (1937).

(19) Melting points are uncorrected. Elemental analyses were performed by Midwest Microlab Inc., Indianapolis, Ind., and by Dr. A. Bernhardt, Mülheim, Germany.

(20) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961).

petroleum ether (Skelly F) gave adduct **19** (0.626 g, 84%), mp 225–253° dec.

Anal. Calcd for $C_{28}H_{18}O_4$: C, 80.37; H, 4.34. Found: C, 80.08; H, 4.63.

Crystallization of **19** from carbon tetrachloride afforded crystals containing one molecule of solvent of crystallization. The following analysis was based on the assumption that the CCl₄ escaped oxidation and passed through the combustion furnace unchanged.

Anal. Calcd for $C_{28}H_{18}O_4 \cdot CCl_4$ (on a C_{28} basis): C, 58.77; H, 3.17. Found: C, 58.70; H, 3.18.

Adduct of 9 with Tetracyanoethylene. 2,2,3,3-Tetracyano-1,4-diphenyl-1,4-oxido-1,2,3,4 tetrahydroanthracene (20).—Solid tetracyanoethylene was added to a solution of furan **9** (0.353 g) in benzene (25 ml) until the red color of **9** disappeared. Evaporation of the solvent and crystallization of the residue from methylene chloride–petroleum ether (Skelly B) afforded pure adduct **20** (0.353 g, 71%), mp 238–255° dec.

Anal. Calcd for $C_{30}H_{16}N_4O$: C, 80.33; H, 3.60; N, 12.51. Found: C, 80.39; H, 3.96; N, 12.52.

Adduct of 9 with ω-Nitrostyrene. 1,2,4-Triphenyl-3-nitro-1,4-oxido-1,2,3,4-tetrahydroanthracene (22).—A solution of furan **9** (3.566 g) in methylene chloride (50 ml) was stirred at room temperature with an excess of ω-nitrostyrene. The red color of the solution faded within several minutes. Concentration of the solution, followed by addition of petroleum ether (Skelly B), gave adduct **22** (3.293 g, 82%), mp 243–253° dec. Recrystallization from the same solvent mixture afforded prisms of pure **22**, mp 422–255° dec.

Anal. Calcd for $C_{32}H_{23}NO_3$: C, 81.86; H, 4.94; N, 2.98. Found: C, 81.54; H, 5.07; N, 2.88.

Adduct of 9 with 1,4-Naphthoquinone. 6,13-Diphenyl-6,13-oxido-5,5a,6,13,13a,14-hexahydropentacene-5,14-dione (23).—A solution of furan **9** (0.517 g) and 1,4-naphthoquinone (0.283 g) in benzene (10 ml) was stirred at room temperature until the red color faded (2 min). Addition of petroleum ether (Skelly B) precipitated adduct **23** (0.668 g, 86%), mp 186–203° dec. Recrystallization from methylene chloride–petroleum ether (charcoal decolorization) afforded analytically pure **23** as white needles, mp 198–203° dec.

Anal. Calcd for $C_{34}H_{22}O_3$: C, 85.33; H, 4.63. Found: C, 85.30; H, 4.72.

Adduct of 9 with 1,4-Benzoquinone. 6,8,15,17-Tetraphenyl-6,17:8,15-dioxido-6,6a,7,7a,8,15,15a,16,16a,17-decahydroheptacene-7,16-dione (24).—A solution of furan **9** (1.155 g, 0.0036 mole) and 1,4-benzoquinone (0.196 g, 0.0018 mole) in benzene (20 ml) was stirred at room temperature for 3 min. Adduct **24**, mp 248–258° dec (0.972 g, 72%), crystallized upon addition of petroleum ether (Skelly B). An analytically pure sample of **24** could not be obtained because of its tendency to dissociate (observable red color of **9**) upon attempted recrystallization.

Anal. Calcd for $C_{54}H_{36}O_4$: C, 86.61; H, 4.85. Found: C, 84.76; H, 4.76.

Adduct of 9 with Acenaphthylene. 7,14-Diphenyl-7,14-oxido-6b,7,14,14a-tetrahydronaphtho[2,3-k]fluoranthene (25).—A solution of furan **9** (1.13 g) and excess acenaphthylene in benzene (30 ml) was refluxed until the red color faded (less than 5 min). Concentration of the solution, followed by addition of hexane, yielded adduct **25** (1.46 g, 87%) as a mixture of stereoisomers. The isomers were partially resolved by chromatography on alumina (grade I neutral, benzene eluent) followed by crystallization from benzene–hexane. Isomer A had mp 274–276° dec.

Anal. Calcd for $C_{36}H_{24}O$: C, 91.50; H, 5.12. Found: C, 91.16; H, 5.34.

Isomer B had mp 232–236° dec.

Anal. Calcd for $C_{36}H_{24}O$: C, 91.50; H, 5.12. Found: C, 91.16; H, 5.16.

Adduct of 9 with Hexafluoro-2-butyne. 1,4-Diphenyl-1,4-oxido-2,3-bistrifluoromethylanthracene (26).—Hexafluoro-2-butyne was bubbled slowly through a warm solution (55–65°) of furan **9** (0.960 g) in benzene (100 ml) for about 10 min, at which time the red color faded. Chromatography (grade III acid alumina, benzene eluent), followed by crystallization from cyclohexane, afforded colorless rosettes (1.043 g, 72%) of adduct **26**, mp 162–164°.

Anal. Calcd for $C_{28}H_{16}F_6O$: C, 69.71; H, 3.34; F, 23.63. Found: C, 69.90; H, 3.62; F, 23.36.

7,14-Diphenylnaphtho[2,3-k]fluoranthene (27).—Adduct **25**

(0.199 g, mixture of stereoisomers) was heated on the steam bath for 19.5 hr with a mixture of acetic acid (10 ml) and 48% aqueous hydrobromic acid (2.5 ml). Addition of water to the resulting solution gave hydrocarbon **27** (0.184 g, 96%), mp 270–274°. Crystallization from methylene chloride–hexane gave the analytical sample, mp 273–274°.

Anal. Calcd for $C_{36}H_{22}$: C, 95.12; H, 4.88. Found: C, 94.87; H, 4.97.

6,13-Diphenylpentacene-5,14-quinone (28).—A mixture of adduct **23** (0.246 g), acetic acid (10 ml), and 48% hydrobromic acid (4 ml) was heated for 12 hr on the steam bath. Addition of water gave crude quinone **28**, which was purified by charcoal treatment (methylene chloride solution) followed by crystallization from petroleum ether (Skelly B). Pure quinone **28** (0.113 g, 48%) was obtained as yellow-orange needles, mp 331–332°.

Anal. Calcd for $C_{34}H_{20}O_2$: C, 88.67; H, 4.38. Found: C, 88.85; H, 4.22.

Adduct of 9 with Dimethyl Acetylenedicarboxylate. Dimethyl 1,4-Diphenyl-1,4-oxido-1,4-dihydroanthracene-2,3-dicarboxylate (21).—A solution of dimethyl acetylenedicarboxylate (0.124 g) and furan **9** (0.204 g) in benzene (25 ml) was stirred at room temperature for 203 min. Evaporation of the solvent and crystallization of the residue from chloroform–methanol gave adduct **21** (0.277 g, 77%), mp 234–238°.

Anal. Calcd for $C_{30}H_{22}O_5$: C, 77.91; H, 4.80. Found: C, 77.81; H, 4.88.

4b-Bromo-5,12-diphenyl-5,12-oxido-4b,5,12,12a-tetrahydronaphtho[2,3-b]biphenylene (35).—To a large excess of a suspension of potassium *t*-butoxide in benzene (25 ml) was added at room temperature furan **9** (1.55 g), followed by *trans*-1,2-dibromobenzocyclobutene (1.494 g). After stirring for 6 min, the reaction mixture was poured into water and the product was extracted into benzene. Evaporation of the dried extract, followed by chromatography on alumina (grade III neutral, cyclohexane eluent), yielded, after crystallization from cyclohexane, adduct **35** (1.213 g, 52%), mp 233–234°. The analytical sample (mp 233–236°) was obtained by crystallization from benzene–petroleum ether (bp 60–90°).

Anal. Calcd for $C_{32}H_{21}BrO$: C, 76.67; H, 4.22; Br, 15.94. Found: C, 76.74; H, 4.55; Br, 16.19.

5,12-Diphenyl-5,12-oxido-4b,5,12,12a-tetrahydronaphtho-[2,3-b]biphenylene (34).—To a solution of adduct **35** (4.842 g) in warm benzene (100 ml) was added ethanol (100 ml), 5% palladium on charcoal (2.2 g), and 85% hydrazine hydrate (33 ml). After refluxing for 15 min on the steam bath, the solution was filtered (Celite), concentrated, and shaken with water and benzene. Evaporation of the dried benzene extract followed by crystallization from cyclohexane yielded adduct **34** (3.652 g, 90%), mp 185–190°.

Anal. Calcd for $C_{32}H_{22}O$: C, 90.96; H, 5.25. Found: C, 90.27; H, 5.42.

5,10-Diphenyl-5,10-oxido-5,5a,9b,10-tetrahydrobenzo[b]biphenylene (31).—To a solution of the bromo adduct **32** (0.265 g) in 1:1 benzene–ethanol (40 ml) was added 5% palladium on charcoal (0.6 g) and 85% hydrazine hydrate (12 ml). After refluxing for 15 min, the reaction product was worked up as described in the preceding experiment. Crystallization from petroleum ether (Skelly F) gave crude adduct **31** (0.116 g, 53%), mp 172–175°. Recrystallization from petroleum ether gave pure **31**, mp 195–197° (lit.[10] mp 200–202°), the infrared spectrum of which was identical with that of authentic material.

5,12-Diphenylnaphtho[2,3-b]biphenylene (36).—A suspension of reduced adduct **34** (0.156 g) and phosphorus pentasulfide (1.5 g) in carbon disulfide (30 ml) was stirred at room temperature for 70 hr. The reaction mixture was evaporated and the product extracted with benzene. Chromatography of the crude product on alumina (grade III acid, benzene eluent) afforded, after crystallization from petroleum ether (Skelly B), hydrocarbon **36** as golden yellow needles (0.091 g, 61%): mp 228–229°; λ_{max}^{EtOH} 240 mμ (log ε 4.49), 293 sh (4.69), 303 (4.81), 325 (4.66), 347 (4.13), 364 (4.06), 386 (3.92), 410 (3.55), and 434 (3.41).

Anal. Calcd for $C_{32}H_{20}$: C, 95.02; H, 4.98. Found: C, 94.95; H, 5.21.

Reaction of 5,12-Diphenylnaphtho[2,3-b]biphenylene with N-Phenylmaleimide.—A solution of hydrocarbon **36** (0.306 g) and N-phenylmaleimide (0.245 g) in toluene (100 ml) was refluxed for 13 days. The solvent was removed and the residue was chromatographed on alumina (grade III neutral). Benzene-

cyclohexane (1:3) eluted some unreacted **36**. Elution with benzene, followed by crystallization from chloroform–methanol, gave yellow crystals (0.271 g, 62%) of adduct **40**, mp 291–293°.

Anal. Calcd for C₄₂H₂₇NO₂: C, 87.32; H, 4.11; N, 2.43. Found: C, 86.67; H, 4.74; N, 2.67.

5,10-Diphenylbenzo[b]biphenylene (33).—A suspension of **31** (0.156 g) and phosphorus pentasulfide (1.5 g) in carbon disulfide (30 ml) was stirred at room temperature for 4 days. Evaporation of the filtered solution, followed by chromatography on alumina (grade III acid, benzene eluent) afforded, after crystallization from cyclohexane, hydrocarbon **33** as yellow needles (0.122 g, 82%), mp 220–222°, identical with an authentic sample (lit.¹⁰ mp 218–220°), λ_max^{EtOH} 230 mμ (log ε 4.43), 250 (4.41), 278 (4.59), 304 (4.53), 355 sh (4.43), 3.80 (3.49), and 400 (3.50).

The Reaction of Adduct 31 with Polyphosphoric Acid.—Polyphosphoric acid (50 ml) was added to a solution of adduct **31** (0.323 g) in methylene chloride (3 ml). The stirred solution was gradually heated to 140° over a period of 80 min, and then kept at 125 ± 15° for an additional 3 hr. The product was isolated by dilution with water and extraction with benzene. Crystallization from cyclohexane afforded homogeneous dark brown crystals (0.162 g, 32%), mp 228–235°. Thin layer chromatography (silica, CCl₄) indicated that the crystals consisted of two components, identified as 5,10-diphenylbenzo[b]-biphenylene (**33**) and 3,6-diphenyl-1,2,4,5-dibenzopentalene (**39**) by comparison (tlc and infrared) with an artificially prepared mixture of **33** and **39**.¹¹ An ultraviolet study of artificially prepared mixtures of **33** and **39** showed that the brown reaction product consisted of about 21% of the pentalene **39** and 79% of the biphenylene **33**. Attempts to separate the mixture of **33** and **39** by crystallization, chromatography, or complex formation failed. Finally, treatment of pure **33** with polyphosphoric acid under the aromatization conditions described above led to the recovery of 74% of crystalline **33** uncontaminated (ir, uv) by **39**.

The Reaction of Reduced Adduct 34 with Polyphosphoric Acid.—A stirred mixture of compound **34** (1.125 g) and polyphosphoric acid (75 ml) was heated between 130 and 170° for 3 hr. After cooling, the mixture was diluted with water and extracted with benzene. Work-up in the usual manner, followed by chromatography on alumina (grade III neutral, benzene eluent) and crystallization from benzene–petroleum ether (bp 60–90°), gave brown-black needles (0.631 g, 59%), mp 228–231°. Thin layer chromatography and infrared studies showed this material to be a mixture of the naphthobiphenylene **36** and 3,6-diphenyl-1,2-benzo-4,5-naphthopentalene (**37**). A solution of the mixture in benzene gave a dark complex with 2,4,7-trinitrofluorenone. Repeated recrystallization of this complex from benzene (final mp 246–247°), followed by complex decomposition on neutral alumina (grade I, benzene eluent) and crystallization from petroleum ether, gave a sample of pure **37** as deep brown needles: mp 240–242°; λ_max^{cyclohexane} 275 mμ (log ε 4.74), 320 (4.69), 441 (4.07), and 470 (4.10).

4,9-Diphenyl-4,9-oxido-1,3,3a,4,9,9a-hexahydronaphtho[2,3-c]-thiophene 2,2-Dioxide (42).—A solution of furan **7** (14.14 g) and 3-sulfolene (**41**, 21.31 g) in benzene (140 ml) was refluxed for 64 hr. After cooling to room temperature, the solid product was removed by filtration and the filtrate was evaporated to dryness *in vacuo*. The solid residue was combined with that which had been removed by filtration and heated on the steam bath with water to dissolve excess sulfolene. The air-dried precipitate of crude **42** (19.77 g, 97%), mp 223–264°, was suitable for direct aromatization by acid (see below). The analytical sample, mp 257–287°, was crystallized from benzene–petroleum ether (bp 60–90°); its broad melting range suggests that it may be a mixture of stereoisomers.

Anal. Calcd for C₂₄H₂₀O₃S: C, 74.21; H, 5.19; S, 8.24. Found: C, 74.32; H, 5.11; S, 8.14.

4,9-Diphenyl-1,3-dihydronaphtho[2,3-c]thiophene 2,2-Dioxide (43).—A mixture of crude adduct **42** (13.503 g), 48% hydrobromic acid (20 ml), and acetic acid (110 ml) was heated for 7 hr on the steam bath, and then allowed to stand at room temperature for 12 hr. The mixture was poured into water and the precipitate was removed by filtration to give sulfone **43** (12.268 g, 94%), mp 301–302°. An analytical sample, mp 301–302°, was obtained by chromatography on acid alumina (grade III, methylene chloride eluent), followed by crystallization from methylene chloride–hexane.

Anal. Calcd for C₂₄H₁₈O₂S: C, 77.82; H, 4.90; S, 8.64. Found: C, 77.27; H, 4.94; S, 8.82.

3,8-Diphenylnaphtho[b]cyclobutene (44).—A solution of sulfone **43** (6.710 g) in diethyl phthalate (93 ml) was refluxed for 5 hr and 20 min. After cooling, the solution was mixed with 15% aqueous sodium hydroxide (200 ml) and ethanol (150 ml) and the mixture was warmed on the steam bath until the phthalate ester was saponified. (*Caution:* the hydrolysis may take place exothermically, resulting in loss of product.) The reaction product was extracted into benzene and subjected to a preliminary purification by chromatography on acid alumina (grade II, chloroform eluent). The crude product was chromatographed again on neutral alumina (grade I). The benzene eluent, after evaporation, was crystallized from methylene chloride–petroleum ether (Skelly B) to give hydrocarbon **44** (3.177 g), mp 207–208° (lit.¹³ mp 201–202°); the infrared spectrum of **44** is in agreement with that previously recorded.¹³

Elution of the column with chloroform–methanol gave material which, after charcoal treatment and crystallization from benzene–petroleum ether, afforded recovered sulfone **43** (1.747 g, 26%), mp 301–302°. The yield of hydrocarbon **44** based upon unrecovered sulfone was 77%.

4,11-Diphenyl-4,11-oxido-1,3,3a,4,11,11a-hexahydroanthra-[2,3-c]thiophene 2,2-Dioxide (45).—A mixture of furan **9** (7.534 g), 3-sulfolene (20 g), and benzene (140 ml) was refluxed for 25 min. The solvent was removed *in vacuo* and the residue was heated with water to dissolve the excess sulfolene. The air-dried precipitate of crude **45** (10.6 g, 100% = 10.3 g), mp 252–265° dec, was sufficiently pure for direct aromatization by acid (see below). Crystallization from benzene–petroleum ether (bp 60–90°) gave the analytical sample, mp 314–315° dec. The high melting point of this sample suggests that it may be the least soluble of two stereoisomeric constituents of the crude product.

Anal. Calcd for C₂₈H₂₂O₃S: C, 76.70; H, 5.04; S, 7.30. Found: C, 76.87; H, 5.47; S, 7.06.

4,11-Diphenyl-1,3-dihydroanthra[2,3-c]thiophene 2,2-Dioxide (46).—A mixture of crude adduct **45** (5.278 g), 48% hydrobromic acid (15 ml), and acetic acid (75 ml) was heated for 12.5 hr on the steam bath. The reaction mixture was poured into water and the precipitate was filtered, purified by charcoal treatment (benzene solution), and crystallized from benzene–petroleum ether (Skelly B) to yield sulfone **46** (4.159 g, 82%), mp 288–289°. Recrystallization from the same solvent pair afforded the analytical sample, mp 288–289°.

Anal. Calcd for C₂₈H₂₀O₂S: C, 79.98; H, 4.79; S, 7.61. Found: C, 79.85; H, 4.92; S, 7.55.

3,10-Diphenylanthra[b]cyclobutene (47).—A solution of sulfone **46** (3.739 g) in diethyl phthalate (150 ml) was refluxed for 11 hr. The cooled solution was added to a hot solution of sodium hydroxide (200 g) in water (350 ml) contained in a 3000-ml beaker. Upon addition of some ethanol a vigorous hydrolysis of the phthalate ester took place. The product was isolated by benzene extraction, followed by chromatography on neutral alumina (grade I). Evaporation of the yellow benzene eluate, followed by crystallization from methylene chloride–petroleum ether (Skelly B), gave hydrocarbon **47** (0.406 g), mp 271–272°. Recrystallization from the same solvent pair afforded the analytical sample: mp 280–282°; λ_max^{cyclohexane} 214 mμ (log ε 4.58), 261 (5.01), and 373 (4.02).

Anal. Calcd for C₂₈H₂₀: C, 94.34; H, 5.66. Found: C, 94.06; H, 5.76.

Elution of the column with chloroform–methanol gave material which crystallized from benzene–petroleum ether, yielding unreacted sulfone **46** (2.638 g, 71%), mp 284–287°. The yield of hydrocarbon **47** based on unrecovered sulfone was 43%.

1,3-Diphenylnaphtho[2,3-c]thiophene (10).—A mixture of phosphorus pentasulfide (2.0 g) and carbon disulfide (100 ml) was stirred at room temperature for 1 hr. Solid furan **9** (0.675 g) was added and stirring was continued for 21.5 hr at room temperature in the dark under nitrogen. The insoluble solid was removed by filtration and the precipitate was washed with methylene chloride. Evaporation of the dark solution gave a residue which was purified by extraction into benzene and chromatography on acid alumina (grade IV, benzene eluent). The deep red eluent was concentrated and a benzene solution of 2,4,7-trinitrofluorenone was added; addition of methanol caused crystallization of the 2,4,7-trinitrofluorenone complex of **10** (0.526 g, 38%) as deep purple needles, mp 169–171°.

Anal. Calcd for $C_{37}H_{21}N_3O_7S$: C, 68.19; H, 3.25; N, 6.45; S, 4.92. Found: C, 68.16; H, 3.27; N, 6.47; S, 4.93.

Chromatography of a benzene solution of the above-described complex on basic alumina (grade II), followed by crystallization from ether, afforded the free thiophene **10** as deep red needles, mp 198–202°, $\lambda_{max}^{benzene}$ 513 mμ (log ϵ 8700).

Anal. Calcd for $C_{24}H_{16}S$: C, 85.67; H, 4.80; S, 9.53. Found: C, 85.61; H, 4.88; S, 9.48.

Adduct of 10 with Tetracyanoethylene. 1,4-Diphenyl-1,4-epithio-2,2,3,3-tetracyano-1,2,3,4-tetrahydroanthracene (48).—A solution of thiophene **10** in benzene was prepared by alumina chromatography of its 2,4,7-trinitrofluorenone complex (0.929 g). To this red solution, tetracyanoethylene was added until the color vanished. Removal of the solvent *in vacuo*, followed by crystallization from methylene chloride–petroleum ether (Skelly F), afforded adduct **48** (0.548 g, 83%) as colorless plates, mp 268–280° dec.

Anal. Calcd for $C_{30}H_{16}N_4S$: C, 77.57; H, 3.47; N, 12.06; S, 6.90. Found: C, 77.40; H, 3.65; N, 11.78; S, 6.84.

A solution of thiophene **10** and N-phenylmaleimide in benzene

gave no indication of the formation of an adduct (tlc) after standing at room temperature for 22 hr.

Bicyclic Ketones. I. Decomposition of Terpene Ketone Tosylhydrazones

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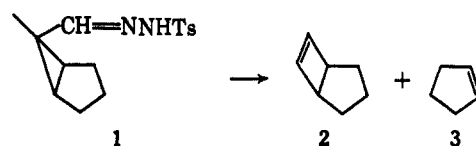*Department of Chemistry, Howard University, Washington, D. C. 20001*

Bicyclic ketone tosylhydrazone sodium salts of the 3.1.0 and 4.1.0 systems decompose to hydrocarbons isomeric with the generated carbene. The structure of these hydrocarbons is related to the position of the cyclopropyl ring relative to the carbenoid carbon. α-Ketocyclopropanes give acetylenic alkenes as major products while β-ketocyclopropanes hydrogen abstract giving bicyclic alkenes. No evidence has been found for the formation of insertion or ring-expansion products.

The preparation of bi- and tricyclic systems from carbenoid precursors is an established preparative reaction.[2] The decomposition of sodium salts of tosylhydrazones (the Bamford–Stevens reaction[3]) has led to a large variety of ring-expanded,[4] ring-contracted,[5] or insertion[6] products depending upon the structure of the starting material, and, as recently found, both the solvent[7] and the base concentration.[8] Evidence has been presented[7,8] that these products are produced as a result of either a carbenoid or cationic precursor.
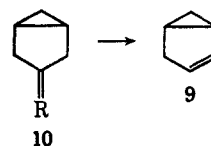
Simple cyclopropylcarbinyl systems have been examined in some detail.[5a,6,7] The nature of the products appears to depend more on the position of the cyclopropane ring relative to the carbenoid carbon than on any other factor. Thus although bicyclo[3.1.0]hexane-6-*endo*-carboxaldehyde tosylhydrazone (**1**) gives *cis*-bicyclo[3.2.0]hept-6-ene (**2**) and cyclopentene (**3**),[9a] incorporation of the carbenoid carbon into a bicyclic system gives no ring-expansion products.[9]

(1) Abstracted from the M.S. Theses of R. H. Chung and Y. N. Vaishnav and the Ph.D. Thesis of C. C. Shroff, Howard University, 1968.

(2) See, for example, W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963).

(3) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

(4) J. W. Wilt, J. M. Kosturik, and R. C. Orowski, *J. Org. Chem.*, **30**, 1052 (1965).

(5) (a) L. Friedman and H. Schechter, *J. Amer. Chem. Soc.*, **82**, 1002 (1960); (b) J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, *J. Org. Chem.*, **30**, 1040 (1965).

(6) H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964).

(7) J. A. Smith, H. Schechter, J. Bayless, and L. Friedman, *J. Amer. Chem. Soc.*, **87**, 659 (1965); K. B. Wiberg and J. M. Lavanish, *ibid.*, **88**, 365 (1966).

(8) R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *ibid.*, **89**, 471, 1442 (1967).

(9) (a) P. K. Freeman and D. G. Kuper, *J. Org. Chem.*, **30**, 1047 (1965); (b) S. J. Cristol and J. K. Harrington, *ibid.*, **28**, 1413 (1963); (c) D. M. Lemal and A. J. Fry, *ibid.*, **29**, 1673 (1964).

The primary products from such bicyclic α-cyclopropylcarbenes are formed by a fragmentation reaction as observed by Cristol and Harrington[9b] and Lemal and Fry[9c] for nortricyclanone (**4**) (R = O) and by Freeman and Kuper[9a] for bicyclo[3.1.0]hexan-2-one (**7**) (R = O).
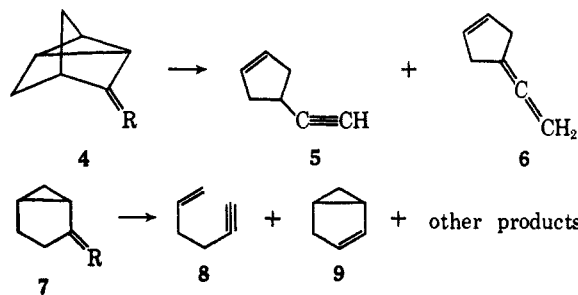
Freeman and Kuper[9a] have also examined bicyclo[3.1.0]hexan-3-one (**10**) (R = O). In this instance, where the cyclopropyl is β to the generated carbene, the only product is formed as a result of hydrogen abstraction (**9**).