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Reactions of 1,4-Quinone *N,N'*-Dibenzenesulfonylimines, 1,4-Quinones, and 1,4-Quinone *N,N'*-Dibenzoylimines with Secondary Diazo Compounds. Structures of Alleged Arocyclopropenes

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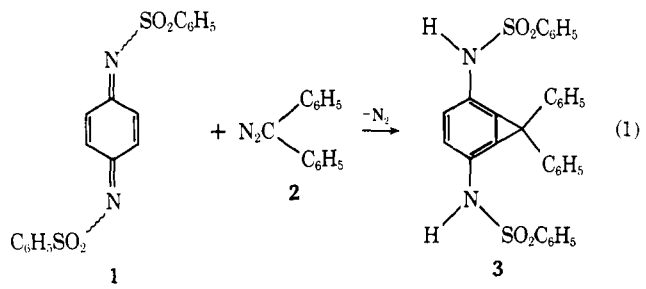
1,4-Benzoquinone *N,N'*-dibenzenesulfonylimine (1) reacts with diphenyldiazomethane (2) with loss of nitrogen to give cyclopropane **8**. Similarly reactions of 2 and of 9-diazofluorene (5) with 1,4-naphthoquinone dibenzenesulfonylimine (4) yield cyclopropanes **9** and **10**. Benzocyclopropene **3** and naphthocyclopropenes **6** and **7** are not obtained. Sulfonylimine 1 and 5 produce mono- and biscyclopropanes, **14** and **15**. Reaction of 8 with cyclopentadiene yields **11**; 8 undergoes acid-catalyzed ring opening of its cyclopropyl group and tautomerization in aqueous acetic acid and in methanol to form **12** and **13**. Rapid syn-anti isomerization about its benzenesulfonylimine nitrogens occurs when 1 is warmed; at 25° the benzenesulfonylimine groups in 4 are syn to the hydrogens at C-2 and C-3 of the 1,4-naphthoquinone moiety. In refluxing benzene, 1,4-benzoquinone (17) reacts with 5 with loss of nitrogen to give cyclopropane **16** and biscyclopropane **23**. Similarly 1,4-naphthoquinone (18) and 5 at 78° yield cyclopropane **22**. Quinones 17 and 18 also react with 1-diazoacenaphthenone (21) to form cyclopropanes **24** and **25**. Cyclopropanes 16 and 22, in the presence of hydrogen chloride, incorporate methanol (2 equiv) and undergo ring opening to yield **30** and **31**, respectively. Thermolysis of 22 results in its isomerization to quinone **32** and decomposition to **18**, bifluorenylidene (**33**), and 9,9'-bifluorenyl (**34**). The reactions of 2 and 5 with 1,4-benzoquinone *N,N'*-dibenzoylimine (**35**), and with the naphtho analog **37**, are successful only in the synthesis of cyclopropane **36** from **35** with 2. Attempts to isomerize **8**, **9**, **10**, **16**, and **22** to arocyclopropenes have been unsuccessful.

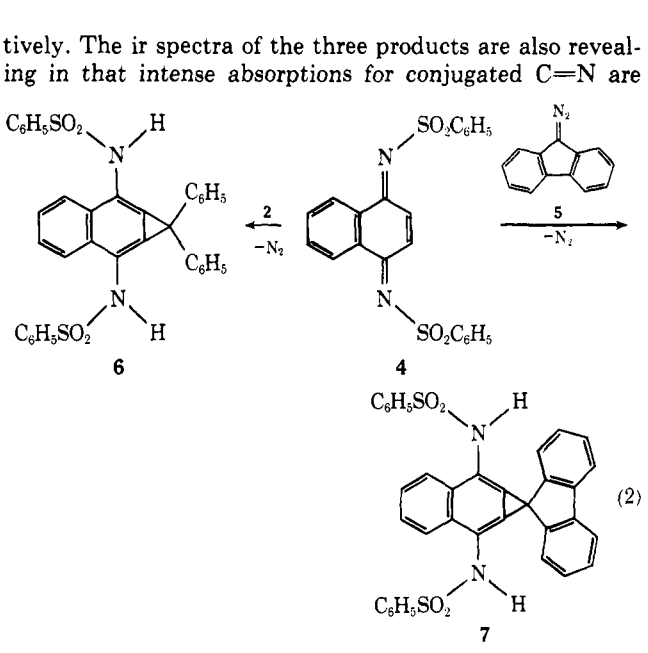
Benzocyclopropenes have recently been synthesized and characterized.[2] It had been earlier reported[3] that 1,4-benzoquinone *N,N'*-dibenzenesulfonylimine (1) and diphenyldiazomethane (2) yield benzocyclopropene **3**[4a] (eq 1) and



(1)

that 1,4-naphthoquinone *N,N'*-dibenzenesulfonylimine (4) reacts with 2 and with 9-diazofluorene (5) to give naphthocyclopropenes **6**[4b] and **7**[4c] (eq 2). We now wish to report a reinvestigation of the products in the prior study[3] of quinone *N,N'*-dibenzenesulfonylimines and diazo compounds. The present summary also includes an investigation of the products of reactions of diazo compounds with 1,4-quinones and 1,4-quinone *N,N'*-dibenzoylimines.

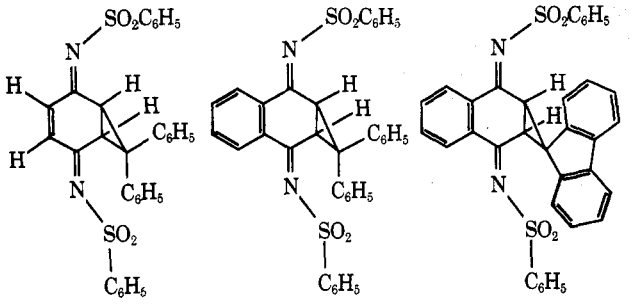
Reactions of 1 and of 4 with 2 and of 4 with 5 do indeed give compounds whose properties match those reported;[3,5] however, they do not show infrared absorption (KBr) for NH stretching. The nmr of the product from 1 and 2 is highly revealing (see Experimental Section) in that singlets for two cyclopropyl hydrogens at δ 4.3 ($CDCl_3$) and for two olefinic hydrogens at δ 6.2 are displayed. Similarly the compounds from 4 with 2 and with 5 show nmr singlets (see Experimental Section) for 2-cyclopropyl hydrogens at δ 4.6 ($CDCl_3$) and 4.55 (DMSO-d_6, 120°), respectively. The ir spectra of the three products are also revealing in that intense absorptions for conjugated C=N are



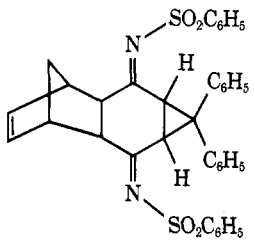
(2)

exhibited at 6.33–6.40 μ. Reactions of 1 with 2 and of 4 with 2 and with 5 thus yield cyclopropanes **8**, **9**, and **10**, respectively, the products of dipolar reaction of the diazo compounds with the quinone sulfonylimines and loss of nitrogen.

The structure of 8 is further confirmed by its reaction with cyclopentadiene to yield **11**[6] (48%). The chemistry of 8 and its resistance to isomerization to 3 are of some note in that 8 is converted by aqueous hydrochloric acid in refluxing acetic acid and by hydrogen chloride in methanol at

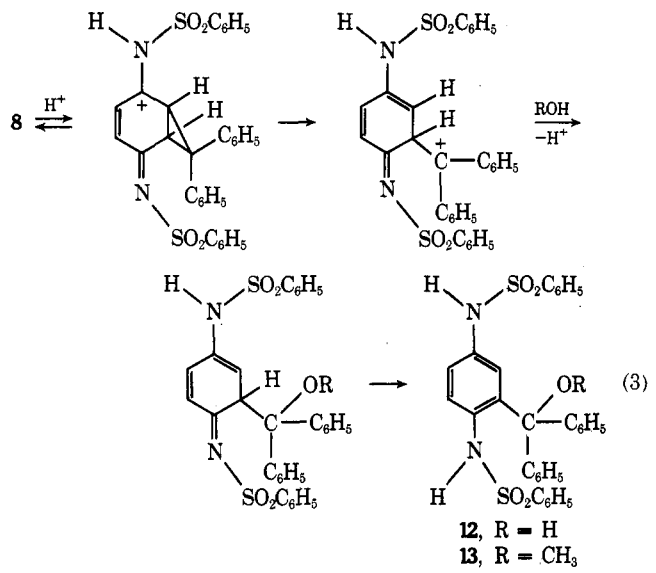


8 9 10



11

25° to ring-opened derivatives **12** (88%) and **13** (73%), respectively, possibly as in eq 3.

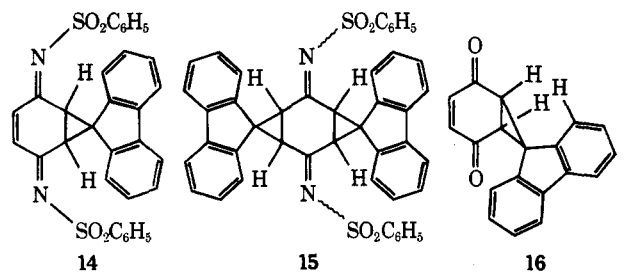


(3)

12, R = H
13, R = CH_3

The structures of **12** and **13** are assigned on the basis of their nmr properties (see Experimental Section) and by conversion of **12** to **13** by reaction with methanolic hydrogen chloride. Efforts to isomerize **8**, **9**, and **10** to **3**, **6**, and **7**, respectively, were unsuccessful; apparently the strain energies of **3**, **6**, and **7** are too great to allow their facile preparation.

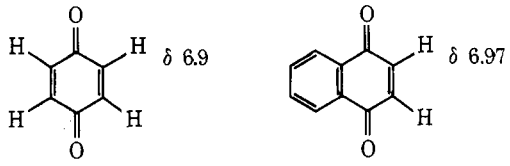
A study has also been made of reactions of **1** with **5**. From **1** and 1 equiv of **5**, cyclopropanes **14** and **15** are



14 **15** **16**

formed. Adduct **14** is difficult to isolate and is hydrolyzed upon chromatography on silica gel to cyclopropane **16**. The properties and a more direct synthesis of **16** are described later in this paper. Sulfonylimine **1** reacts efficiently with 2 equiv of **5** with total loss of nitrogen to give **15**. It is not yet possible to assign the stereochemistry of **15**.

The stereochemistries of the benzenesulfonyl groups in quinone *N,N'*-dibenzenesulfonylimines **1** and **4** and in cyclopropane *N,N'*-dibenzenesulfonylimines **8**, **9**, **10**, and **14** are of interest. 1,4-Benzoquinone (**17**) and 1,4-naphthoquinone (**18**) display nmr singlets for their olefinic protons



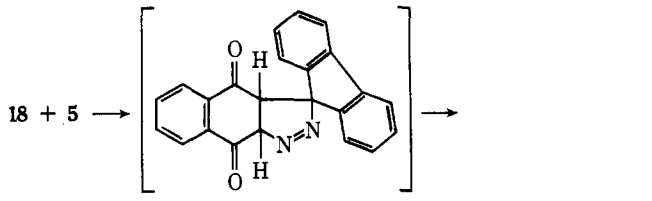
17 **18**

at δ 6.9 and 6.97, respectively. Disulfonylimine **1** shows a complex "doublet" for its olefinic protons at δ 6.9 (100 MHz, $CDCl_3$, −10°); additional resonance for its olefinic protons at δ 8.1 is partially masked by that of the ortho hydrogens of the phenyl groups. As the temperature of **1** in 1,2-dibromoethane is increased, the nmr signals at δ 6.9 and 8.1 fade, the nmr coalescence temperature of **1** being greater than 123°. The nmr properties of **1** at elevated temperatures thus reveal rapid syn-anti isomerization about the benzenesulfonylimine nitrogens and it is not yet possible to assign the stereochemistry of **1** definitely.[7] The results appear to indicate that the olefinic protons in **1** are deshielded ~δ 1.2 by a *syn-N*-benzenesulfonylimino group when compared with a quinone carbonyl and that a *N*-benzenesulfonylimino group has essentially the same nmr influence relative to carbonyl when anti to the olefinic protons.

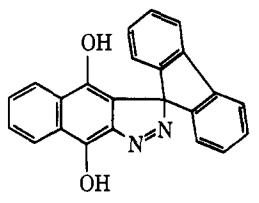
Naphthoquinone *N,N'*-disulfonylimine **4** exhibits a two-proton nmr singlet at δ 8.2 ($CDCl_3$, 25°) for its olefinic hydrogens. This singlet indicates only one isomer to be present; both *N*-benzenesulfonyl groups must be either syn or anti to the olefinic protons. On the basis that the deshielding value of a *syn-N*-benzenesulfonylimino group is ~δ 1.2, the *N*-benzenesulfonyl groups in **4** appear to be syn to the olefinic protons. The stereochemical assignment also agrees with the expectation (on the basis of molecular models) that the interaction of the *N*-benzenesulfonyl groups with the peri hydrogens in the "anti" isomer will be greater than with the hydrogens at C-2 and C-3 in **4**.

Disulfonylimines **8**, **9**, **10**, and **14** display nmr singlets for cyclopropyl protons at δ 4.3–4.6, whereas the ketone (**22**, to be discussed) corresponding to **10** shows a cyclopropyl hydrogen singlet at δ 3.55. The shift (~1 ppm) in the resonance of the cyclopropyl hydrogens compares favorably with that (~1.2 ppm) for olefinic protons in the analogous syn and anti disulfonylimines. On the basis of molecular models, the steric interactions of the sulfonylimino groups with the cyclopropyl hydrogens in **8**, **9**, **10**, and **14** are less than that for the peri or olefinic hydrogens in their geometric isomers. It thus appears likely that the sulfonylimino groups are syn and deshielding as represented in **8**, **9**, **10**, and **14**.

Quinones **17** and **18** have been previously reported to react with secondary diazo compounds to give dihydroxy-3*H*-indazole derivatives,[8] as illustrated for **18** and **5** in eq 4, to give **19**,[8b] presumably by dienolization and aromatization of the initial dipolar adducts. For 2-methyl-1,4-naphthoquinone and diphenyldiazomethane, a system designed to prevent dienolization upon dipolar addition, reaction occurs at 100° with loss of nitrogen to give cyclopropanaphthalenedione **20**.[9] A study has now been made of reactions of **17** and of **18** with **5** and 1-diazoacenaphthenone (**21**), respectively. An initial objective of this effort was to determine if dipolar reactions of these unblocked quinones could be effected with loss of nitrogen to give bi-



(4)



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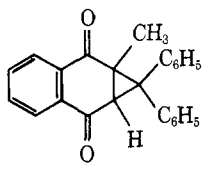

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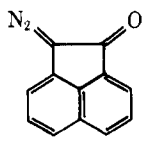
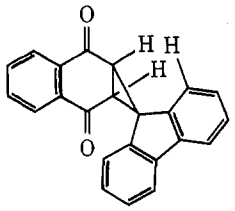


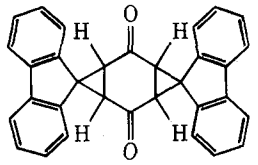
21

cyclo[4.1.0]hept-3-ene-2,5-dione derivatives, analogs of **8–10** and **14**, rather than dihydroxy-3*H*-indazoles derived by dipolar addition and dienolization as in eq 4; the bicyclo[4.1.0]hept-3-ene-2,5-diones are of interest with respect to their possible tautomerization to dihydroxybenzocyclopropene and dihydroxynaphthocyclopropene analogs of **3** and **7**.

It has been found that, in refluxing benzene, **17** and **18** react with **5** to give cyclopropanes **16** (73%) and **22** (61%), respectively. With excess **5** in refluxing benzene, **17** yields the biscyclopropane derivative **23** (50%). The point of note



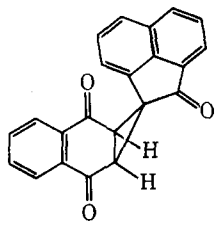
22



23

with respect to synthesis in these systems is that, upon raising the temperature sufficiently, dipolar reaction and loss of nitrogen occur to give cyclopropanes while dipolar addition and dienolization to form 3*H*-indazole derivatives can be effectively avoided. The structures of **16** and **22** are established by their nmr spectra for cyclopropyl hydrogens (**16**, δ 3.5; **22**, δ 3.6) and their infrared absorption for conjugated carbonyl groups (**16**, 6.0 μ; **22**, 6.1 μ). Biscyclopropane **23** is so insoluble that its nmr could not be obtained. The structure of **23** is indicated from its analysis, method of synthesis, and nonconjugated carbonyl absorption (5.90 μ). The stereochemistry of **23** is unknown.

Reactions of **17** and **18** with **21** occur with loss of nitrogen in refluxing benzene to yield cyclopropanes **24** (35%) and **25** (42%), respectively. The structures of **24** and **25**



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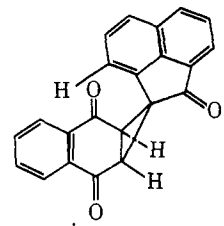
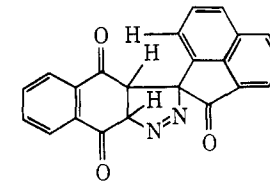


25

are indicated by their nmr singlets (see Experimental Section) for cyclopropyl hydrogens (δ 3.50 and 3.35, respectively). The nmr of **25** also shows a one-proton doublet at δ 5.9 (J = 7 Hz). The resonance is similar to that displayed by **22** (1 H at C-1 of fluorenyl moiety, δ 6.1) and arises from the stereochemistry indicated for **25** which leads to shielding of the hydrogen at C-3 in the acenaphthenone moiety by the benzenoid ring of the naphthoquinone unit. The stereochemistry of the process leading to **25** may possibly be determined in dipolar addition of **18** and **21** to give **26** rather than **27**. In **26** the interaction of



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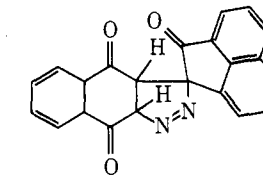
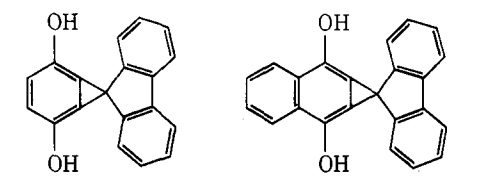


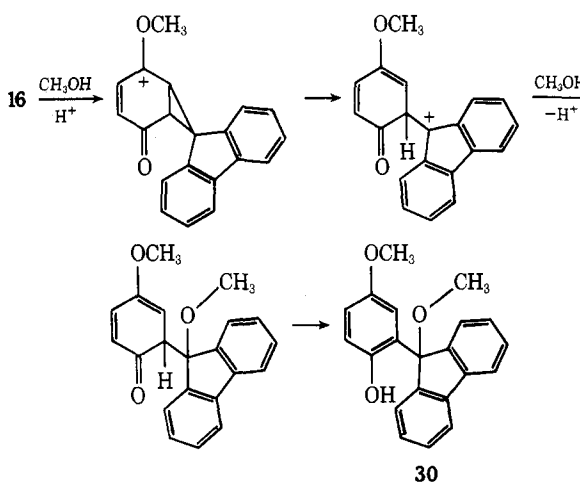
27

hydrogen at C-3 of the acenaphthenone moiety with hydrogen at C-2 and C-3 of the 1,4-dione unit is less than that for the acenaphthenone carbonyl with the C-2 and C-3 hydrogens of **27**. The nmr of the product from **17** and **21** does not allow stereochemical assignment;[10] the stereochemistry illustrated for **24** is based on analogy with **25**.

Possible isomerization of **16** and **22** to benzocyclopropene **28** and naphthocyclopropene **29** has been investigated. Attempted acid-catalyzed enolization of **16** to **28** by hydrogen chloride in methanol results, however, in incorporation of 2 equiv of methanol and ring opening to give **30**, possibly as in eq 5. Analogously **22** is converted by hydrogen chloride–methanol to **31**. Addition of 2 equiv of methanol to **16** and **22** is indicated by the analyses, mass spectra, and nmr of the products. Adducts **30** and **31** each exhibit nmr signals for two methoxy groups and one phenolic hydrogen (see Experimental Section). That the 9-methoxy-9-fluorenyl group in **30** and in **31** is ortho rather

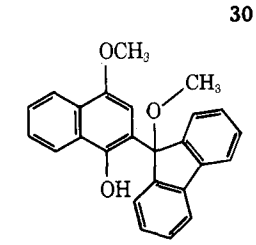


28 29



(5)

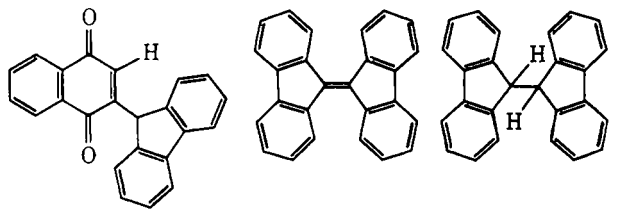
30



31

than meta to the phenol hydroxyls is indicated by the downfield shifts of the phenolic protons. The general range for nmr of phenolic protons is δ 4.0–7.5; however, when phenol groups are intramolecularly hydrogen bonded, their proton resonance is shifted to *ca.* δ 10.0–12.0.[11] In **30** and **31** the phenol protons resonate at δ 9.15 and 10.0, respectively. The assignments of the phenolic groups as indicated in **30** and **31** are thus based on the downfield shifts of the phenol protons presumably resulting from favorable six-membered ring hydrogen bonding with methoxyl of the ortho 9-methoxy-9-fluorenyl groups.

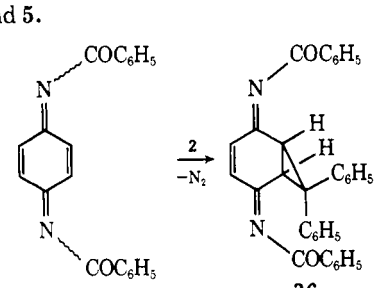
An attempt to effect thermal isomerization of **22** to **29** resulted, however, in its isomerization to **32** (16%) and its decomposition to **18** (30%), bifluorenylidene (**33**, 16%), and 9,9′-bifluorenyl (**34**, 4%), apparently *via* a carbenic



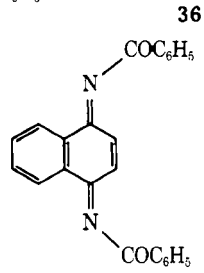
32 **33** **34**

process involving 9-fluorenylidene. Alcoholic bases effect deep-seated decomposition of **16** and **22** to complex unidentified products. As yet, there is no evidence for isomerization of **16** or **22** to arocyclopropenes **28** or **29**.

In addition to the reactions of *N,N′*-dibenzenesulfonylimines **1** and **4** discussed above, the behavior of the analogous benzoylimines **35** and **37** has also been examined with **2** and **5**. Whereas **1** and **4** each yield cyclopropanes with both **2** and **5**, only benzoylimine **35** gives an addition product with **2** (eq 6). The product is assigned as cyclopropane **36** on the basis of its spectroscopic properties (see Experimental Section). Under conditions for preparation of **36**, imine **37** is totally unreactive toward both diazoalkanes **2** and **5**.



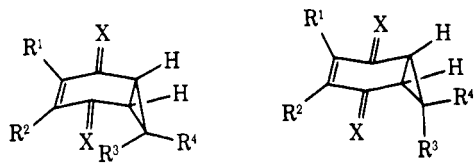
35 **36** (6)



37

The stereochemical assignments for **35–37** are more tentative than those for *N,N′*-dibenzenesulfonylimines **8–10** and **14**. Quinone imine **35** at 25° shows only one resonance signal for its olefinic protons at δ 6.9, similar to that of **17**, and consequently the *N*-benzoyl substituents have no distinctive effect either on the syn or anti olefinic protons.[7] No configurational assignment can thus be made for **35** at 25°. However, with **37** it is reasonable to expect that the configuration is *E,E* with both nitrogen substituents syn to the olefinic protons, since in this isomer steric interference is at a minimum. Cyclopropane **36** exhibits singlet cyclopropyl and olefinic resonances at δ 2.8 and 6.4, respectively. The configuration of **36** is suggested as having both of its *N*-benzoyl substituents syn to the three-membered ring, in which the shielding experienced by the cyclopropyl protons (*ca.* δ 0.8 compared with **16**) is accounted for by the benzoyl groups.

A further aspect of structures **8–10**, **14**, **16**, **22**, **24**, **25**, and **36** is that they may exist in the boat conformation (**38**) or/and the ring-flip isomer (**39**). It has been shown



38 **39**

that 1,6,7,7-tetrasubstituted bicyclo[4.1.0]hept-3-enes exist only in conformation **39** when R^3 is bulky (*e.g.*, Cl or Br).[12] This conformational preference results from a reduced interaction between R^3 and the π electrons of the C_3–C_4 double bond. In the bicycloheptenes **8–10**, **14**, **16**, **22**, **24**, **25**, and **36**, the C_7 substituents are either phenyl, spirofluorenyl, or spiroacenaphthenonyl and molecular models indicate that a minimum interaction is obtained as in **39**. It is thus reasonable to conclude that the bicycloheptene derivatives of the present research are of preferred conformation **39**.

Further studies of arocyclopropenes and their derivatives are in progress in these laboratories.

Experimental Section

(*Z,Z*)-2,5-Bis(*N*-phenylsulfonylimino)-7,7-diphenylbicyclo[4.1.0]hept-3-ene (8). A benzene solution (35 ml) of **1** (1.1 g, 2.9 mmol) and **2** (0.6 g, 3.1 mmol) was refluxed for 3 hr. The solvent was removed and the residue was treated with ether and filtered. Recrystallization of the solid from benzene–hexane gave pale yellow crystals of **8** (0.96 g, 65%): mp 205–206° (lit.[3] mp 202°); ir (KBr) 6.35 (C=N), 6.8, 7.7, 8.6, 9.2, 11.85, and 13.7 μ; nmr ($CDCl_3$) δ 7.0–8.2 (m, 20 H, aromatic), 6.2 (s, 2 H, olefinic), and 4.3 (s, 2 H, cyclopropyl); λ_{max} ($CHCl_3$) 242 nm (log ϵ 4.15) and 283 (4.36).

2′,7′-Bis(*N*-phenylsulfonylimino)-1′a,2′a,3′,6′,6′a,7′a-hexahydro-1,1-diphenyl[3,6]methano[1*H*]cyclopropa[*b*]naphthalene (11). A solution of **8** (600 mg, 1.09 mmol) and cyclopentadiene (1 g, 15.2 mmol) in chloroform (10 ml) was stored at 25° for 45 hr and then evaporated. The yellow residue, after treatment with ethyl ether and repeated recrystallizations from mixtures of ethyl ether, petroleum ether (bp 30–60°), and carbon tetrachloride, yielded Diels–Alder adduct **11** (323 mg, 48%): mp 158–163° (resolidification and remelting at 180–183°); ir (KBr) 3.2, 6.25 (C=N), 6.9, 7.7, 8.65, 9.2, and 12.45 μ; nmr (100 MHz, $CDCl_3$) δ 7.0–8.2 (m, 20 H, aromatic), 6.1 (m, 2 H, olefinic), 4.2 (s, 2 H, cyclopropyl), 3.4 (broad s, 2 H, bridgehead), 2.3 (broad s, 2 H, α-imido), 1.2 (d, 1 H, bridge), and 0.9 (d, 1 H, bridge).

Anal. Calcd for $C_{36}H_{30}N_2O_4S_2$: C, 69.87; H, 4.89; N, 4.53. Found: C, 69.62; H, 5.05; N, 4.27.

2-(Diphenylhydroxymethyl)-1,4-phenylene-*N,N′*-dibenzenesulfonylamine (12). To glacial acetic acid (20 ml) was added sulfonylimine **8** (1.0 g, 1.82 mmol) and concentrated hydrochloric acid (10 ml), and the mixture was refluxed for 3 hr, cooled, and filtered. Recrystallization of **12** (900 mg, 88%) from ethyl acetate–petroleum ether gave white crystals: mp 210–211° dec; ir (KBr) 2.75, 2.95, 6.7, 7.6, 8.7, 9.2, 13.15, 13.75, 14.25, and 14.6 μ; nmr (100 MHz, DMSO-d_6) δ 9.86 (s, 1 H, NH), 9.80 (s, 1 H, NH), 7.82 (s, 1 H, OH), 6.7–7.7 (m, 22 H, aromatic), and 6.25 (d, 1 H, J_{AC} = 3 Hz, aromatic).

Anal. Calcd for $C_{31}H_{26}N_2O_5S_2$: C, 65.24; H, 4.59; N, 4.91; S, 11.24. Found: C, 64.98; H, 4.70; N, 4.85; S, 11.32.

2-(Diphenylmethoxymethyl)-1,1-phenylene-*N,N′*-dibenzenesulfonylamine (13). Gaseous hydrogen chloride was passed into a mixture of **8** (500 mg, 0.91 mmol) and anhydrous methanol (80 ml) until the solution became warm. The suspension was stirred at 25–30° for 18 hr, whereupon a yellow solution was obtained. Evaporation of the mixture *in vacuo* yielded a yellow residue which after treatment with anhydrous methanol gave white

crystals of methoxy ether **13** (388 mg, 73%): mp 168.5–169°; ir (KBr) 3.0, 6.7, 6.95, 8.6, 9.2, 13.2, and 14.6 μ; nmr (DMSO-d_6) δ 9.95 (s, 1 H, NH), 8.9 (s, 1 H, NH), 6.8–7.8 (m, 23 H, aromatic), and 3.0 (s, 3 H, OCH_3).

Anal. Calcd for $C_{32}H_{28}N_2O_5S_2$: C, 65.73; H, 4.83. Found: C, 65.70; H, 4.87.

Conversion of Alcohol 12 by Methanol to Methyl Ether 13. Gaseous hydrogen chloride was padded into a solution of **12** (200 mg, 0.35 mmol) in absolute methanol (30 ml) until heat was generated. After stirring at 25–30° for 15 hr, the mixture was evaporated *in vacuo*. The white solid obtained, **13** (~100%), is identical (melting point, ir, and nmr) to that resulting from **8** and methanol in the presence of hydrogen chloride.

(*E,E*)-1a,7a-Dihydro-2,7-bis(*N*-phenylsulfonylimino)-1,1-diphenyl-1*H*-cyclopropa[*b*]naphthalene (9). A mixture of **4** (0.5 g, 1.2 mmol) and **2** (0.4 g, 2.1 mmol) in benzene (30 ml) was refluxed for 3 hr. After the solvent had been removed, the residue was treated with ether and filtered to yield **9** (0.60 g, 83%) as pale yellow needles from benzene–hexane: mp 248–249° (lit.[3] mp 244–245°); ir (KBr) 3.2, 6.4 (C=N), 7.0, 7.75, 8.65, 9.2, 11.95, and 13.7 μ; nmr ($CDCl_3$) δ 6.8–8.3 (m, 24 H, aromatic) and 4.6 (s, 2 H, cyclopropyl); λ_{max} ($CHCl_3$) 346 nm (log ε 4.35), 266 (sh, 4.33), 274 (sh, 4.31), and 297 (4.25).

(*E,E*)-1a,7a-Dihydro-2,7-bis(*N*-phenylsulfonylimino)spiro[1*H*-cyclopropa[*b*]naphthalene-1,9′-fluorene (10). Sulfonylimine **4** (0.7 g, 1.7 mmol) and **5** (0.4 g, 2.1 mmol) were refluxed in benzene (35 ml) for 2 hr. The precipitated material was filtered, washed with hexane, and dried. The pale yellow crystals of **10** (0.74 g, 73%), on crystallization from chloroform–hexane, melted at 249–250° (lit.[3] mp 250°); ir (KBr) 6.25, 6.4 (C=N), 7.0, 7.65, 8.7, 9.25, 11.55, 12.9, and 13.7 μ; nmr (DMSO-d_6, 120°) δ 8.3–8.5 (m, 2 H, aromatic), 8.15–7.8 (m, 4 H, aromatic), 7.1–7.7 (m, 14 H, aromatic), 6.6–6.9 (m, 1 H, aromatic), 5.85–6.1 (d, 1 H, aromatic), and 4.55 (s, 2 H, cyclopropyl); λ_{max} ($CHCl_3$) 264 nm (log ε 4.55), 288 (sh, 4.30) and 307 (sh, 4.06).[13]

(*Z,Z*)-2′,5′-Bis(*N*-phenylsulfonylimino)spiro[fluorene-9,7′-[3]norcarene] (14). A mixture of **1** (0.6 g, 1.6 mmol) and **5** (0.3 g, 1.7 mmol) in benzene (25 ml) was refluxed for 1.5 hr. The precipitated material was filtered, washed with hexane, and dried to give **15** (0.20 g, 25%; see below). The filtrate was concentrated to a red gum, triturated with benzene (4 ml), and left to stand for 3 days, after which time a mixture of yellow crystals and red-orange prisms had formed. Hand separation of the species showed the yellow material to be **1** (0.04 g, 7%). The major red-orange component was crystallized from ethyl acetate–light petroleum to give **14** (0.40 g, 49%) as orange plates: mp 145–147°; ir (KBr) 6.35 (C=N), 6.9, 7.6, 8.6, 9.2, 11.2, 12.4, and 13.95 μ; nmr (DMSO-d_6, 22°) δ 7.3–8.3 (m, 18 H, aromatic), 7.1 (s, 2 H, olefinic), and 4.45 (s, 2 H, cyclopropyl).

Anal. Calcd for $C_{31}H_{22}N_2O_4S_2$: C, 67.61; H, 4.02; N, 5.13. *Found:* C, 67.49; H, 4.33; N, 4.89.

Subjection of the product mixture to preparative tlc (Merck Keiselgel GF 254) with benzene elution effects quantitative conversion of **14** to cyclopropane **16**.

2′,6′-Bis(*N*-phenylsulfonylimino)dispiro[fluorene-9,4′-tricyclo[5.1.0.0^{3,5}]octane-8′,9″-fluorene] (15). A mixture of **1** (1.0 g, 2.6 mmol) and **5** (2.0 g, 10.04 mmol) in benzene (100 ml) was refluxed for 2 hr and then cooled. The precipitate was filtered, washed with hexane, and dried to give **15** (1.43 g, 77.5%). Recrystallizations of **15** from 1,1,2,2-tetrachloroethane and from 1,2-dichloroethane yielded off-white crystals: mp 265–266°; ir (KBr) 6.25 (C=N), 6.9, 7.6, 8.6, 9.15, 13.5, and 14.25 μ. The nmr of **15** could not be determined because of its insolubility.

Anal. Calcd for $C_{44}H_{30}N_2O_4S_2$: C, 73.95; H, 4.20; N, 3.92; S, 8.96. Found: C, 74.29; H, 4.45; N, 3.91; S, 9.56.

Spiro[fluorene-9,7′-[3]norcarane]-2′,5′-dione (16) and Dispiro[fluorene-9,4′-tricyclo[5.1.0.0^{3,5}]octane-8′,9″-fluorene]-2′,6′-dione (23). A benzene solution (30 ml) of **17** (0.17 g, 1.6 mmol) and **5** (0.35 g, 1.8 mmol) was refluxed for 20 hr. The solid formed on cooling the mixture was filtered and crystallized from a large volume of ethyl acetate to give **16** (0.30 g, 73%) as yellow needles: mp 263–264°; ir (KBr) 6.0, 6.2, 6.9, 7.7, 11.15, 13.0, and 13.6 μ; nmr (DMSO-d_6, 135°) δ 7.7–8.1 (m, 2 H, aromatic), 7.1–7.6 (m, 6 H, aromatic), 7.0 (s, 2 H, olefinic), and 3.5 (s, 2 H, cyclopropyl); λ_{max} (THF) 258 nm (log ε 4.32), 265 (4.32), 284 (sh, 4.03), and 293 (sh, 3.85).

Anal. Calcd for $C_{19}H_{12}O_2$: C, 83.79; H, 4.44. Found: C, 83.93; H, 4.36.

In a separate experiment, **17** (1.0 g, 9.25 mmol) and **5** (3.6 g, 18.7 mmol) were allowed to react as above. Monoadduct **16** was obtained in 5% yield and diadduct **23** was formed in 50% yield (2.01 g). Diadduct **23** is very insoluble in all solvents investigated but was purified upon heating with nitrobenzene: white crystals; mp >300°; ir (KBr) 5.9, 6.9, 7.75, 8.05, 12.9, and 13.6 μ. The nmr of **23** could not be determined because of its insolubility.

Anal. Calcd for $C_{32}H_{20}O_2$: C, 88.02; H, 4.62. Found: C, 87.75; H, 4.88.

1a,7a-Dihydrospiro[1*H*-cyclopropa[*b*]naphthalene-1,9′-fluorene]-2,7-dione (22). Quinone **18** (1.58 g, 10 mmol) and **5** (1.92 g, 10 mmol) were mixed in benzene (100 ml) and the mixture was refluxed for 2 hr. The mixture was concentrated and the residue was extracted with hot hexane (300 ml). The solid, after crystallization from glacial acetic acid, was identified as **22** (2.10 g, 61%): pale yellow crystals; mp 234–235°; ir (KBr) 6.0, 6.3, 6.9, 7.8, 8.1, 9.7, 12.0, 12.6, and 13.7 μ; nmr ($CDCl_3$, 50°) δ 6.9–8.4 (m, 10 H, aromatic), 6.75 (m, 1 H, aromatic), 6.05 (d, 1 H, aromatic), and 3.55 (s, 2 H, cyclopropyl); λ_{max} (THF) 258 nm (log ε 4.34), 283 (sh, 4.02), 291 (3.94), and 310 (3.53).

Anal. Calcd for $C_{23}H_{14}O_2$: C, 85.69; H, 4.38. Found: C, 85.62; H, 4.57.

Evaporation of the hexane extract yielded bifluorenylidene (**33**, 1.05 g), mp 194–195°.

(*r*)-Spiro[acenaphthene-1,7′-bicyclo[4.1.0]hepten[3]ene]-2,2′,5-trione (24). A solution of **17** (540 mg, 5.0 mmol) and **21** (960 mg, 5.2 mmol) in benzene (30 ml) was refluxed for 17 hr. The mixture was then cooled and the brown solid formed (400 mg) was separated. The filtrate was chromatographed on silica gel. Elution with benzene produced biacenedione (32 mg, 4%); further elution with methylene chloride gave **17** (170 mg). Upon use of 2% methanol in methylene chloride as eluent, **24** (480 mg, 35%) was obtained as white crystals: mp 191.5–192°; ir (KBr) 5.80, 5.95, 8.0, 9.1, 12.0, and 12.8 μ; nmr ($CDCl_3$) δ 7.2–8.3 (m, 6 H, aromatic), 7.0 (s, 2 H, olefinic), and 3.35 (s, 2 H, cyclopropyl).

Anal. Calcd for $C_{18}H_{10}O_3$: C, 78.82; H, 3.68. Found: C, 78.38; H, 3.71.

(*r*)-1′a,7′a-Dihydrospiro[acenaphthene-1,1′-[1*H*]cyclopropa-[*b*]naphthalene]-2,2′,7′-trione (25). A solution of **18** (0.79 g, 5.0 mmol) and **21** (0.97 g, 5.25 mmol) in benzene (30 ml) was refluxed for 11 hr. The mixture was cooled and filtered, and the brown residue (0.79 g) was washed with benzene. The filtrate was chromatographed on silica gel. Elution with methylene chloride yielded biacenedione (72 mg); further elution with 4% methanol in chloroform gave additional product (0.47 g) which was combined with the brown residue. Recrystallization from tetrahydrofuran yielded crystals of **25** (0.74 g, 42%): mp 235–236°; ir (KBr) 5.8, 5.95, 6.25, 7.75, 8.0, 9.05, 10.0, 12.8, and 13.4 μ; nmr ($CDCl_3$) δ 7.3–8.5 (m, 9 H, aromatic), 5.9 (d, 1 H, J_{AH} = 7 Hz, aromatic), and 3.5 (s, 2 H, cyclopropyl).

Anal. Calcd for $C_{22}H_{12}O_3$: C, 81.47; H, 3.73. Found: C, 81.73; H, 3.56.

4-Methoxy-2-(9′-methoxy-9′-fluorenyl)phenol (30). On passing hydrogen chloride into a suspension of **16** (500 mg, 1.84 mmol) in anhydrous methanol (25 ml), heat was generated and the mixture turned maroon and became homogeneous in 12 hr. Evaporation of the solution, treatment of the residue with methanol, and cooling yielded white crystals of dimethoxyphenol **30** (350 mg, 60%): mp 111–112.5°; ir (KBr) 2.85, 3.3 6.7, 8.25, 9.4, 9.5, 12.2, and 13.4 μ; nmr ($CDCl_3$) δ 9.15 (s, 1 H, OH), 7.15–7.75 (m, 8 H, aromatic), 6.95 (d, 1 H, J_{xy} = 9.0 Hz, aromatic), 6.7 (d_0/d, 1 H, J_{ax} = 3.0 Hz, aromatic), 6.0 (d, 1 H, J_{ax} = 3.0, J_{ay} = 1 Hz, aromatic), 3.4 (s, 3 H, OCH_3), 2.9 (s, 3 H, OCH_3); *m/e* 318 [P − 32 and P − 33 (100%) were very large].

Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.03; H, 5.79.

4-Methoxy-2-(9′-methoxy-9-fluorenyl)-1-naphthol (31). Gaseous hydrogen chloride was passed into a solution of **22** (1.0 g, 2.60 mmol) in absolute methanol (50 ml). The mixture warmed, was stirred at room temperature for 24 hr, and then was evaporated. A methanol solution of the residue was treated with charcoal, concentrated, and filtered. The brown crystals (90 mg) of **31** turned purple on standing for 24 hr. The product, mp ~60°, resisted purification *via* recrystallization or chromatography on silica gel. The structure of **31** was assigned from the following properties: ir (KBr) 2.95, 6.25, 6.90, 7.35, 9.1, 10.1, 13.1, and 13.45 μ; nmr ($CDCl_3$) δ 10.0 (s, 1 H, OH), 7.1–8.2 (m, aromatic), 5.75 (s, aromatic), 3.5 (s, 3 H, OCH_3), and 3.05 (s, 3 H, OCH_3).

Anal. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47. Found: C, 81.68; H, 5.07.

Thermolysis of 1a,7a-Dihydrospiro[1*H*-cyclopropa[*b*]naphthalene-1,9′-fluorene]-2,7-dione (22). Dione **22** (300 mg, 0.93 mmol) was heated until the yellow solid melted (265°) and turned dark. The residue was cooled and extracted with methylene chlo-

ride. Evaporation of the extract *in vacuo* produced a dark residue which upon treatment with hot hexane left a purple solid (77 mg). The hexane solution was chromatographed on silica gel. Elution with increasing amounts of ether–hexane gave (1) a red material (30 mg), (2) **32** (47 mg, 16%), and (3) **18** (45 mg, 30%), respectively. The red product on further chromatography on silica gel using 5% benzene in hexane yielded **33** (24 mg, 16%) and **34** (6 mg, 4%). The structures of **18**, **32**, **33**, and **34** were assigned upon comparison with authentic samples or spectral data of such samples.

Dione **32** is a yellow solid: ir (KBr) 6.0, 6.25, 6.9, 7.5, 7.7, 7.9, 10.35, 10.9, 12.8, 13.0, and 13.6 μ; nmr ($CDCl_3$, 100 MHz) δ 7.15–8.3 (m, 12 H, aromatic), 6.3 (s, 1 H, olefinic), and 4.5 (s, 1 H, 9-fluorenyl).

Anal. Calcd for $C_{23}H_{14}O_2$: C, 85.70; H, 4.38. Found: C, 85.42; H, 4.36.

(*Z*,*Z*)-2,5-Bis(*N*-benzoylimino)-7,7-diphenylbicyclo[4.1.0]hept-3-ene (36). A benzene solution (45 ml) of **35** (1.88 g, 6.0 mmol) and **2** (1.32 g, 7.0 mmol) was refluxed for 3 hr. The white amorphous precipitate was filtered and vacuum sublimed to give 1,4-phenylene-*N*,*N*′-dibenzoylamine (0.16 g, 8%), mp 338–340° (lit.[14] mp >300°). The filtrate was concentrated and subjected to preparative tlc over Merck Kieselgel GF 254 with benzene–hexane (1:1) elution. The band with R_f 0.5,[15] extracted with chloroform, gave a pale yellow oil which slowly solidified. Recrystallization from benzene–hexane gave **36** (1.87 g, 65%): mp 264°; ir (KBr) 6.05 (C=O), 6.2, 6.8, 7.6, 7.8, 8.0, 8.5, 9.4, 12.4, and 14.4 μ; nmr ($CDCl_3$) δ 7.9–8.2 (m, 4 H, aromatic), 7.1–7.7 (m, 16 H, aromatic), 6.39 (s, 2 H, olefinic), and 2.78 (s, 2 H, cyclopropyl).

Anal. Calcd for $C_{33}H_{24}N_2O_2$: C, 82.47; H, 5.13; N, 5.83. Found: C, 82.57; H, 5.40; N, 5.71.

Registry No.—**1**, 1050-82-4; **2**, 883-40-9; **4**, 42976-05-6; **5**, 832-80-4; **8**, 42976-06-7; **9**, 42976-07-8; **10**, 42976-08-9; **11**, 42976-09-0; **12**, 42976-10-3; **13**, 43021-10-9; **14**, 42976-11-4; **15**, 42976-12-5; **16**, 42976-13-6; **17**, 106-51-4; **18**, 130-15-4; **21**, 42976-14-7; **22**, 42976-15-8; **23**, 42976-16-9; **24**, 42976-17-0; **25**, 42976-18-1; **30**, 42976-19-2; **31**, 42976-20-5; **32**, 42976-21-6; **33**, 746-47-4; **35**, 16720-35-7; **36**, 42976-23-8.

References and Notes

(1) We should like to acknowledge support of this research by (a) the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the National Institutes of Health, and (b) the New Zealand Universities Grants Committee.
(2) For a review see B. Halton, *Chem. Rev.*, **73**, 113 (1973).
(3) A Mustafa and M. Kamel, *J. Amer. Chem. Soc.*, **75**, 2934 (1953).
(4) Arocyclopropenes **3**, **6**, and **7** may be named (a) 2,5-bis(*N*-phenylsulfonylamino)-1,1-diphenyl-1*H*-cyclopropabenzene (**3**), (b) 2,7-bis(*N*-phenylsulfonylamino)-1,1-diphenyl-1*H*-cyclopropa[*b*]naphthalene (**6**), and (c) 2,7-bis(*N*-phenylfulfonylamino)-spiro[1*H*-cyclopropa[*b*]naphthalene-1,9′-fluorene] (**7**), respectively.
(5) Minor products from **1** and from **4** with **2** are tetraphenylethylene (<10%) and benzophenone azine (<10%).
(6) The structure of **11** is based on its analysis, nmr and ir spectra (see Experimental Section), and origin. The stereochemistry of **11** is not known.
(7) The mechanisms of isomerization and the temperature dependence of the nmr of *N*-benzenesulfonylimines are discussed by M. Raban, E. Carlson, and F. Jones, *Chem. Commun.*, 1235 (1969). For further discussion and leading references concerning isomerization of imines, see R. Moriarty, C. Yeh, K. Ramey, and P. Whitehurst, *J. Amer. Chem. Soc.*, **92**, 6360 (1970).
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(10) In **24** the hydrogen at C-3 of the acenaphthenone moiety is not shielded by the cyclohexenedione unit; a fused benzene ring as in **25** is necessary to effect the shielding. Similarly the hydrogen at C-1 in the fluorene moiety of **16** is not shielded whereas it is in the benzo analog **22**.
(11) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1970, p 122.
(12) D. C. F. Law and S. W. Tobey, *J. Amer. Chem. Soc.*, **90**, 2376 (1968).
(13) In these experiments **33** and fluorenone azine were also formed (<10%).
(14) R. Adams and J. L. Anderson, *J. Amer. Chem. Soc.*, **72**, 5154 (1950).
(15) Bands with R_f 0.7 and 0.9 gave benzophenone azine (15%) and tetraphenylethylene (3%), respectively.

Benzocyclopropenes *via* Reactions of *p*-Quinonebenzenesulfonimides with Diphenyldiazomethane: a Reinvestigation. Quinone Imide Isomerism[1]

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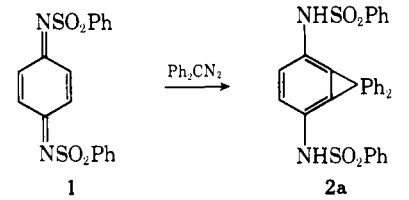
The product from the reaction of *p*-quinonedibenzenesulfonimide (**1**) and diphenyldiazomethane does not have the benzocyclopropene structure (**2a**) as reported by Mustafa and Kamel. On the basis of conclusive ir and ^1H nmr studies, the correct structure in solution and in the crystalline state is that of a novel substituted biocyclo[4.1.0]-3-heptene (**2b**). Two types of crystals (higher melting tablets and lower melting needles) were isolated from *p*-quinonedibenzenesulfonimide prepared by the oxidation of *p*-phenylenedibenzenesulfonamide by lead tetraacetate. The two forms are identified as syn and anti isomers (**1a** and **1b**, respectively) on the basis of moderate differences in melting point and ir spectra and marked differences in behavior on standing.

According to a recent review on benzocyclopropenes,[2] the two earliest reports claiming syntheses of benzocyclopropenes were in 1930 by De and Dutt[3] and in 1953 by Mustafa and Kamel;[4] neither of these reports has been substantiated or refuted in a published paper. Mustafa and Kamel[4] claimed that substituted benzocyclopropenes (*e.g.*, **2a**) were formed in reactions of diphenyldiazomethane with *p*-quinonebenzenesulfonimides (*e.g.*, **1**). Halton[2] cast doubt on the structures assigned to these products as well as to that in the analogous reaction between **1** and 9-diazofluorene on the basis that recent attempts by Halton and Milsom[5] to obtain 7,7-diphenylbenzocyclopropenes led to the isolation of fluorene derivatives.

Because of the importance of benzocyclopropene as a unique structure, we undertook a study of the reaction of



1 **2a**

p-quinonedibenzenesulfonimide with diphenyldiazomethane. Recent interest in this topic as indicated by the above reports[2,5-7] prompts us to present our earlier work[8]