358 (82), 211 (3), 187 (7), 186 (16), 185 (100), 179 (11), 118 (4), 167 (4), 140 (3).

Anal. Calcd for $C_{21}H_{14}O_2N_2S$: C, 70.37; H, 3.94; N, 7.82; S, 8.95. Found: C, 70.62; H, 3.82; N, 7.89; S, 8.72.

***N*-Phenylmaleimide Adducts of Naphtho[2,3-*c*]thiophene.**—Into a 250-ml flask was added 1,3-dihydronaphtho[2,3-*c*]thiophene 2-oxide (**10**, 1.0 g, 4.95 mmol), *N*-phenylmaleimide (0.86 g, 4.96 mmol), and 20 ml of acetic anhydride under dry nitrogen. The mixture was refluxed for 20 min. The yellow solution was cooled slightly and the excess acetic anhydride removed under reduced pressure to leave 1.80 g (101%) of a yellow crystalline solid. The separation of the isomeric adducts is detailed as follows.

Exo Adduct.—The yellow solid was recrystallized from acetonitrile to give 0.60 g (34%) of white solid. An analytical sample was obtained by recrystallization from chloroform–hexane: mp 281.5–282.5°; ir (KBr) 1765, 1700 (broad, imido C=O), 790 (m), 745 (s), 740 (sh), 690 cm^{-1} (m); nmr (DMSO-d_6) τ 2.2–3.05 (m, 11, aromatic), 4.89 (s, 2, bridgehead), 6.50 (s, 2, endo H); mass spectrum (70 eV; source 250°, probe 150°) *m/e* (rel intensity) 357 (9.7), 325 (3.1), 186 (5.9), 185 (13.8), 184 (100), 178 (10).

Anal. Calcd for $C_{22}H_{15}NO_2S$: C, 73.92; H, 4.23; N, 3.92; S, 8.97. Found: C, 73.89; H, 4.06; N, 3.73; S, 9.10.

Endo Adduct.—This isomer was separated by preparative thin layer chromatography on a 20 × 20 cm 1000-μ silica gel PF_{254} plates which had been activated 3 hr at 120°. Samples of 100 mg each, obtained in ether, were spread on the plates. Each plate was developed twice in 95% benzene–5% ethyl acetate in a presaturated chamber. Each plate was allowed to dry thoroughly between developments. The slower moving band from seven plates was scraped off and extracted with chloroform to yield 0.318 g of white solid. An analytical sample was obtained by recrystallization from ethanol: mp 214.5–215.5°; ir (KBr) 1775, 1700 (broad, imido C=O), 745 (s), 715 (s), 680 cm^{-1} (m); nmr ($CDCl_3$) τ 2.2–2.85, 2.9–3.3 (m, 9, aromatic), 3.8–4.15 (m, 2, H-1 and -4 on the naphthalene ring), 4.9 (m, 2, bridgehead), 5.8–6.0 (m, 2, exo hydrogens); mass spectrum (70 eV; source 275°, probe 110°) *m/e* 357 (9.3), 325 (2), 186 (6.4), 185 (13.7), 184 (100), 178 (6.4).

Anal. Found: C, 73.96; H, 4.23; N, 3.99; S, 9.05.

Registry No.—**4**, 28237-98-1; **5**, 28237-99-2; **6**, 28238-00-8; **7**, 28238-01-9; **8**, 28312-62-1; **10**, 28238-02-0; **11**, 28238-03-1; **12**, 28238-04-2; **13**, 28238-04-2.

Acknowledgment.—The authors wish to thank Messrs. Bruce Heitke and James C. Wisowaty for recording the nmr spectra and Mr. Robert Smith for recording the mass spectra.

The Aromatization of Some Cyclopropene Adducts. An Approach to the Naphtho[*b*]cyclopropene System

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1,3-Diphenylisobenzofuran (**4**) reacts with cyclopropene, 1-methylcyclopropene, and 1,2,3-triphenylcyclopropene to give the Diels–Alder adducts **5**, **16**, and **17**, all of which are the exo isomers. Attempted dehydration of **5** to 2,7-diphenylnaphtho[*b*]cyclopropene (**3**) could not be effected, although a variety of transformation products of **5** was isolated and identified. Several acid-catalyzed transformations of **16** and **17** were also studied. All evidence points to the nonintermediacy of **3** in the acid-catalyzed reactions of **5**.

Benzocyclopropene (**1**) is the most highly strained member of the benzocycloalkene series. Since 1964 the synthesis of the very reactive but isolable **1**[2a] and of a number of its substitution products[2b] has been reported. No example of any other condensed cyclopropane aromatic system exists in the literature.[3]

The work described in this paper had as its main goal the synthesis of a derivative of naphtho[*b*]cyclopropene (**2**), a system in which the central ring might be expected to show a high degree of bond fixation. 2,7-Diphenylnaphtho[*b*]cyclopropene (**3**) was chosen as a convenient synthetic objective, since it appeared to be readily accessible by the Diels–Alder addition of cyclopropene to 1,3-diphenylisobenzofuran (**4**), followed by acid-catalyzed dehydration of the resulting adduct **5**. The corresponding naphtho[*b*]cyclobutene derivative **6** has indeed been synthesized from cyclobutene by an exactly analogous route.[4]

Results and Discussion

Cyclopropene was found to add to 1,3-diphenylisobenzofuran (**4**) to give a single crystalline adduct, mp 95–96°. This adduct was assigned the structure of the exo isomer **5** on the basis of its nmr spectrum, which indicated considerable deshielding of one of the two cyclopropane methylene protons (δ ~1.75 and ~1.15) by the oxido bridge.[5,6]

Reaction of adduct **5** with hydrogen chloride in benzene at room temperature led to a good yield of 1,4-diphenyl-2-chloromethylnaphthalene (**7**), no other product being detectable by tlc. The formation of chloride **7** could be explained as involving the formation of the desired cyclopropene **3** as a transient intermediate, followed by ring opening of **3** by hydrogen chloride. On the other hand, **3** might never be formed and formation of **7** could proceed by way of direct nucleophilic attack of chloride ion on the methylene of the cyclopropyl carbinyl cation **8**.

In an attempt to dehydrate **5** under milder conditions, it was heated in chloroform solution in the presence of a cation exchange resin (Dowex 50W X-2), which was later found to contain some chloride ion. The minor reaction product (16%) was again chloride **7**, but the

(1) Author to whom correspondence should be directed.

(2) (a) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965). (b) R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 525 (1964); G. L. Closs, *Advan. Alicycl. Chem.*, **1**, 64 (1966); G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967); E. Vogel, S. Korte, W. Grimme, and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **7**, 289 (1968).

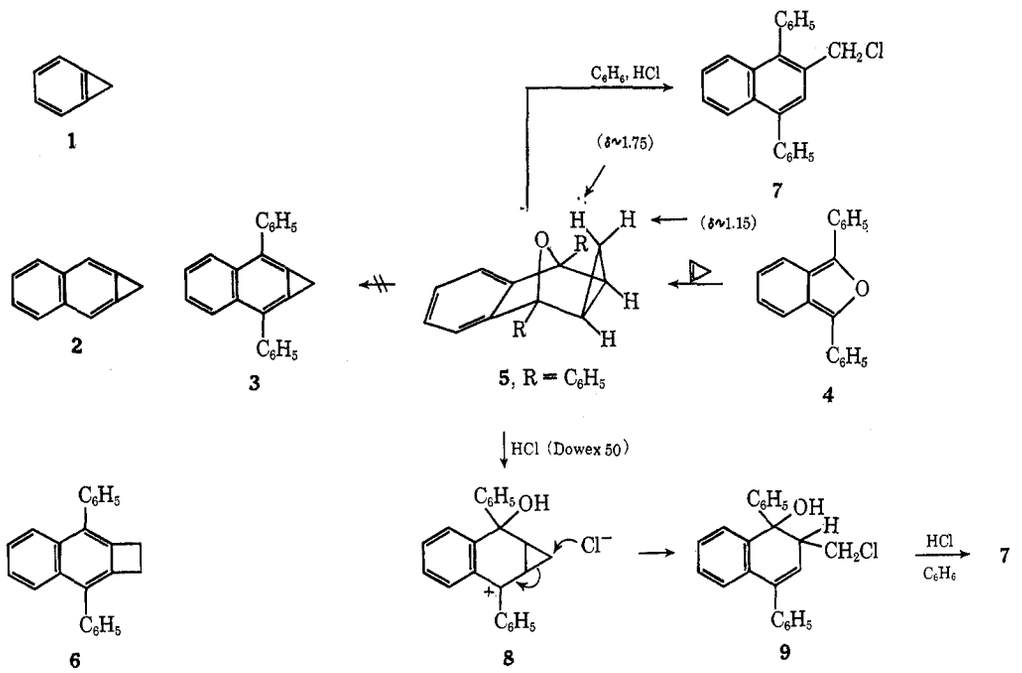
(3) A compound originally believed to be a keto tautomer of a naphtho[*b*]cyclopropenediol was subsequently shown not to contain a three-membered ring: L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, **53**, 4080 (1931); A. R. Bader and M. G. Ettlinger, *ibid.*, **75**, 730 (1953).

(4) C. D. Nenitzescu, M. Avram, I. G. Dinulescu, and G. Mateescu, *Justus Liebigs Ann. Chem.*, **653**, 79 (1962).

(5) M. P. Cava and F. M. Scheel, *J. Org. Chem.*, **32**, 1304 (1967).

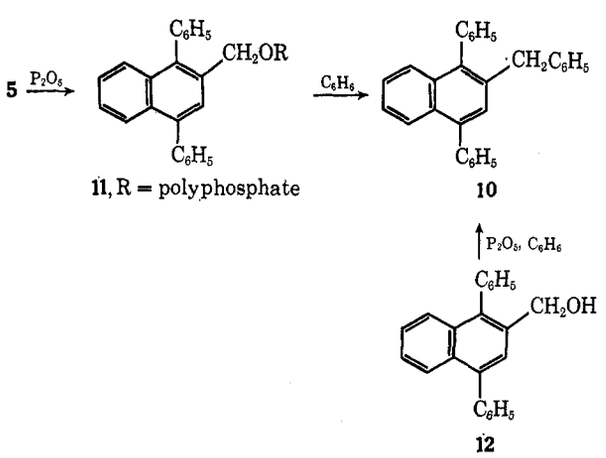
(6) Other investigators have mentioned in the footnote of a recent paper that they have synthesized adduct **5**: M. A. Battiste and C. T. Sprouse, Jr., *Tetrahedron Lett.*, 3165 (1969).

SCHEME I

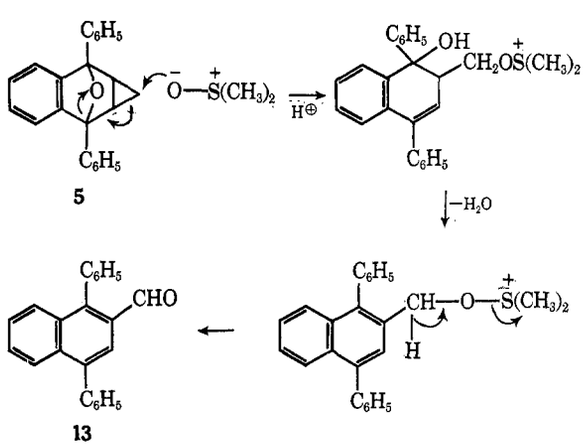


major reaction product (70%) was a compound which was assigned the chlorohydrin structure **9** on the basis of mass spectral, nmr, and analytical data. In accord with structure **9**, the mass spectrum of the compound showed significant peaks due to the loss of either water or hydrogen chloride. Its nmr spectrum showed an exchangeable hydroxyl proton at δ 2.35 and a single olefinic proton doublet (J = 2.5 Hz) at δ 6.15, as well as aromatic protons and a three-proton multiplet in the region δ 3.45–3.65. As anticipated, **9** reacted immediately with hydrogen chloride in benzene to give the fully aromatic halide **7**. The isolation of chlorohydrin **9** in this experiment strongly suggests that the naphthocyclopropene **3** is in fact not an intermediate in the conversion of adduct **5** to the benzylic chloride **7** (Scheme I).

The reaction of adduct **5** with phosphorus pentoxide in benzene afforded a single product which was assigned the structure of 1,4-diphenyl-2-benzylnaphthalene (**10**) on the basis of mass spectral, nmr, and analytical data. The initial naphthalenic reaction product is probably a polyphosphate ester **11** of the benzyl alcohol **12**, which then attacks the solvent in a Friedel–Crafts alkylation process. In accord with this scheme, the known alcohol **12** was found to give hydrocarbon **10** on reaction with phosphorus pentoxide in benzene.



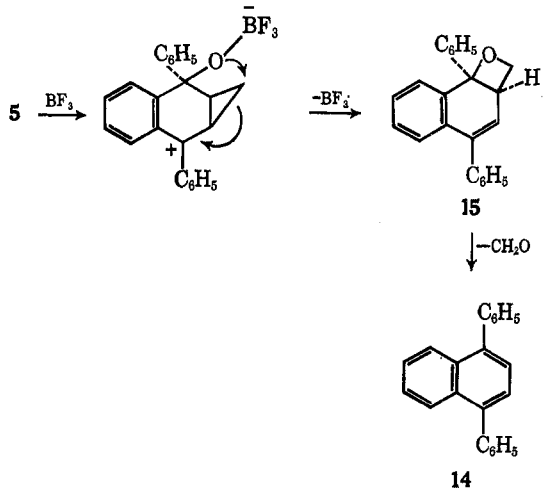
In an attempt to dehydrate **5** thermally under neutral conditions, the adduct was heated for a short time to 180° in dimethyl sulfoxide solution. The sole reaction product isolated (42% yield) was the known 1,4-diphenylnaphthalene-2-carboxaldehyde (**13**). The key step in the formation of **13** would appear to be a nucleophilic opening of the cyclopropane ring of **5** by the sulfoxide oxygen as shown below. Related ring-opening reactions of three-membered heterocycles by dimethyl sulfoxide have been recorded.[7]



Still different results were obtained when adduct **5** was treated with boron trifluoride etherate in ether solution. In addition to an unidentified product of molecular weight 392, 1,4-diphenylnaphthalene (**14**) was isolated. The unexpected formation of **14** may be rationalized by a reaction path involving formation of an oxetane intermediate **15** which aromatized to a naph-

(7) T. Durst, *Advan. Org. Chem.*, **6**, 354 (1965).

thalene by loss of formaldehyde. It will be noted that the assigned exo configuration of **5** is required for this mechanism.

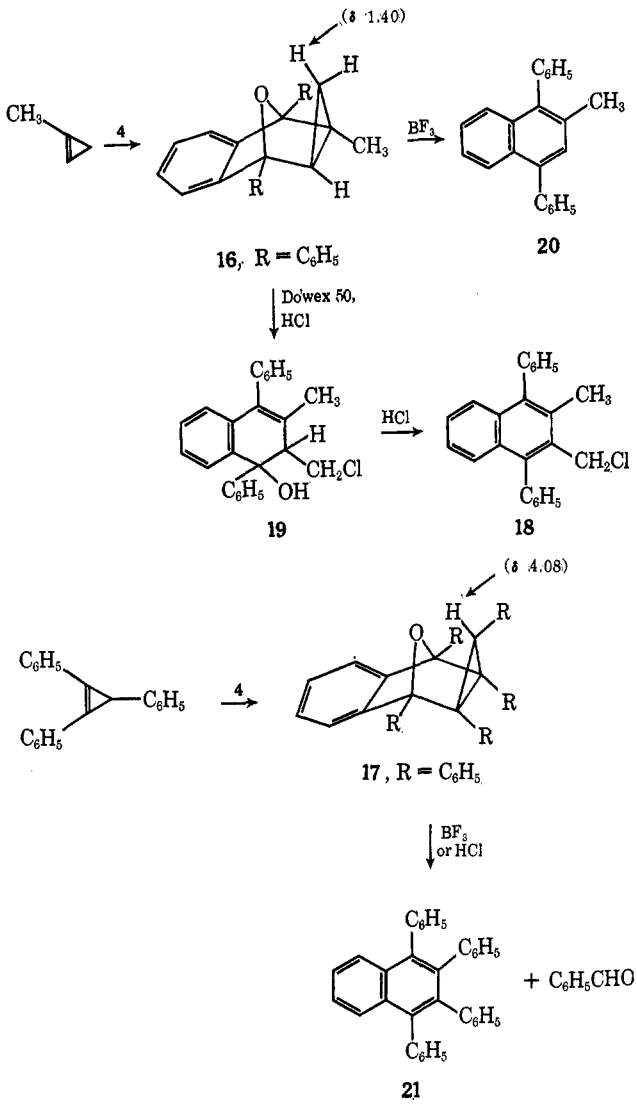


It seemed of interest to compare a few of the aromatization reactions of **5** with those of some related adducts which differ from **5** structurally in being incapable of giving a naphthocyclopropene by any direct dehydration process. In this connection, the adducts **16** and **17** were prepared from 1,3-diphenylisobenzofuran, 1-methylcyclopropene, and 1,2,3-triphenylcyclopropene, respectively. Although **16** was an oil, both **16** and **17** were homogeneous; they were assigned the exo configuration on the basis of their nmr spectra, both of which showed deshielding of one of the cyclopropane methylene protons by the oxido bridge.[5] The observed values for **16** (δ 1.40 and 1.00, J = 7 Hz) were comparable to the corresponding values for **5**; coupling of the proton at 1.40 with the *trans*-cyclopropane proton at the ring junction (δ 2.10, J = 2.5 Hz) was readily discernible. It should be pointed out, however, that these apparently obvious values were obtained by a first-order analysis, and they may not be entirely accurate. In the case of **17**, the deshielded proton appeared at δ 4.08, or 1.33 ppm further downfield than the aliphatic protons of the model compound *cis*-1,2,3-triphenylcyclopropane.[8-10]

Hydrogen chloride reacted with **16** in a manner strictly analogous to its reaction with the unmethylated adduct **5**. Thus, hydrogen chloride in benzene gave the naphthylmethyl chloride **18**; using Dowex 50 resin, the intermediate chlorohydrin **19** could be isolated. The reaction of boron trifluoride etherate with **16** was also similar to that of **5**; 1,4-diphenyl-2-methylnaphthalene (**20**) and an unidentified compound of mol wt 406 were isolated.

Adduct **17** underwent the expected fragmentation reaction in the presence of boron trifluoride etherate, affording 1,2,3,4-tetraphenylnaphthalene (**21**) in high yield. Hydrocarbon **21** was also formed from **17** by treatment with hydrochloric acid in acetic acid; in this experiment the second cleavage product, benzaldehyde, was also isolated in quantitative yield as its 2,4-dinitrophenylhydrazone (Scheme II).

SCHEME II



Conclusion

We conclude from the experiments described that the naphtho[*b*]cyclopropene derivative **3** is not formed, even as an intermediate, in any of the aromatization reactions of adduct **5** which we have studied.[11] The reaction of **5** with acidic reagents follows a course quite different from that of the corresponding adduct of **4** with cyclobutene, which affords the normal dehydration product **6**.

(8) R. Breslow and P. Dowd, *J. Amer. Chem. Soc.*, **85**, 2729 (1963).

(9) The tendency of cyclopropenes to give exo adducts with **4** was pointed out during our study in a paper in which some adducts of **4** with various chlorinated cyclopropenes were reported: R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970).

(10) For a very recent report of the formation of an exo adduct from **4** and 1,2-diphenylcyclopropene, see D. T. Longone and D. M. Stehouwer, *Tetrahedron Lett.*, 1017 (1970).

(11) After the completion of the manuscript of our paper, the following communication appeared [K. Geibel and J. Heindl, *ibid.*, 2133 (1970)] in which the reaction of cyclopropene with furan **4** was reported to give a 5.8:1 mixture of isomeric adducts, for which no physical data were given. The major adduct was converted by hydrochloric acid into compound **7** as in our study. The minor adduct was apparently obtained only in impure form and suffered ring cleavage (unlike the major adduct) simply on being passed through neutral alumina. Since our Diels–Alder products from cyclopropene and methylcyclopropene were purified by initial neutral alumina chromatography, it is apparent why we did not detect minor adducts from our reactions. Geibel and Heindl have assigned the endo configuration to their major stable adduct (our **5**) and the exo configuration to their minor unstable adduct. We believe that these assignments, for which no justification was given, must be reversed for reasons given in our discussion and in ref 9. (Note particularly in ref 9 the detection by nmr of a minor endo adduct, from **4** and chlorocyclopropene, which was too unstable to survive isolation by silica chromatography.)

Experimental Section

Melting points were taken with a Thomas-Hoover apparatus and are uncorrected. Nmr spectra were obtained in deuteriochloroform with a Varian A-60 nmr spectrometer. Infrared spectra were taken with a Perkin-Elmer Model 137 infrared spectrophotometer. Elemental analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind. Molecular weights of all new compounds were confirmed by mass spectrometry using a Perkin-Elmer Model 270 instrument.

Isolation in the usual manner refers to extraction with ether or the organic solvent mentioned, washing the organic extract with water, followed by drying over magnesium sulfate, and evaporation of solvent under reduced pressure. Preparative tlc was carried out using silica gel (EM Reagent GF-254) coated on 20 × 20 cm glass plates (1-mm thickness) with hexane as the developer unless otherwise stated. The zones were detected by ultraviolet light, collected, and extracted with chloroform containing 3% MeOH.

The identity of known compounds was established by a comparison of ir spectra and by mixture melting point determinations with authentic samples obtained according to literature references given.

Reaction of 1,3-Diphenylisobenzofuran (4) with Cyclopropene. Adduct 5.—A stream of cyclopropene in nitrogen, generated from sodium amide (12 g, 0.3 mol) and allyl chloride (25 g, 0.3 mol),[12] was passed through a trap cooled in Dry Ice and then led into a solution of 1,3-diphenylisobenzofuran (4.05 g, 0.015 mol) in 250 ml of benzene at 20°. After the fluorescence had disappeared (2 hr), the benzene solution was worked up in the usual manner and the residue was chromatographed over neutral alumina using benzene as the eluent. The resulting oil (3.1 g), which was homogeneous by tlc, crystallized from hexane (50 ml) to give adduct **5** as colorless plates (1.95 g), mp 93–94°. In another run **5** was obtained from the same solvent as prisms, mp 66–67°. The two products are dimorphous as shown by comparison of nmr and ir spectra: nmr δ 1.1 (m, 1 H), 1.7–1.8 (m, 3 H), 7.0 (t, 4 H), 7.3–7.4 (m, 6 H), and 7.7 (m, 4 H).

Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 89.27; H, 5.99.

Reaction of 5 with Hydrogen Chloride in Benzene.—Adduct **5** (50 mg) was dissolved in 10 ml of dry benzene, and the solution was saturated with dry hydrogen chloride and then stirred at room temperature for 10 hr. The benzene solution was worked up in the usual manner to give a residue (45 mg) which crystallized from hexane to give chloride **7** (33 mg, 62%), mp 115–117° (lit.[13] 123°). Tlc examination of the mother liquor revealed the absence of any other product.

Reaction of 5 with Phosphorus Pentoxide in Benzene. 1,4-Diphenyl-2-benzylnaphthalene (10).—Adduct **5** (50 mg) was dissolved in 10 ml of dry benzene, 100 mg of P_2O_5 was added, and the reaction mixture was stirred at room temperature for 10 hr. The dark brown reaction mixture was then decomposed with ice and the product was isolated in the usual manner after preparative tlc as colorless crystals (31 mg, 52%) of **10**: mp 125–126°; nmr δ 3.95 (s, 2 H), 7.1 (t, 4 H), 7.2 (s, 1 H), 7.4 (m, 13 H), and 7.8 (m, 1 H).

Anal. Calcd for $C_{25}H_{22}$: C, 94.01; H, 5.99. Found: C, 93.71; H, 5.98.

Hydrocarbon **10** was prepared independently by stirring a solution of 1,4-diphenylnaphthalene-2-methanol[13] (**12**, 200 mg) in benzene (10 ml) with phosphorus pentoxide (500 mg) at room temperature for 2.5 hr. Isolation in the usual manner (ether) followed by preparative tlc (hexane–benzene, 5:1) afforded **10** (0.110 g) as feathery needles, mp 126–127°, after crystallization from hexane.

Reaction of 5 with Cation Exchange Resin.—Adduct **5** (500 mg) was dissolved in 20 ml of chloroform, Dowex 50W X-2 cation exchange resin (1 g) was added, and the mixture was stirred at room temperature for 4 hr. The solution was filtered and the filtrate was evaporated. The residue was resolved by preparative tlc into 70 mg of **7** (14.7%) and 406 mg (70%) of **9**. Compound **9** was purified by recrystallization from benzene–hexane (1:1) to give colorless plates: mp 125–127° (320 mg); nmr δ 2.35 (s, 1 H), 3.45 (m, 2 H), 3.65 (d, J = 2.5 Hz, 1 H), 6.15 (d, J = 2.5 Hz, 1 H), 6.92 (m, 1 H), 7.1 (q, 4 H), and 7.3 (m, 10 H).

Only erratic carbon analyses for this compound were obtained, although it analyzed well for chlorine and its molecular weight was confirmed by mass spectrometry.

Anal. Calcd for $C_{23}H_{19}ClO$: Cl, 10.22. Found: Cl, 10.48.

Reaction of 9 with Hydrogen Chloride in Benzene.—Compound **9** (30 mg) was dissolved in 10 ml of dry benzene, and the solution was saturated with dry hydrogen chloride and then stirred at room temperature for 10 min. Isolation in the usual manner gave chloride **7** (12 mg, 47%). Tlc examination of the mother liquor showed the absence of any other product.

Reaction of 5 with Dimethyl Sulfoxide.—Adduct **5** (50 mg) was dissolved in 3 ml of dimethyl sulfoxide and the solution was maintained at mild reflux for 15 min. After dilution with water, the product was isolated in the usual manner followed by silica gel chromatography (benzene eluent). Crystallization from hexane gave 23 mg (42%) of 1,4-diphenyl-2-naphthaldehyde (**13**) as colorless crystals, mp 146–148 (lit.[14] mp 145–147°).

Reaction of 5 with Boron Trifluoride Etherate.—Adduct **5** (50 mg) was dissolved in 10 ml of dry ether, a few drops of freshly distilled BF_3 etherate were added, and the colorless solution was stirred at room temperature for 12 hr. The usual isolation, followed by careful separation by preparative tlc, gave the following products: (a) 1,4-diphenylnaphthalene (**14**) (11 mg), colorless needles (hexane), mp 135–136° (lit.[14] mp 135–137°); (b) unidentified compound of mol wt 392, prisms (20 mg) from hexane.

Reaction of Furan 4 with 1-Methylcyclopropene. Adduct 16.—1-Methylcyclopropene, generated by the reaction of methallyl chloride (12 g) and sodium amide (5 g),[15] was led into a solution of furan **4** (1.0 g) in 30 ml of benzene. After the fluorescence had disappeared (5 hr), the solvent was removed and the residue was purified by chromatography over neutral alumina. A viscous oil (homogeneous by tlc) was obtained which could not be crystallized. However, the compound could be purified by distillation [bath temperature 160–180° (6 mm)]. A pale yellow liquid (602 mg) was obtained: nmr δ 1.0 (d, J = 7 Hz, 1 H), 1.12 (s, 3 H), 1.4 (dd, J = 7 Hz, J = 2.5 Hz), 2.1 (t, J = 2.5 Hz), 7.0–7.3 (m, 10 H), and 7.5–7.8 (m, 4 H).

Anal. Calcd for $C_{24}H_{20}O$: C, 88.85; H, 6.21. Found: C, 89.13; H, 6.27.

Reaction of Adduct 16 with Hydrogen Chloride in Benzene.—Adduct **16** (200 mg) was dissolved in 30 ml of dry benzene. The solution was saturated with hydrogen chloride and stirring was continued at room temperature for 0.5 hr. Isolation in the usual manner gave 162 mg (77%) of crystalline product which was recrystallized from hexane: mp 164–165°; 129 mg; nmr δ 2.35 (s, 3 H), 4.58 (s, 2 H), 7.2–7.6 (m, 14 H).

Anal. Calcd for $C_{24}H_{19}Cl$: C, 84.10; H, 5.58; Cl, 10.34. Found: C, 83.85; H, 5.58; Cl, 10.27.

Reaction of Adduct 16 with Cation Exchange Resin.—Adduct **16** (95 mg) was dissolved in 20 ml of dry chloroform, Dowex 50W X-2 cation exchange resin (1 g) was added, and the mixture was refluxed with stirring for 5 hr. The solution was filtered and the filtrate was evaporated. The residue was separated by preparative tlc into 11 mg of chloride **18** (4.7%) and 32 mg of chlorohydrin **19** (14.4%). Recrystallization of compound **19** from hexane gave colorless prisms, mp 150–152°. Its nmr spectrum showed, in addition to aromatic protons (14 H) centered around δ 2.8 and a methyl (3 H, s) at 1.62, the following pattern due to the nonequivalent protons (H_A and H_B) of the chloromethyl group and a single proton (H_C) of the adjacent carbon: δ 4.12 (H_A, q), 3.66 (H_B, q), 3.10 (H_C, q), J_{AB} = 10 Hz, J_{AC} = 6 Hz and J_{BC} = 7.5 Hz. Since attempted recrystallization of **19** resulted in decomposition, a satisfactory sample could not be prepared for analysis, although mass spectrometry confirmed its molecular weight.

Reaction of Adduct 16 with Boron Trifluoride Etherate.—Adduct **16** (100 mg) was dissolved in 10 ml of dry ether, a few drops of BF_3 etherate were added, and the solution was stirred at room temperature overnight. Tlc separation led to the isolation of the following products: (a) 1,4-diphenyl-2-methylnaphthalene (**20**, 25 mg), colorless needles (hexane), mp 128–129° (lit.[16] 129°); (b) unidentified compound of mol wt 406 (14 mg).

Reaction of Furan 4 with 1,2,3-Triphenylcyclopropene. Adduct 17.—A solution of 1,2,3-triphenylcyclopropene[8] (1.00 g)

(12) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966).
(13) J. Robert, *C. R. Acad. Sci., Ser. C*, **223**, 906 (1946).
(14) A. Weiss, *Monatsh. Chem.*, **61**, 167 (1932).
(15) F. Fischer and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965).
(16) A. Etienne, A. Spire, and E. Toromanoff, *Bull Soc. Chim. Fr.*, 750 (1952).

and furan 4 (1.00 g) in benzene (10 ml) was refluxed for 5 hr. Crystallization from benzene–hexane yielded adduct **17** (1.50 g, 75%): mp 222–224° dec; nmr δ 4.1 (s, 1 H), 6.1–7.1 (m, 13 H), and 7.15–7.4 (m, 16 H).

Anal. Calcd for $C_{41}H_{30}O$: C, 91.41; H, 5.61. Found: C, 91.67; H, 5.90.

Reaction of Adduct 17 with Acetic Acid and Hydrochloric Acid.—Adduct **17** (100 mg) was dissolved in 2 ml of glacial acetic acid, two drops of concentrated hydrochloric acid were added, and the solution was heated under reflux for 3 hr. The solvent was removed *in vacuo* and the residue, which had a strong odor of benzaldehyde, was diluted with water. Isolation in the usual manner (ether) and separation by preparative tlc gave 1,2,3,4-tetraphenylnaphthalene (**21**), 64 mg (80%), mp 198–200°, identical with an authentic sample.

In another run, before extraction with ether, the reaction mixture was treated with 40 mg of 2,4-dinitrophenylhydrazine in ethanol solution. After stirring for 10 min, the precipitated hydrazone was filtered and washed with hexane to give 52 mg of 2,4-dinitrophenylhydrazone, mp 220–250°. Recrystallization from ethanol gave the pure derivative, mp 237–238°, identical with an authentic sample.

Registry No.—**5**, 28273-58-7; **9**, 28273-59-8; **10**, 28273-60-1; **16**, 28273-66-7; **17**, 28312-69-8; **18**, 28273-61-2; **19**, 28273-62-3.

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The Tricyclo[5.2.0.0^{2,5}]nonane System[1,2]

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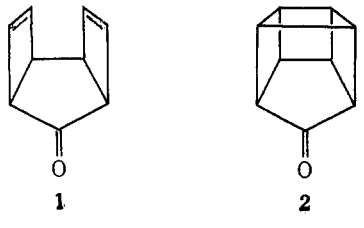
Received October 16, 1970

This paper describes the synthesis of *anti*-tricyclo[5.2.0.0^{2,5}]nonan-6-one (**6**), *syn*- and *anti*-tricyclo[5.2.0.0^{2,5}]-non-3-en-6-one (**4** and **5**), and *anti*-tricyclo[5.2.0.0^{2,5}]nona-3,8-dien-6-one (**21**), as well as some methylated derivatives of these tricyclic ketones. Irradiation of dienone **21** leads efficiently to homocubanone (**2**) *via* the syn dienone **1**. Some transformations of the above tricyclic ketones, especially the β,γ-unsaturated ketones, are discussed.

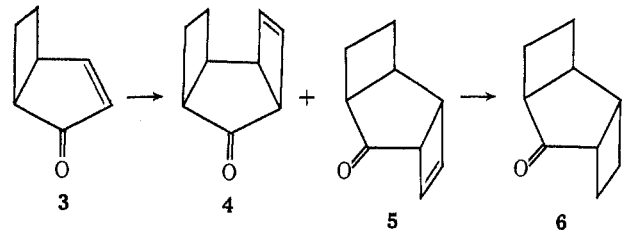
The obvious relationship of *syn*-tricyclo[5.2.0.0^{2,5}]-nona-3,8-dien-6-one (**1**) and homocubanone (**2**) led



1 **2**

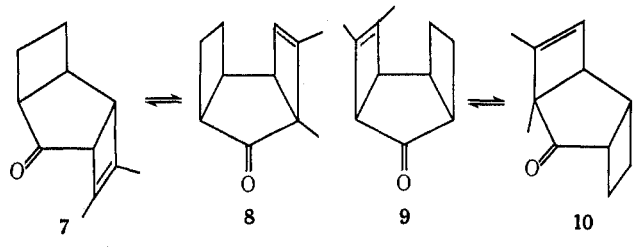
us to explore synthetic approaches to **1**. In this paper we report syntheses of several members of the tricyclo-[5.2.0.0^{2,5}]nonane family as well as some of the transformations of these compounds.[3] In particular, the details of an efficient synthesis of homocubanone from cyclopentenone (14% overall yield) are presented.

Irradiation of bicyclo[3.2.0]hept-3-en-2-one (**3**)[4] with 1,2-chloroethylene followed by ketalization of the cycloadducts, dehalogenation, and hydrolysis provided a mixture of tricyclic ketones **4** and **5**, ratio 2:98, in 75% overall yield.[5] The major isomer is assigned the anti configuration **5**, since cycloaddition should occur predominantly from the less hindered face of **3**. This assignment was confirmed by the identity of the hydrogenation product of the major enone and an authentic sample of *anti*-tricyclo[5.2.0.0^{2,5}]nonan-6-one (**6**) obtained as outlined later in this paper.



3 **4** **5** **6**

Photocycloaddition of ketone **3** and 2-butyne in methylene chloride produced a mixture of four isomeric tricyclic ketones **7**–**10** in 66% yield. The primary adducts **7** and **9** undergo subsequent photisomerization *via* the well-known allylic shift of carbonyl[6] to the isomeric ketones **8** and **10**, respectively. Separate irradiation of pure **7** and of pure **8** gave the same photostationary-state mixture containing 73% of **7** and 27% of **8**. Lack of material precluded similar experiments with **9** and **10**.



7 **8** **9** **10**

In contrast to the photoisomerizations of the substituted enones **7**–**10**, irradiation of the unsubstituted anti enone **5** in methylene chloride yielded the saturated

(1) Grateful acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) A preliminary report of a portion of this work has appeared: R. L. Cargill and T. Y. King, *Tetrahedron Lett.*, 409 (1970).

(3) The tricyclo[5.2.0.0^{2,5}]nonane system has previously been described by L. I. Smith, C. L. Agre, R. M. Leekley, and W. W. Prichard, *J. Amer. Chem. Soc.*, **61**, 7 (1939); R. Criegee, J. Dekker, and H. A. Brune, *Chem. Ber.*, **96**, 2368 (1963).

(4) R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *J. Amer. Chem. Soc.*, **92**, 3809 (1970).

(5) Spectroscopic data for all new compounds are presented in the Experimental Section.

(6) G. Büchi and E. M. Burgess, *J. Amer. Chem. Soc.*, **82**, 4333 (1960).