as a solution of EPA (ether–isopentane–ethanol, 5:5:2 v/v) or isopentane. The solvent was checked for emission at each time. No interference due to emission of solvent was observed. The solution contains *ca.* 10^{-5} *M* solute and they formed clear glasses without micro crystals at 77°K.

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Photochemical and Thermal Reactions of Naphthoquinones and Ynamines. Formation of Intermediate Cyclobutadienes

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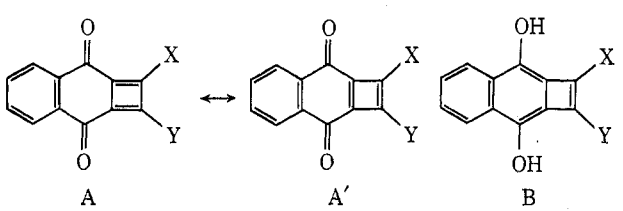
Photochemical and thermal reactions of naphthoquinones with ynamines were found to give cyclobutene, quinone methine, and naphthothiophene products. The reaction course was governed by naphthoquinone and ynamine substituents and reaction conditions. Conversions of the cyclobutenes to naphthocyclobutadienes, the corresponding naphthoquinones, and their dimerizations were studied.

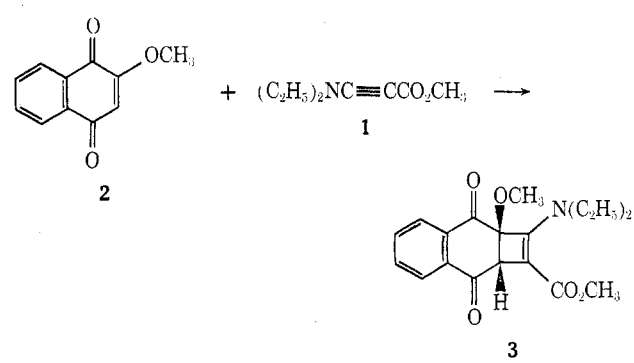
The acid-promoted dimerization of ynamines to four-membered ring imonium salts and their subsequent treatment with base gave stable, tetrasubstituted cyclobutadiene compounds.[1,2] In order to study the limits of stability of these long elusive smallest cyclic polyenes, we undertook studies which should lead to the cyclobutadiene–naphthoquinone and cyclobutadiene–dihydroxynaphthalene systems A and B, in which one might expect some measurable π bond localization, depending on the substituents X and Y.



While enamines react with quinones, quinone imines, and naphthoquinones to form substituted hydroquinones or their corresponding derivatives,[3-8] ynamines were found to give products derived from addition to the quinone carbonyl group.[9] The formation of intermediate oxirans was again observed in the photochemical reactions of other acetylenes with naphthoquinones, but these reactions also gave fused cyclobutene products.[10-13] This paper describes studies of the photochemical and nonphotochemical reactions of naphthoquinones with ynamines and subsequent conversions designed to give A and B.

Irradiation of a solution of carbomethoxydiethylaminoacetylene (**1**) and 2-methoxynaphthoquinone (**2**) in acetonitrile through a Pyrex filter (λ >280 mμ) produced a 58% yield of the adduct **3**. Since ir, uv, and nmr spectra did not allow a rigorous exclusion of the isomeric cyclobutene product with adjacent carbomethoxy and methoxy groups (though there was no double-bond isomerization evident in our product), a single-crystal X-ray analysis was enlisted.[14] This firmly established the structure of **3**.

A uv spectrum of the reaction mixture prior to irradiation did not reveal formation of an initial complex of the reactants, and the isolated product **3** proved to be stable to further irradiation. The 1,3-photorearrangement[15] through Norrish type I cleavage, which has been observed for other naphthoquinone–acetylene adducts, would not be expected in this case, since it would lead to the cyclobutene where amine and ester group conjugation is lost. No adduct **3** was formed in acetonitrile without irradiation.



Similarly, the cyanoynamine **4** was found to react with 2-methoxynaphthoquinone (**2**) to form the cyclobutene **5** in 70% yield. The structure of this product was suggested by a close spectroscopic correlation with **3**. (Profound differences were found in the isomeric cyclobutenes obtained in the acetoxy series, below.)

Together with the cyclobutene **5**, a quinone methine **6** was obtained in 2–5% yield. This product arises on opening of the oxirane obtained by addition of the ynamine to one of the naphthoquinone carbonyl groups.

A cyclobutene product was also formed from diethylaminophenylacetylene (**7**) and 2-methoxynaphtho-

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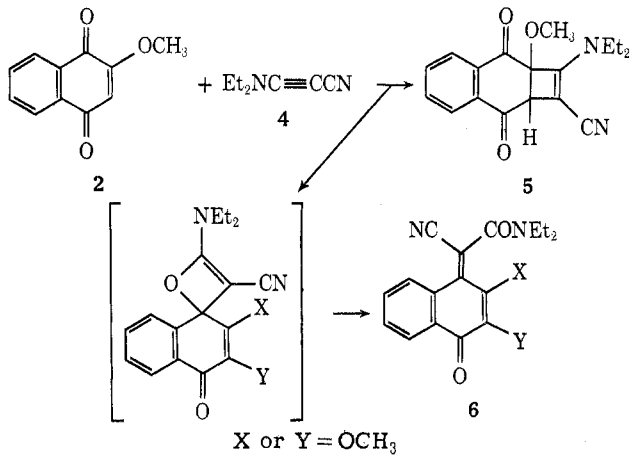
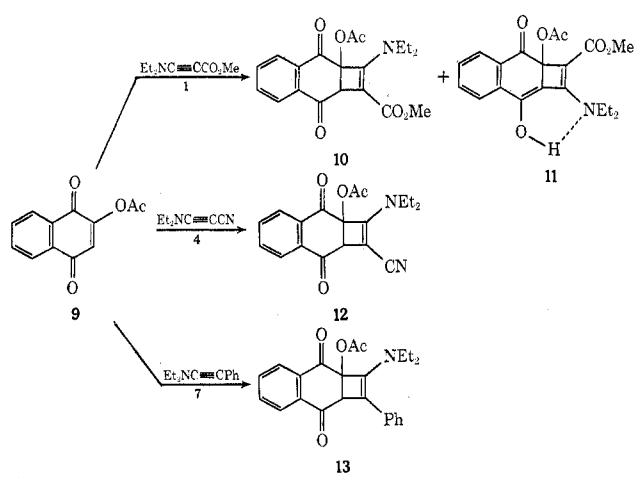


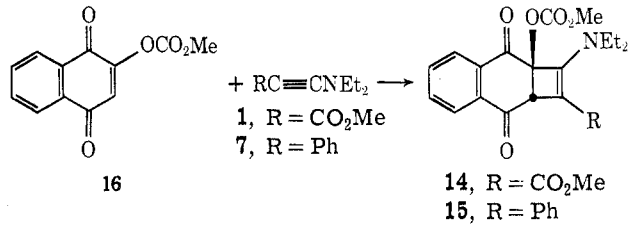
quinone (2), but this compound decomposed on purification and was not investigated further. No product could be obtained from a reaction with diethylaminomethylacetylene (8), possibly because of the increased reactivity of the unconjugated cyclobutene enamine system.

When 2-acetoxynaphthoquinone (9) was irradiated in the presence of the carbomethoxy ynamine 1, two cyclobutene products were obtained. While one showed all of the spectroscopic characteristics associated with the corresponding methoxy product 3, and could thus be assigned structure 10, the other showed one enolic hydroxyl group in nmr and ir spectra and intramolecular hydrogen bonding to nitrogen. The isomeric structure 11 was thus assigned to this compound. In addition to these products, some 20 others were formed and seen on chromatography of the reaction mixture. A large number of colored products were also obtained without irradiation in benzene or acetonitrile, but the cyclobutene compounds could not be isolated from those reactions.

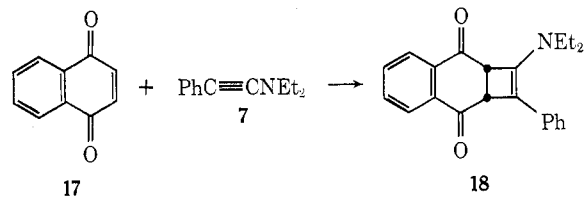
Irradiation of 2-acetoxynaphthoquinone (9) with the cyanoynamine 4 or the phenylynamine 7 led to the cyclobutene compounds 12 and 13 as well as a large number of unidentified products. Again 12 and 13 were not produced in benzene or acetonitrile without irradiation.



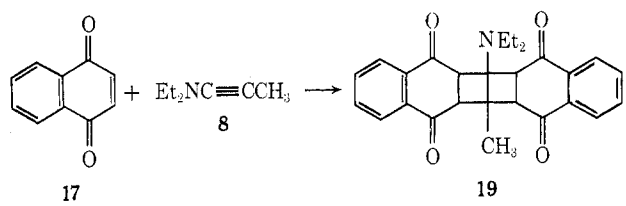
However, it was found that the cyclobutenes 14 and 15 were formed without irradiation from the methyl carbonate compound 16 and the carbomethoxy and phenyl ynamines 1 and 7. These reactions gave better yields of 14 and 15 when acetonitrile, rather than benzene, was used as solvent. No addition products of the methyl carbonate 16 could be obtained with the cyano ynamine 4 or the methyl ynamine 8, with or without irradiation.



Addition of the phenyl ynamine 7 to the unsubstituted naphthoquinone 17 and formation of the cyclobutene 18 without irradiation was also observed.[13a]



Addition of the methyl ynamine 8 to naphthoquinone (17) without irradiation led to a 1:2 adduct. In view of the known reactions of enamines with naphthoquinones, addition of a second equivalent of naphthoquinone to the initial cyclobutene is expected. While previous examples led to the formation of only one carbon–carbon bond, the formation of a second cyclobutane ring, in 19, became evident by the simplicity of the nmr spectrum, which did not allow for phenolic or benzodihydrofuranoid structures.

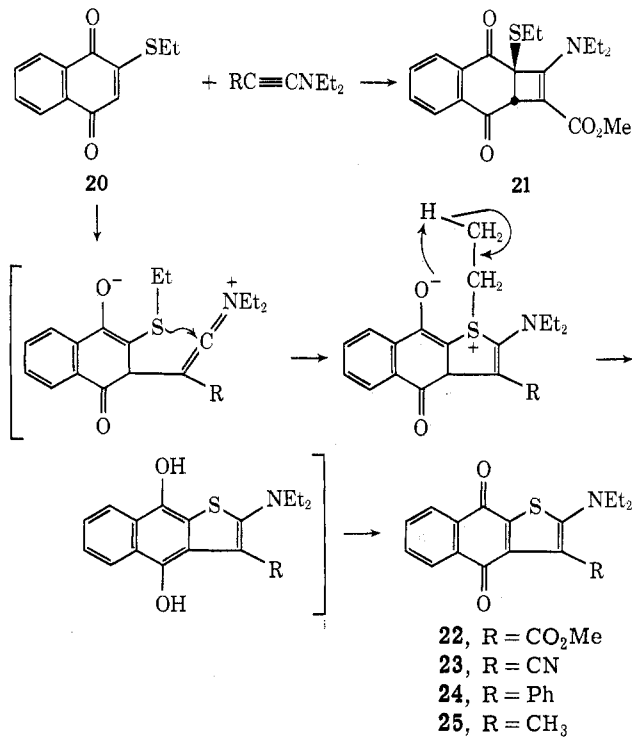


A complex product mixture resulted from irradiation of 2-ethylthionaphthoquinone (20) and the ynamine ester 1 in acetonitrile. From this mixture the cyclobutene 21 was isolated as well as the aminothiophene 22. Structural assignment of 22 was based on loss of the *S*-ethyl group, apparent in the nmr spectrum, with retention of sulfur. Extended conjugation was evident in uv and visible spectra of 22 and the molecular weight was found from the mass spectrum. These conclusions were confirmed by a single-crystal X-ray analysis of 22.[16]

The thiophene product 22 was also formed without irradiation and similar additions of the cyano, phenyl, and methyl ynamines 4, 7, and 8 led to analogous thiophene products 23, 24, and 25. A speculative mechanism for the formation of these compounds is shown. In accord with this mechanism, one observes higher yields of the thiophene products with the carbomethoxy and cyano ynamines 1 and 4 *vs.* the phenyl and methyl

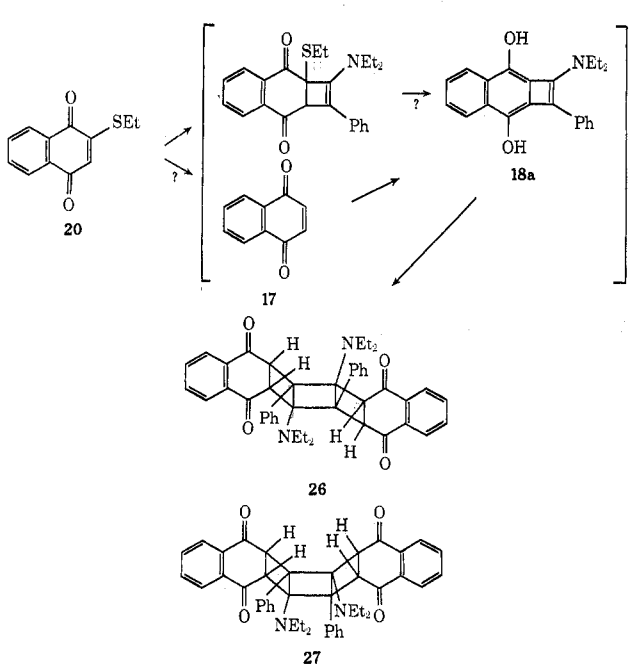
(16) We thank Drs. J. Lerbscher, C. Gibbons, and J. Trotter for their valuable cooperation. The results are to be published by the University of British Columbia group.

ynamines **7** and **8** owing to relative facility of electrophilic attack on sulfur.



22, R = CO_2Me
23, R = CN
24, R = Ph
25, R = CH_3

The last step in the proposed pathway involves oxidation of hydroquinones to the quinone products **22–25**. A clue to this step may be seen in the isolation of the dimeric ynamine adducts **26** and **27** on fractionation of the corresponding reaction mixture. These compounds were formed on preparative chromatography and were absent from the original reaction mixture. Dimerization may proceed through the phenolic tautomer **18a** of an initial naphthoquinone–ynamine adduct **18** lacking the sulfur substituent. Reduction of 2-ethylthionaphthoquinone (**20**) to naphthoquinone (**17**) and addition of the phenyl ynamine **7**, or reduction of a thioethylcyclobutene, would give **18** and **18a**. The dimeric compounds **26** and **27** could also be isolated from the



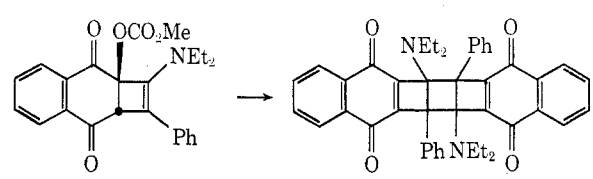
reaction of naphthoquinone (**17**) with the phenyl ynamine **7**.

The dimeric nature of compounds **26** and **27** was evident from mass spectra. The proposed orientation and stereochemistry for **26** and **27** is tentative and based on nmr spectra which showed two pairs of methyl groups for **27** with one pair deshielded relative to the other and relative to the identical methyl groups found in **26**. This effect can be ascribed to deshielding of two ethyl groups by phenyl substituents in **27**, but alternative stereostructures with dissimilar ethyl groups are possible.

Elimination of the angular substituents in the cyclobutene products **3**, **5**, **10–15**, and **21** was studied next. The methoxy group was not lost under a variety of elimination conditions. Thus the cyclobutenes **3** and **5** were recovered unchanged from sodium methoxide in methanol, sodium hydride in benzene, or the cation exchange resin Rexin 101 in benzene after 18 hr at reflux. The compounds could also be recovered from *p*-toluenesulfonic acid and ethylene glycol in benzene, at reflux for 3 days, and an attempted reduction with zinc in ethanol. The thioethyl compound **21** was also stable to sodium hydride in benzene.

The acetates **10** and **11** could be recovered unchanged from attempted vapor-phase pyrolyses at 430° under vacuum. Treatment with collidine at 280° led to formation of numerous decomposition products, and reduction with zinc and acetic acid for 10 min led to loss of the methyl ester group in **10** (ester exchange) but not loss of the acetate group.

The carbonate esters **14** and **15** also proved to be stable to attempted pyrolytic cleavage below 200°, but were destroyed at higher temperatures. Elimination of the ester function from **15** with sodium hydride in refluxing benzene led to the formation of a dimeric naphthoquinone for which the head-to-tail structure **28** is suggested.



15 **28**

Present Status of This Research.—While it was possible to generate the cyclobutadienes A, A′, and B, the present examples were found to dimerize. However, the compounds studied did not have the optimum substituents X and Y for push–pull stabilization, and conditions for the final step in cyclobutadiene generation were not favorable for preservation of products with limited stability. Further studies to overcome these barriers are in progress.

Experimental Section

Irradiation of 2-Methoxy-1,4-naphthoquinone with *N,N*-Diethylcarbomethoxyethynylamine.—A solution of the quinone[10] (1.0 g, 5.32 mmol) and the carbomethoxy ynamine[17] (1.00 g, 6.40 mmol), in 125 ml of dry acetonitrile, was saturated with nitrogen and irradiated for 3.5 hr employing a Pyrex filter. The brown solution was vacuum evaporated to a black gum which crystallized. Chromatography of the mixture on a 1.5 × 23 cm

(17) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4406 (1968).

column of Anasil in dichloromethane gave a yellow band at the solvent front. Evaporation under vacuum and recrystallization from benzene–hexane gave 1.1 g (58%) of orange crystals (**3**): mp 120–121°; uv max (95% C_2H_5OH) 232, 270, and 288 mμ; ir (KBr) 2940, 1690, 1620, and 1450 cm^{-1}; nmr ($CDCl_3$) δ 1.10 (t, 6 H), 3.43 (s, 3 H), 3.60 (q, 4 H), 3.62 (s, 3 H), 3.98 (s, 1 H), and 7.9 (m, 4 H).

Anal. Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 66.64; H, 6.07; N, 4.35.

A reaction employing a filter transmitting wavelengths greater than 400 mμ, in place of the Pyrex filter, gave back predominantly starting material after 4 hr of irradiation.

Irradiation of 2-Methoxy-1,4-naphthoquinone with *N,N*-Diethylcyanoethynylamine.—A solution of 2-methoxynaphthoquinone (1.0 g, 5.32 mmol) and freshly distilled cyano ynamine[18] (1.16 g, 9.5 mmol) in 125 ml of dry acetonitrile was saturated with nitrogen. The system was irradiated for 2.75 hr using a Pyrex filter. The red solution was vacuum evaporated to a red syrup, which was chromatographed on a column of Anasil. Elution with dichloromethane gave 1.20 g (69.5%) of orange crystals (**5**) which were recrystallized from benzene–hexane: mp 139–140°; uv max (95% C_2H_5OH) 235, 263, and 305 mμ (shoulder); ir (KBr) 2965, 2930, 2190, 1690, 1650, 1590, and 1450 cm^{-1}; nmr ($CDCl_3$) δ 1.12 (t, 6 H), 3.43 (s, 3 H), 3.40 (broad q, 4 H), 3.98 (s, 1 H), and 8.0 (m, 4 H).

Anal. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03. Found: C, 69.94; H, 5.95; N, 9.21.

Continued elution with ether gave a 1:1 adduct which was rechromatographed yielding 0.042 g (2.5%) of purple solid (**6**): mp 64–67°; uv max (95% C_2H_5OH) 208, 242, 248, 279, 310, and 515 mμ; ir (KBr) 2965, 2935, 2190, 1650, 1600, 1550, and 1425 cm^{-1}; nmr ($CDCl_3$) δ 1.33 (t, 6 H), 3.58 (q, 4 H), 4.20 (s, 3 H), 7.10 (s, 1 H), and 7.9 (m, 4 H).

Irradiation of 2-Methoxy-1,4-naphthoquinone with *N,N*-Diethylphenylethynylamine.—Irradiation through Pyrex, for 2.75 hr, of a solution of 2-methoxynaphthoquinone (1.00 g, 5.32 mmol) and the phenyl ynamine[19] (1.00 g, 5.79 mmol), in 125 ml of acetonitrile, yielded an orange-brown solid upon vacuum evaporation of the solvent. Chromatography on Anasil in dichloromethane gave a fast-running, yellow-orange band (however, the crystals of this compound decomposed upon recrystallization from benzene–hexane or other solvents; no stable adduct could be isolated): nmr ($CDCl_3$) δ 1.10 (split t, 6 H), 3.34 (superimposed q, five-line pattern, 4 H), 3.70 (s, 3 H), 3.86 (s, 1 H), 7.30 (s, 5 H), and 7.42 (m, 4 H).

Irradiation of 2-Acetoxy-1,4-napthoquinone with *N,N*-Diethylcarbomethoxyethynylamine.—A solution of freshly distilled ynamine (3.0 g, 0.0193 mol) and 2-acetoxynaphthoquinone (2.0 g, 9.0 mmol), in dry acetonitrile, was irradiated for 21 hr using a Corex filter. Chromatography on Anasil in toluene–ether (4:1) eluted starting quinone, followed closely by a pink fraction which crystallized upon evaporation. Recrystallization from ethyl acetate gave 0.121 g (3.5%) of **11**: mp 184.5–185.5°; uv max (95% C_2H_5OH) 214, 269, and 306 mμ, in base 246 mμ (shoulder); ir (KBr) 3450, 2910, 2740, 1760, 1660, 1620, 1590, 1575, and 1520 cm^{-1}; nmr ($CDCl_3$) δ 1.32 (t, 6 H), 2.52 (s, 3 H), 3.66 (q, 4 H), 4.00 (s, 3 H), 7.8 (m, 4 H), and 11.80 (s, 1 H).

Anal. Calcd for $C_{20}H_{21}NO_6$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.86; H, 5.68; N, 3.87.

Continued elution with ether–ethanol (10%) gave a brown gum which crystallized after continued scratching. Recrystallization from ether yielded 73 mg (2.1%) of **10**: mp 143–143.5°; uv max (95% C_2H_5OH) 227, 263, and 286 mμ; ir (KBr) 2960, 1752, 1695, 1670, 1630, 1600, and 1460 cm^{-1}; nmr (CCl_4) δ 1.10 (t, 6 H), 2.17 (s, 3 H), 3.58 (s) and 3.63 (q) (total 8 H), and 7.83 (m, 4 H).

Anal. Calcd for $C_{20}H_{21}NO_6$: C, 64.68; H, 5.70; N, 3.77. Found: C, 64.73; H, 5.64; N, 3.77.

Irradiation of 2-Acetoxy-1,4-naphthoquinone with *N,N*-Diethylcyanoethynylamine.—Irradiation of the quinone (1.25 g, 5.8 mmol) with the cyano ynamine (1.25 g, 0.010 mol), in acetonitrile through Corex optics for 19.5 hr, gave 52 mg (2.6%) of the cyclobutene **12**: mp 178°; uv max (95% C_2H_5OH) 229 and 260 mμ; ir (KBr) 2950, 2180, 1732, 1690, 1648, 1595, and 1450 cm^{-1}; nmr ($CDCl_3$) δ 1.20 (t, 6 H), 2.25 (s, 3 H), 3.50 (q, 4 H), 3.90 (s, 1 H), and 8.18 (m, 4 H).

Anal. Calcd for $C_{19}H_{18}N_2O_4$: C, 67.44; H, 5.36; N, 8.28. Found: C, 67.36; H, 5.49.

Chromatography of the reaction mixture on Anasil in dichloromethane and dichloromethane–ethanol (5%) recovered a large amount of starting quinone.

Irradiation of 2-Acetoxy-1,4-naphthoquinone with *N,N*-Diethylphenylethynylamine.—Irradiation of the quinone (2.00 g, 9.25 mmol) with the phenyl ynamine (1.46 g, 8.44 mmol), in acetonitrile through Corex optics for 19.5 hr, gave 41 mg (1.2%) of the cyclobutene **13**. Separation of the reaction mixture on silica gel in toluene–20% ether gave a fast-running brown oil which was rechromatographed in toluene on Anasil. The initial orange oil was crystallized from ether and hexane, yielding red diamonds of **13**: mp 163.5–164°; uv max (95% C_2H_5OH) 227, 263, and 300 mμ; ir (KBr) 1735, 1690, 1678, 1640, 1595, and 1422 cm^{-1}; nmr ($CDCl_3$) δ 0.99 (t, 6 H), 2.20 (s, 3 H), 3.30 (q, 4 H), 4.00 (s, 1 H), 7.22 (s, 5 H), and 7.85 (m, 4 H).

Anal. Calcd for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.60. Found: C, 73.72; H, 6.21; N, 3.57.

Irradiation of 2-Ethylthio-1,4-naphthoquinone with *N,N*-Diethylcarbomethoxyethynylamine.—Irradiation of the quinone[20] (2.18 g, 10.0 mmol) and the ynamine (2.00 g, 12.9 mmol) through Corex optics for 6 hr in acetonitrile gave a sanguine solution which was vacuum evaporated and chromatographed on silica gel in dichloromethane. Starting quinone (0.445 g), a purple band, and a brown fraction were eluted (5% ethanol). Slow crystallization of the purple fraction from ethanol gave the yellow 1:1 adduct **21** and purple crystals, 0.225 g (6.5%), which were identified as the thiophene-fused naphthoquinone (**22**): mp 158–160°; uv max (95% C_2H_5OH) 241, 246, 308, and 348 mμ (shoulder); ir (KBr) 1725, 1660, 1628, 1510, 1450, 1434, 1325, 1275, and 1260 cm^{-1}; nmr ($CDCl_3$) δ 1.27 (t, 6 H), 3.48 (q, 4 H), 3.93 (s, 3 H), and 7.88 (m, 4 H); *m/e* 343.

Anal. Calcd for $C_{18}H_{17}NSO_4$: C, 62.95; H, 4.99; N, 4.08; S, 9.32. Found: C, 63.08; H, 5.14; N, 3.82; S, 9.49.

The yellow C_4 adduct **21**, which runs slightly behind the purple thiophene on tlc in benzene–dichloromethane, was isolated: 0.306 g (8.2%); mp 104.5–105.5°; uv max (95% C_2H_5OH) 231, 261, and 289 mμ; ir (KBr) 1690, 1628, 1600, and 1450 cm^{-1}; nmr ($CDCl_3$) δ 1.08 (t, 6 H), 1.28 (t, 3 H), 2.62 (q, 2 H), 3.63 (s, 3 H), 3.70 (eight-line pattern, 4 H), 3.99 (s, 1 H), and 7.85 (m, 4 H).

Anal. Calcd for $C_{20}H_{23}NSO_4$: C, 64.33; H, 6.21; N, 3.75; S, 8.57. Found: C, 64.27; H, 6.21; N, 3.58; S, 8.63.

Crystallization of the brown fraction from ethanol gave a second yellow crystalline product. Photolysis of the C_4 adduct **21** above, in acetonitrile for 2 hr through Pyrex, gave this product exclusively as seen by tlc: nmr ($CDCl_3$) δ 0.60 (t, 2 H), 1.08 (m, 6 H), 1.45 (t, 2 H), 3.3 (m, 6 H), 6.64 (s, 1 H), 7.20 (s, 4 H), and 7.68 (m, 4 H).

Reaction of 2-Ethylthio-1,4-naphthoquinone and *N,N*-Diethylcarbomethoxyethynylamine without Light.—Stirring an acetonitrile solution of the quinone (1.00 g, 4.6 mmol) and the ynamine (1.0 g, 6.45 mmol) overnight, and chromatographing the solvent-free mixture on silica gel plates in dichloromethane, yielded 99 mg (6.3%) of the thiophene adduct **22**. Tlc and spectral data match the information given previously; no C_4 adduct could be isolated.

Irradiation of 2-Ethylthio-1,4-naphthoquinone and *N,N*-Diethylphenylethynylamine.—Irradiation of a solution of the quinone (1.5 g, 6.9 mmol) and the phenyl ynamine (2.0 g, 11.6 mmol), in acetonitrile for 4.5 hr, was carried out through Vycor optics. Chromatography of the vacuum-evaporated mixture on Anasil in dichloromethane gave 0.137 g (5.5%) of the purple thiophene **24**, the C_4 adduct as a yellow gum, and 0.034 g (1.5%) of a yellow compound, at the origin, which was derived from photolysis of the C_4 adduct.

The purple thiophene **24** was separated from starting quinone by chromatographing on silica gel in petroleum ether (bp 30–60°)–benzene (60:40): mp 155–156°; uv max (95% C_2H_5OH) 227, 245, 285, 313, and 347 mμ (shoulder); ir (KBr) 1660, 1620, 1588, 1493, 1440, 1330, 1275, and 1260 cm^{-1}; nmr ($CDCl_3$) δ 1.05 (t, 6 H), 3.15 (q, 4 H), 7.39 (s, 5 H), and 7.83 (m, 4 H).

Anal. Calcd for $C_{22}H_{19}NSO_2$: C, 73.11; H, 5.30; N, 3.88; S, 8.85. Found: C, 72.90; H, 5.56; N, 3.60; S, 9.10.

The yellow C_4 adduct was identified by its nmr spectrum. However, it decomposed at a moderate rate so that its purity was always in question: ir (KBr) 1635, 1600, 1575, 1450, 1105, 760,

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752, 717, 695, and 658 cm^{-1}; nmr ($CDCl_3$) δ 1.12 (broad t, 8 H), 3.38 (borad q, 5 H), 3.72 (s, 1 H), 7.31 (s, 5 H), 7.40 (s, 3 H), 7.67 (m, 1 H), and 8.1 (m, 1 H).

The yellow crystals derived by ethanol crystallization from the origin region of the chromatograms were also prepared by photolyzing the C_4 adduct through Vycor for 2 hr in acetonitrile: mp 150–153°; uv max (95% C_2H_5OH) 220, 229 (shoulder), 256, 275, 290, 301, and 380 mμ; ir (KBr) 1628, 1590, 1570, 1530, 1515, and 1440 cm^{-1}.

Reaction of 2-Ethylthio-1,4-naphthoquinone and *N,N*-Diethylphenylethynylamine without Light (Formation of Cyclobutadienoid Dimers 26 and 27).—Stirring the quinone (1.0 g, 4.6 mmol) with the phenyl ynamine (1.0 g, 5.8 mmol), in 20 ml of acetonitrile overnight, yielded 0.079 g (4.75%) of the purple thiophene **24**, upon chromatography in dichloromethane on silica gel plates. Spectral ir and nmr matches were obtained with this adduct and the photochemical product.

Also isolated from this reaction were two isomeric compounds of lower R_f. These isomers were initially isolated as a broad band on chromatography, and were rechromatographed. This purification step resolved the mixture to a single orange band of R_f 0.5. Slow crystallization from ethanol yielded yellow and red crystals; separation with tweezers and recrystallization from ethanol yielded 119 mg (7.8%) of the red (**27**) and 131 mg (8.6%) of the yellow isomer (**26**).

Yellow isomer **26** had mp 197–198°; uv max (95% C_2H_5OH) 222, 237, 299, 307, and 352 mμ, in acid or base; ir (KBr) 1685, 1640, 1600, 1585, 1560, and 1465 cm^{-1}; nmr ($CDCl_3$) δ 1.00 (five-line pattern of two triplets, 6 H), 2.90 (q, 2 H), 3.76 (q, 2 H), 4.52 (s, 1.5 H), 7.33 (s, 5 H), and 7.67 (s, 4 H); mass spectrum *m/e* 662 and 331.

Anal. Calcd for $C_{44}H_{42}N_2O_4$: C, 79.73; H, 6.39; N, 4.23; S, 0.00. Found: C, 79.43; H, 6.24; N, 4.10; S, 0.00.

Red isomer **27** had mp 197–198°; uv max (95% C_2H_5OH) 222, 238, 297, 307, and 356 mμ, in acid or base; ir (KBr) 1680, 1640, 1600, 1585, 1560, and 1465 cm^{-1}; nmr ($CDCl_3$) δ 1.20 (q, from two triplets, 6 H), 3.10 (q, 2 H), 4.00 (m, 2 H), 4.59 (s, 1.5 H), 7.24 (s, 5 H), and 7.7 (m, 4 H); mass spectrum *m/e* 662 and 331.

Anal. Calcd for $C_{44}H_{42}N_2O_4$: C, 79.73; H, 6.39; N, 4.23; S, 0.00. Found: C, 79.70; H, 6.18; N, 4.15; S, 0.00.

Reaction of Cyclobutadienoid Dimer 27 with Sodium Hydride and Subsequently Acetic Anhydride.—Treatment of the red isomer **27** (30 mg) with washed sodium hydride, in dimethoxyethane for 6 hr, gave a deep, blue-green solution. The suspension was filtered and the blue-green color was dispelled by the addition of a few drops of acetic anhydride. The solvent was evaporated and the residue was taken up in water and extracted with ether. Drying and evaporation of the ether gave 9 mg (28%) of a white, gummy material which slowly crystallized: mp >270°; uv max (95% C_2H_5OH) 253 mμ; ir (KBr) 1720, 1640, 1555, and 1450 cm^{-1}.

Reaction of Cyclobutadienoid Dimer 26 with Sodium Hydride and Subsequently Ammonium Chloride Solution.—Treatment of a filtered solution of the blue anion, derived as above from the yellow isomer **26**, with a few drops of saturated ammonium chloride solution gave immediate discoloration. The solution was extracted with ether and evaporated to a white, amorphours gum: ir (KBr) 3300, 1665, 1640, 1590, and 1445 cm^{-1}.

Irradiation of 2-Ethylthio-1,4-naphthoquinone with *N,N*-Diethylcyanoethynylamine.—Irradiation of the quinone (1.00 g, 4.6 mmol) with the cyano ynamine (1.00 g, 8.2 mmol), in acetonitrile, was carried out through Corex. The resulting solution was vacuum evaporated and chromatographed on silica gel plates in dichloromethane. The purple thiophene **23** was isolated, 0.080 g (5.6%), and was the only identifiable product: mp 195–196°; uv max (95% C_2H_5OH) 243, 246, 307, and 333 mμ (shoulder); ir (KBr) 2210, 1668, 1640, 1592, 1528, 1468, 1455, 1332, and 1265 cm^{-1}; nmr ($CDCl_3$) δ 1.43 (t, 6 H), 3.72 (m, 4 H), and 7.89 (m, 4 H).

Anal. Calcd for $C_{17}H_{14}N_2SO_2$: C, 65.78; H, 4.55; N, 9.03; S, 10.33. Found: C, 65.63; H, 4.78; N, 8.80; S, 10.59.

Reaction of 2-Ethylthio-1,4-naphthoquinone with *N,N*-Diethylpropynylamine without Light.—Stirring a solution of 2-thioethylnaphthoquinone (1.00 g, 4.6 mmol) and the methyl ynamine[21] (1.00 g, 9.0 mmol), in acetonitrile overnight, and chromatographing the solvent-free mixture on silica gel plates, gave 41 mg (3%) of the purple thiophene **25**: uv max (95% C_2H_5OH) 242, 247, 285, 305, and 345 mμ (shoulder); ir (KBr) 1660, 1625, 1588, 1440, 1330, and 1260 cm^{-1}; nmr ($CDCl_3$) δ 1.18 (t, 6 H), 2.47 (s, 3 H), 3.25 (q, 4 H), and 7.98 (m, 4 H).

Reaction of 1,4-Naphthoquinone with *N,N*-Diethylphenylethynylamine without Light.—Vacuum evaporation of the reaction mixture of naphthoquinone (1.00 g, 6.34 mmol) with the phenyl ynamine (1.00 g, 5.8 mmol), which had been stirred in acetonitrile for 24 hr in the dark, produced a dark, amorphous solid. Chromatography on silica gel plates in dichloromethane–ethanol (1%) produced three orange bands; no naphthoquinone remained.

The region of R_f 0.6 was crystallized from ethanol, after rechromatography, and was identified as the mixture of dimeric adducts **26** and **27** previously isolated from the 2-thioethylnaphthoquinone–phenyl ynamine reaction, 26 mg (1.3%). Spectral matches (nmr, ir, and uv) and a tlc match in dichloromethane on silica gel were obtained with **26** and **27**.

A combination of naphthoquinone with the carbomethoxy ynamine gave no isolatable adducts as seen by tlc. It should be noted that difficulty was encountered in the purification of both of these reaction mixtures, since decomposition occurred rapidly while the mixtures were in solution.

Reaction of 1,4-Naphthoquinone with *N,N*-Diethylpropynylamine.—To a solution of naphthoquinone (1.00 g, 6.34 mmol), in 20 ml of acetonitrile, was added the methyl ynamine (0.98 g, 8.8 mmol). The solution was shaken without irradiation for 20 hr. Chromatography on a column of Anasil in dichloromethane, with some added ethanol, gave a yellow solid **19**, 0.105 g, which was recrystallized from ethyl acetate: mp 186–186.5° dec; uv max (95% C_2H_5OH) 240, 255, 301, and 362 mμ; ir (KBr) 1690, 1620, 1595, 1575, and 1535 cm^{-1}; nmr (DMSO) δ 0.78, 0.87 (overlapping s and t, total 8 H), 1.77 (s, 1 H), 2.48 (s, 1 H), 3.0–4.0 (m, 3.5 H), 6.10 (s, 1 H), and 7.38 (m, 7 H).

Anal. Calcd for $C_{27}H_{23}NO_4$: C, 75.86; H, 5.90; N, 3.28. Found: C, 75.73; H, 6.11; N, 2.98.

Preparation of 2-Methylcarbono-1,4-naphthoquinone (16).—An ether solution of methyl chloroformate (4.9 g, 0.0518 mol) was added dropwise to a well-agitated solution of 2-hydroxynaphthoquinone (9.0 g, 0.0518 mol) in 4 g of pyridine and 50 ml of ether in an ice bath. The mixture was stirred overnight. Dichloromethane (150 ml) was added and the suspension was vacuum filtered. The residue was washed with small portions of dichloromethane until the washes were colorless. The orange solution was vacuum evaporated to a yellow solid, which was chromatographed on Florisil in dichloromethane, yielding 9.5 g (79%) of product **16**: mp 95°; uv max (95% C_2H_5OH) 247, 253, 262, 338, and 351 mμ; ir (KBr) 1768, 1678, 1662, 1640, 1590, and 1449 cm^{-1}; nmr ($CDCl_3$) δ 3.96 (s, 3 H), 6.83 (s, 1 H), and 7.92 (m, 4 H).

Anal. Calcd for $C_{12}H_8O_5$: C, 62.07; H, 3.47. Found: C, 62.32; H, 3.55.

Reaction of 2-Methylcarbono-1,4-naphthoquinone with *N,N*-Diethylphenylethynylamine.—Stirring a solution of the ynamine (1.00 g, 5.8 mmol) and the methylcarbonoquinone (1.00 g, 4.3 mmol), in 20 ml of acetonitrile, caused precipitation of clean, red plates after 2 hr. After 4 hr the mixture was chromatographed on Anasil in dichloromethane, yielding 1.36 g (78%) of red crystals of **16** which were recrystallized from ethyl acetate [in a second run a mixture of quinone (2.0 g) and ynamine (2.0 g) yielded 2.75 g of the adduct]: mp 173°; uv max (95% C_2H_5OH) 237, 245, 261, 301, and 345 mμ; ir (KBr) 1745, 1684, 1640, 1288, and 1250 cm^{-1}; nmr ($CDCl_3$) δ 0.98 (t, 6 H), 3.29 (q, 4 H), 3.82 (s, 3 H), 4.00 (s, 1 H), 7.21 (sharp m, 5 H), and 7.8 (m, 4 H).

Anal. Calcd for $C_{24}H_{23}NO_5$: C, 71.10; H, 5.72; N, 3.46. Found: C, 71.10; H, 5.81; N, 3.21.

Reaction of 2-Methylcarbono-1,4-naphthoquinone with *N,N*-Diethylcarbomethoxyethynylamine.—Stirring a solution of the ynamine (1.00 g, 6.45 mmol) and the methylcarbonoquinone (1.00 g, 4.3 mmol), in 20 ml of acetonitrile, yielded a dark solution after 6 hr. Chromatography of the mixture on Anasil in dichloromethane and recrystallization from ethyl acetate produced 0.510 g (30%) of the 1:1 adduct **14**: mp 145°; uv max (95% C_2H_5OH) 231, 264, and 287 mμ; ir (KBr) 1751, 1698, 1668, 1630, 1288, and 1258 cm^{-1}; nmr ($CDCl_3$) δ 1.12 (t, 6 H), 3.63 (s, 3 H), 3.82 (s, 3 H), 3.70 (m, 4 H), 3.89 (s, 1 H), and 7.9 (m, 4 H).

Anal. Calcd for $C_{20}H_{21}NO_7$: C, 62.01; H, 5.46; N, 3.62. Found: C, 62.17; H, 5.63; N, 3.46.

Elimination Conditions Employed with 2-*N,N*-Diethylamino-1-phenyl-2a,8a-dihydro-2a-methylcarbonocyclobuta[*b*]naphthalene-3,8-dione. (15).—The phenyl ynamine adduct was sublimed at

(21) Purchased from Fluka A. G., Buchs, Switzerland.

165° (0.03 mm) but pyrolized at 220° (0.25 mm) to a tar and a small amount or yellow gummy material that was carbonate-free in the ir.

Stirring a sample of this compound (**15**) in benzene with either acid ion exchange resin or sodium hydride for 18 hr gave no reaction (tlc and ir).

Addition of 1.00 g (2.47 mmol) of the adduct **15** to a suspension of benzene-washed sodium hydride in benzene (0.5 g), and refluxing the mixture for 6 hr, produced 0.137 g (17%) of a yellow dimeric adduct (**28**) after chromatography on silica gel plates in dichloromethane: mp 192–193°; uv max (95% C_2H_5OH) 225, 251, 290 (shoulder), 325, and 410 mμ; ir (KBr) 1700, 1540, 1190, and 1094 cm^{-1}; nmr ($CDCl_3$) δ 0.97 (t, 6 H), 3.08 (q, 4 H), and 7.17 and 7.52 (two m, total 9.5 H).

Anal. Calcd for $(C_{22}H_{19}NO_2)_2$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.43; H, 5.83; N, 4.01.

Registry No.—**1**, 17691-75-7; **2**, 2348-82-5; **3**, 36623-54-8; **4**, 26391-04-8; **5**, 36623-56-0; **6**, 36623-57-1; **7**, 4231-26-9; **8**, 4231-35-0; **9**, 1785-65-5; **10**, 36623-61-7; **11**, 36674-94-9; **12**, 36623-62-8; **13**, 36623-63-9; **14**, 36674-95-0; **15**, 36623-64-0; **16**, 36674-96-1; **17**, 130-15-4; **19**, 36623-65-1; **20**, 36623-66-2; **21**, 36623-67-3; **22**, 36623-68-4; **23**, 36623-69-5; **24**, 36623-70-8; **25**, 36623-71-9; **26**, 36674-97-2; **27**, 36623-72-0; **28**, 36674-98-3.

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Deamination of Nerylamine and Geranylamine[1]

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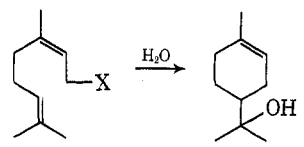
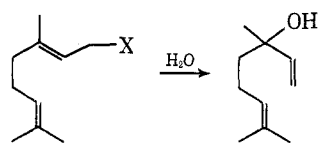
The products of deamination of nerylamine and geranylamine in water and acetic acid have been compared with the products of hydrolysis of neryl and geranyl chlorides, phosphates, and pyrophosphates. Deamination of nerylamine gives less cyclic products than hydrolysis of the neryl compounds, and deamination of geranylamine gives a much lower ratio of linalyl to geranyl products than do the corresponding hydrolyses. Alcohols as well as acetates are formed in the deamination in glacial acetic acid, and the product compositions suggest that ion pairs of the diazonium ions with hydroxide or acetate ions are reaction intermediates and that the substitution products can be formed either by ion-pair collapse or attack of an external nucleophile. Differences between the olefinic products of deamination and hydrolysis can also be explained in these terms.

The solvolysis of derivatives of nerol (I, X = OH) and geraniol (II, X = OH) have been studied extensively as models for cyclization and rearrangement in terpene biosynthesis. Neryl derivatives give largely cyclic products, *e.g.*, α-terpineol (III) and olefins



I III

related to it, whereas geranyl derivatives give largely linalool (IV) and olefins related to it.[2–5] These results



II IV

are readily understandable in that the configuration of nerol allows a carbonium ion derived from it or its derivatives to take up a conformation which favors cyclization, whereas a carbonium ion derived from geraniol has to rotate about the 2,3 double bond before it can cyclize to terpineol.[6] Phosphates,[3,4] alcohols,[4] and chlorides,[9] have been used in these experiments, and the product compositions are relatively insensitive to the solvent composition or the nature of the leaving group.

Carbonium ions are often invoked as intermediates in deaminations by nitrous acid which can be regarded as SN1 reactions of an unstable diazonium ion, but the products of such reactions are often very different from those of solvolyses, and a number of workers have speculated on the nature of the intermediates.[10–12] Deaminations of neryl and geranylamine (I, II, X = NH_2) were therefore examined, because of the possibility that a major change in the leaving group would markedly change the products.

Experimental Section

Materials.—Nerol and geraniol were obtained from Fluka, Chemical Samples Co. or Columbia Organics. Their purities were tested by glc, and samples having >95% overall purity and <0.1% of the other geometrical isomer were used. Preparation of geranyl chloride by reaction of the alcohol with PCl_3 or $SOCl_2$ has been reported,[13] but in our hands these methods gave mix-

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