1380, 1090, 1030, 915, and 735 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 1.10 (3 H, s), 1.47 (3 H, s), 1.58 (3 H, s), 1.60 (3 H, s), 1.68 (3 H, s), 5.01 (1 H, br d, J = 8 Hz), 5.14 (2 H, br m), and 5.31 (1 H, br t, J = 6 Hz); ^1H NMR (benzene-d_6, 220 MHz) δ 1.15 (3 H, s), 1.34 (3 H, s), 1.49 (3 H, s), 1.61 (3 H, s), 1.69 (3 H, s), 4.86 (1 H, br m), 4.87 (1 H, br d, J = 8 Hz), 5.07 (1 H, br d, J = 8 Hz), and 5.26 (1 H, br t, J = 6 Hz); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 16.6, 17.7, 23.5, 24.4, 24.7, 25.7, 41.5, 68.8 (d), 76.6 (s), 124.4 (d), 131.7 (s), and 133.3 (s); MS m/e 288 ($M^+ - H_2O$), 273, 270, 255, 219, 207, 187, 177, 167, 147, 135, 121, 119, 109, 94, 83, 81, 79, 69, 55, 43, and 41; calculated for $C_{20}H_{32}O$ ($M^+ - H_2O$) 288.245, found 288.245.

Acetylation of Hydroxydilophol (1). A solution of 28 mg (0.096 mmol) of 1 and excess acetic anhydride in 2 mL of anhydrous pyridine was allowed to react at room temperature for 24 h. Approximately 2 mL of distilled water was added, and the mixture was extracted with three 5-mL portions of CCl_4. After drying with anhydrous $MgSO_4$, concentrating, and TLC in 5:5:1 hexane–dichloromethane–ethyl acetate, 10 mg (30%) of 3 was obtained as an oil: IR (CCl_4) ν_{max} 3600, 2950, 2870, 1730, 1450, 1380, 1250, 1220, 1025, 985, and 855 cm^{-1}; ^1H NMR (CCl_4) δ 1.06 (3 H, s), 1.56 (6 H, s), 1.61 (3 H, s), 1.68 (3 H, s), 1.99 (3 H, s), 4.79 (1 H, br d, J = 8 Hz), 4.89 (1 H, br dd, J = 14, 7 Hz), 5.08 (1 H, br t, J = 6 Hz), and 5.77 (1 H, br d, J = 8 Hz); MS m/e 288 (M^+ – AcOH), 270, 255, 227, 203, 185, 173, 161, 159, 147, 133, 119, 109, 105, 93, 91, 81, 79, 69, 55, 43, and 41.

Ozonolysis of Hydroxydilophol (1). Ozone was bubbled through a solution of 1 (170 mg, 0.56 mmol) in 20 mL of CH_2Cl_2 at −78 °C until the solution became blue. The solvent was removed in vacuo, the residue taken up in acetone, and Jones' reagent added until an orange color persisted. The solution was stirred an additional 10 min, then diluted with water and extracted with diethyl ether. The ether extract was dried with $MgSO_4$ and concentrated in vacuo to give a brown oil. Preparative silica gel TLC of this oil in ethyl acetate gave 20 mg of levulinic acid (31%) as a colorless oil. ^1H NMR, infrared, and mass spectra obtained from this product were identical with those obtained from a commercial sample.

Tetrahydrohydroxydilophol (4). A solution of 183 mg (0.598 mmol) of 1 in 10 mL of CH_3OH and 40 mg of 10% palladium on carbon catalyst, was stirred for 48 h under an atmosphere of hydrogen. The catalyst was filtered off and the solvent was removed in vacuo to yield a yellow oil which when purified by LC (μ-Porasil, 20% EtOAc–hexanes) gave 69 mg (37%) of the tetrahydro derivative 4 as a colorless oil: IR (CCl_4) ν_{max} 3380, 2960, 1470, 1380, 1105, 1020, 935, 910, and 850 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 0.86 (3 H, d, J = 7 Hz), 0.88 (3 H, d, J = 7 Hz), 1.00 (3 H, d, J = 7 Hz), 1.20 (3 H, s), 1.71 (3 H, s), 2.09 (1 H, br dd, J = 13, 6 Hz), 2.59 (1 H, dddd, J = 13, 13, 13, 4 Hz), 2.66 (1 H, br s, D_2O exch), 2.76 (1 H, br dd, J = 13, 13 Hz), 3.41 (1 H, br s, D_2O exch), 4.50 (1 H, br dd, J = 13, 6 Hz), and 5.17 (1 H, br dd, J = 13, 4 Hz); ^{13}C NMR ($CDCl_3$, 20 MHz) δ 19.9, 22.4, 22.5, 22.8, 23.8, 24.9, 25.9, 26.4, 27.2, 28.0, 36.5, 37.7, 38.1, 39.7, 40.2, 42.7, 69.6 (d), 77.1 (s), 127.9 (d), and 131.3 (s); MS m/e 310 (M^+), 292, 277, 274, 225, 207, 189, 179, 161, 149, 137, 121, 111, 109, 95, 81, 71, 69, 57, 55, 43, and 41.

Jones' Oxidation of Tetrahydrohydroxydilophol (4). Jones' reagent was cautiously added to an ice-cooled solution of 60 mg (0.194 mmol) of 4 in 5 mL of acetone until the orange color persisted. After stirring for an additional 15 min, the mixture was diluted with water and extracted with diethyl ether. The ether extract was dried (anhydrous $MgSO_4$) and reduced in vacuo to give the ketone 5 (84%) as a colorless oil: IR (CCl_4) ν_{max} 3350, 2960, 1700, 1540, 1460, 1370, and 980 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 0.87 (6 H, d, J = 6 Hz), 0.90 (3 H, d, J = 6 Hz), 1.16 (3 H, s), 1.89 (3 H, s), 2.17 (1 H, dddd, J = 12, 12, 12, 4 Hz), 2.40 (1 H, br s, D_2O exch), 2.82 (1 H, br d, J = 18 Hz), 3.14 (1 H, dd, J = 12, 3 Hz), 3.37 (1 H, br d, J = 18 Hz), and 5.38 (1 H, br dd, J = 12, 4 Hz); MS m/e 308 (M^+), 290, 275, 265, 237, 223, 205, 180, 155, 137, 123, 111, 109, 95, 81, 69, 55, 45, 43.

1,5-Dimethylcyclodecen-7-one (6). Two milliliters of an aqueous saturated Na_2CO_3 solution was combined with a solution of 5 (44 mg, 0.143 mmol) in 5 mL of methanol and stirred for 24 h. The solution was diluted with water and extracted with 3 × 5 mL portions of pentane. The combined pentane extracts were dried (anhydrous $MgSO_4$) and concentrated in vacuo to yield a colorless oil: IR (CCl_4) ν_{max} 2950, 1700, 1460, and 1125 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 0.88 (3 H, d, J = 6 Hz), 1.83 (3 H, s), 2.28 (1 H, dddd, J = 11, 11, 11, 5 Hz), 2.70 (1 H, br d, J = 17 Hz), 2.79 (1 H, ddd, J = 12, 12, 3 Hz), 3.47 (1 H, br d, J = 17 Hz), 5.36 (1 H, br dd, J = 11, 5 Hz); MS m/e 180 (M^+), 165, 149, 137, 121, 109, 105, 97, 95, 93, 81, 79, 69, 67, 55, 43, and 41.

Transannular Cyclization of 1. A solution of 1 (40 mg, 0.131 mmol) in 3 mL of dioxane was heated to reflux for 8 h. The dioxane was removed in vacuo and the residue was purified by preparative silica gel TLC (2:2:1, hexanes–CH_2Cl_2–EtOAc). Starting material (15 mg, 37%) was recovered, along with the diol 7 (12 mg, 30%) which illustrated the following spectral features: IR (CCl_4) ν_{max} 3450, 2940, 2870, 1450, 1370, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$, 220 MHz) δ 1.19 (3 H, s), 1.23 (3 H, s), 1.60 (3 H, s), 1.68 (6 H, s), 2.67 (1 H, br d, J = 8 Hz), 3.19 (1 H, br s, D_2O exch), 3.45 (1 H, br s, D_2O exch), 3.91 (1 H, br d, J = 8 Hz), 5.08 (1 H, t, J = 6 Hz), and 5.25 (1 H, br t, J = 6 Hz); MS m/e 306 (M^+), 288, 270, 237, 221, 203, 179, 161, 145, 135, 120, 109, 93, 81, 69, 55, 43, and 41.

Acknowledgments. This work is a result of research sponsored by NOAA, Office of Sea Grant, Department of Commerce, under Grant No. 04-7-158-44121. We are grateful for ship support funding from the National Science Foundation in support of our use of R/V E. B. SCRIPPS, which enabled our collection of *Dictyota masonii* at Isla Guadalupe, Mexico. We thank Dr. Jim Norris, Smithsonian Institution, for identifying *D. masonii* and for preparing voucher specimens for deposit in the National Herbarium. The UCSD NMR facility was supported by a grant from the National Institutes of Health (RR-708).

Registry No.—1, 69204-66-6; 3, 69204-67-7; 4, 69204-68-8; 5, 69204-69-9; 6, 69204-70-2; 7, 69204-71-3; levulinic acid, 123-76-2.

References and Notes

(1) D. R. Hirschfeld, W. Fenical, G. H. Y. Lin, R. M. Wing, P. Radlick, and J. J. Sims, *J. Am. Chem. Soc.*, **95**, 4049 (1973).
(2) E. Fattorusso, S. Magno, L. Mayol, C. Santacroce, D. Sica, V. Amico, G. Oriente, M. Piattelli, and C. Tringali, *Chem. Commun.*, 575 (1976).
(3) K. J. Robertson and W. Fenical, Phytochemistry, **16**, 1071 (1977).
(4) D. J. Faulkner, B. N. Ravi, J. Finer, and J. Clardy, *Phytochemistry*, **16**, 991 (1977).
(5) H. H. Sun, S. M. Waraszkiewicz, K. L. Erickson, J. Finer, and J. Clardy, *J. Am. Chem. Soc.*, **99**, 3516 (1977).
(6) F. J. McEnroe, K. J. Robertson, and W. Fenical in "Marine Natural Products Chemistry", D. J. Faulkner and W. Fenical, Eds., Plenum Press, New York, 1977, pp 179–189.
(7) B. Danise, L. Minale, R. Riccio, V. Amico, G. Oriente, M. Piattelli, C. Tringali, E. Fattorusso, S. Magno, and L. Mayol, *Experientia*, **33**, 413 (1977).
(8) V. Amico, G. Oriente, M. Piattelli, C. Tringali, E. Fattorusso, S. Magno, and L. Mayol, *Chem. Commun.*, 1024 (1976).
(9) H. H. Sun and W. Fenical, *Phytochemistry*, in press.
(10) Only 12 bands were observed in the ^{13}C-NMR spectrum of 1 despite recording of the spectrum using a variety of instrumental parameters.
(11) K. Nakanishi, T. Goto, S. Ito, S. Natori, and S. Nozoe, "Natural Products Chemistry", Vol. 1, Kodansha and Academic Press, New York, 1974, pp 97–101.
(12) E. D. Brown, M. D. Solomon, J. K. Sutherland, and T. Torre, *Chem. Commun.*, 111 (1967).
(13) M. A. Schwartz, J. D. Crowell, and J. H. Musser, *J. Am. Chem. Soc.*, **94**, 4361 (1972).

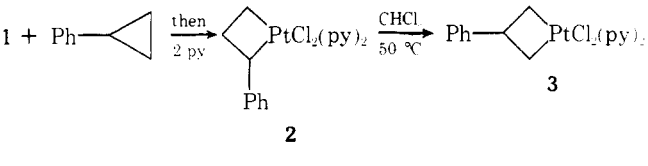
Platinacyclobutanes. Cyclopropane Exchange vs. Rearrangement

Thomas H. Johnson

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506

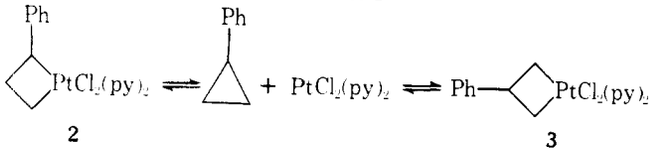
Received November 14, 1978

The reaction of Zeise's dimer[1a] (1) with most monosubstituted cyclopropanes was reported to occur with platinum insertion into the least substituted bond of the cyclopropane.[1b] Thus, the reaction of phenylcyclopropane with 1 followed by treatment with 2 equiv of pyridine was reported to give 3.[1] The structure of 3 was based upon its ^1H NMR spectrum. However, Puddephatt and Tipper established that the initial product was not 3 but 2 which resulted from platinum insertion into the substituted bond.[2] Furthermore, they established that 2 could be partially converted into 3 by heating at 50 °C for 45 min in chloroform.[3] The structures 2 and 3 were easily distinguished by ^{13}C NMR.[2]

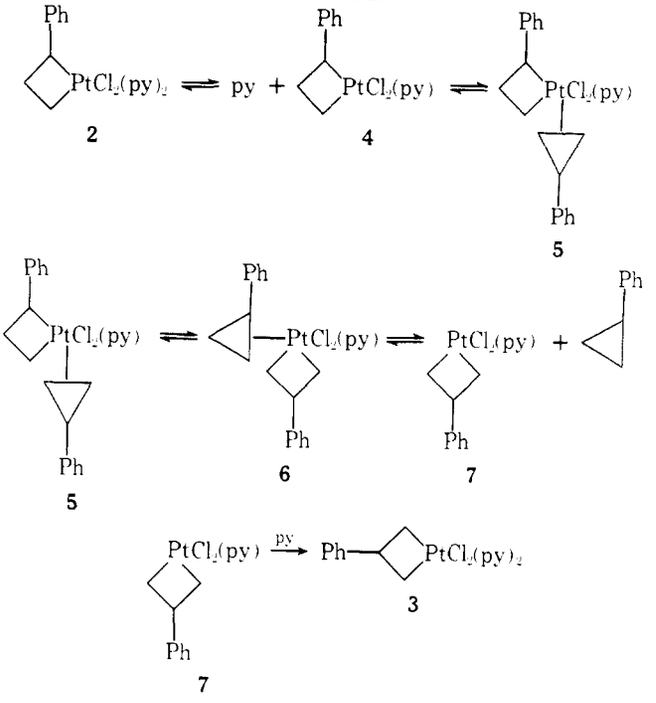


2 3

Scheme I



Scheme II



McQuillin has reported that the unsubstituted platinacycle, prepared from **1** and cyclopropane, could exchange with phenylcyclopropane to give the phenyl-substituted platinacyclobutane.[1] While no experimental details of this reaction were given, a more complete study of this exchange with substituted cyclopropanes in THF has been recently reported by Puddephatt.[4]

These two events have led to speculation that the rearrangement of **2** to **3** may involve an intermediate derived from **2** and external phenylcyclopropane.[5] Hence, the rearrangement process may occur by an exchange mechanism wherein the more favored **3** predominates. The two reports cited above clearly indicate that phenylcyclopropane can displace cyclopropane from a platinacyclobutane. However, the evolution of cyclopropane would certainly favor this process. In this instance, we shall be concerned about the ability of phenylcyclopropane to displace another phenylcyclopropane from a platinacyclobutane.

Unlike the exchange experiments of McQuillin and Puddephatt, the rearrangement of **2** to **3** occurs without the addition of phenylcyclopropane. However, it has been established that the platinacyclobutane **2** thermally decomposes to give phenylcyclopropane and dichlorobis(pyridine)platinum(II).[6] Indeed, small amounts of phenylcyclopropane are found in solutions of **2**. Consequently, a source of phenylcyclopropane is available.

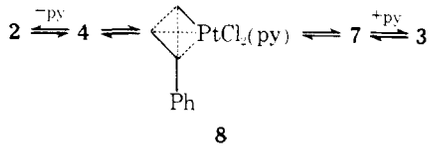
We can envision two possible modes by which phenylcyclopropane may participate in the rearrangement of **2** to **3**. Scheme I depicts a dissociation–association mechanism wherein phenylcyclopropane dissociates and readds to form the favored platinacyclobutane **3**. If the mechanism depicted in Scheme I was operating, then one should be able to prepare the platinacyclobutane **2** (or **3**) from dichlorobis(pyridine)-platinum(II) and phenylcyclopropane. Both *cis*- and *trans*-dichlorobis(pyridine)platinum(II) were prepared according to literature methods[7] and were exposed to phenylcyclopropane under the rearrangement conditions. We were unable to detect either of the platinacyclobutanes in this reaction. Thus, it would seem unlikely that the mechanism depicted in Scheme I would be operating.

Alternatively, the mechanism depicted in Scheme II requires the initial dissociation of pyridine to give the unsaturated platinacycle **4**, which could then undergo addition of phenylcyclopropane to form **5**. Intermediate **5** could equilibrate with **6**, which upon loss of phenylcyclopropane would give **7**. The addition of pyridine to **7** would give the isomerized platinacyclobutane **3**. This mechanism requires the dissociation of a pyridine ligand and small amounts of free phenylcyclopropane. The phenylcyclopropane could be provided by a small amount of thermal decomposition of **2**. The dissociation of pyridine has been previously suggested by Puddephatt[2] by noting that the rearrangement process is retarded in the presence of excess pyridine. We have obtained additional confirmation of the pyridine dissociation process by carrying out the rearrangement of **2** in the presence of free pyridine-d_5. Mass spectral analysis of the recovered platinacyclobutane revealed a complete equilibration of pyridine-d_5 and pyridine-d_0 in the complex.

If Scheme II were operating in the rearrangement of **2** to **3**, then one should be able to carry out a phenylcyclopropane exchange reaction to the extent that **2** rearranges to **3**. This hypothesis was tested by reacting **2** with phenylcyclopropane-d_1 (89% enriched), 1:1, in chloroform under the rearrangement conditions. Mass spectral analysis of the recovered phenylcyclopropane revealed that it was now 85% enriched. Similar analysis of the recovered platinacyclobutane gave a deuterium enrichment of 5%. Clearly, a phenylcyclopropane exchange does occur, but the amount of exchange is too modest to account for the observed amount of rearrangement.[8]

Theoretically, chloride ion could also be dissociating during the rearrangement. To test for possible chloride ion dissociation, a sample of **2** was treated with radioactive chloride-38[9] under rearrangement conditions. Recovery and subsequent analysis of the platinacyclobutane revealed no incorporation of chloride-38. Therefore, under rearrangement conditions, chloride ion appears not to be dissociating.

These results are consistent with a mechanism proposed by Puddephatt and Tipper[2] where an intramolecular rearrangement process occurs.[10] They envisioned the initial loss of a pyridine ligand followed by a concerted rearrangement, shown as **8**, to give **7**. Pyridine addition to **7** would give **3**.



These results also rule against mechanisms requiring phenylcyclopropane exchange as a step in the rearrangement.

Experimental Section

The platinacyclobutane **2** and phenylcyclopropane-d_1 were prepared according to the procedure of McQuillin.[1] The rearrangement reactions were all carried out according to the procedure of Puddephatt and Tipper.[2] Mass spectral data were obtained from an AEI-MS30 double-beam spectrometer, and NMR spectra were obtained from a Varian XL-100 spectrometer. Pyridine-d_5 was purchased from Stohler Isotopes and was 99% deuterium enriched. Chloride-38 was obtained from the Kansas State University reactor and was used immediately.

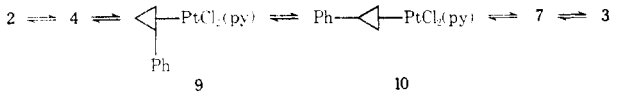
Acknowledgments. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this re-

search. A generous load of platinum chloride by the Matthey-Bishop Co. is also gratefully acknowledged. The author would like to thank Professor J. Paukstelis for obtaining the NMR spectra, Professor H. Moser for assistance with the radioactive chloride experiment, and both them and Professor R. McDonald for helpful discussions. Partial support from the Department of Chemistry, Kansas State University, is also acknowledged.

Registry No.—**2**, 63469-62-5; **3**, 38889-63-3.

References and Notes

(1) (a) Zeise's dimer is di-μ-chloro-dichlorobis(η^2-ethene)diplatinum [12073-35-8]. (b) W. J. Irwin and F. J. McQuillin, *Tetrahedron Lett.*, 1937 (1968); F. J. McQuillin and K. G. Powell, *J. Chem. Soc., Dalton Trans.*, 2123 (1972).
(2) R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Chem. Soc., Chem. Commun.*, 625 (1976).
(3) The ratio of **2/3** was 1:3 under these conditions.
(4) R. J. Al-Essa, R. J. Puddephatt, M. A. Quyser, and C. F. H. Tipper, *J. Organomet. Chem.*, **150**, 295 (1978).
(5) An alternate (olefin)metal–carbene mechanism has been discounted by Puddephatt[2] on the grounds that no styrene was found in the reaction when **2** was converted to **3**.
(6) P. W. Hall, R. J. Puddephatt, K. R. Seddon, and C. F. H. Tipper, *J. Organomet. Chem.*, **81**, 423 (1974).
(7) G. B. Kauffman, *Inorg. Synth.*, **7**, 249 (1963).
(8) The ratio of **2/3** in this experiment was ca. 1:2.5.
(9) Introduced as KCl. Chloride-38 has a half-life at 36 min. A sample was obtained from the Kansas State University reactor and was sufficiently active to be detectec in the products.
(10) An alternate explanation could involve a pair of equilibrating edge complexes, **9** and **10**:



9 10

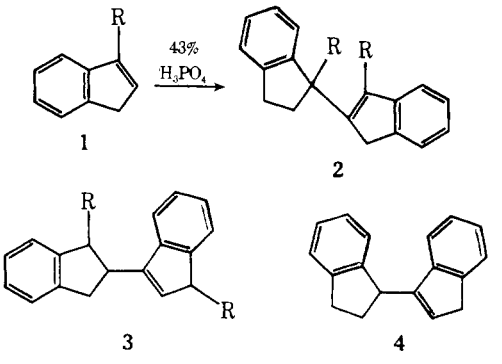
Diindene (Indene Dimer): A Triboluminescent Compound[1]

Wayland E. Noland,* Lawrence L. Landucci,[1a] and James C. Darling[1b]

School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received October 10, 1978

Weissgerber[2] reported in 1911 the preparation of a dimer of 1*H*-indene (diindene) in nearly quantitative yield, a colorless solid, mp 51 °C (recrystallized from acetic acid), by refluxing 1*H*-indene with acetic or phosphoric acids. He suggested as possibilities two cyclobutane ([2 + 2]cycloadduct) structures. Stobbe and Färber[3] reported in 1924 that repetition of the preparation with phosphoric acid gave a colorless sample, mp 50–51 (solidified oil) and 57–58 °C (from acetic acid or ethanol, with a little water). The latter sample was converted to a dibromide, mp 120–121 °C, indicating that a double bond was present, and was oxidized with chromium(VI) oxide to 2,3-dihydro-1*H*-inden-1-one. On the basis of their evidence, they suggested possible structures **2a** and **3a**. Similarly, Marion[4] obtained from a sample of diindene recrystallized from ethanol, mp 55–56 °C, a dibromide, mp 126 °C. Stobbe and Färber[3] left open the question whether the lower melting solidified oil and the higher melting recrystallized sample were isomers or were the same compound in differing states of purity. The possibility of dimorphism does not seem to have been considered. The only appreciable difference they noted was that the lower melting form was autoxidized much more rapidly than the higher melting form. Dansi and Pasini,[5] who prepared their diindene with stronger acid (48% sulfuric acid), argued that at least two isomers were present since their diindene, when crystallized from ethanol or acetic acid, gave fractions having different and variable melting points. Furthermore, they obtained two different dibromides, mp 131–133 and 131–132 °C, and fractions of intermediate and depressed melting points, which were reported to be of different stability and formed in differing yields depending on which sample of diindene they were derived from. On the basis of this evidence they assigned structure **2a** to the lower melting diindene and suggested that the higher melting form was probably structure **4**. It should



a, R = H; b, R = CH_3

be noted, however, that **2a** could give rise to two diastereomeric dibromides. One, the trans, would be the result of normal anti addition of bromine to the double bond, and the other, the cis, could result from syn addition of bromine or from epimerization of a bromine at the benzyl (1) or tertiary (2) carbon atoms of the trans dibromide.

In the present work indene was refluxed with 1:1 water–85% phosphoric acid according to the procedure of Weissgerber,[2] giving diindene in 77% yield as a colorless blue fluorescent oil, bp 158–161 °C (0.9 mm), which solidified on cooling to an extremely hard white crystalline solid, mp 42–52 °C. Two recrystallizations from acetic acid gave white needles, mp 59–60 °C. The NMR spectra of the two samples are the same, indicating that they are dimorphs, except for an impurity peak in the former at δ 0.98. Since the orientation of protonation and carbocation attack on the 1*H*-indene double bond would be expected to produce a benzyl cation, structure **2a** is more probable than **3a** (or **4**), a likelihood which was also recognized[6] before the acceptance of carbonium ion theory. The NMR spectra of diindene are consistent with structure **2a** since the indenyl vinyl proton and methylene group appear as broad singlets (in carbon tetrachloride) at δ 6.53 ($W_{1/2}$ = 3.5 Hz) and 3.21 ($W_{1/2}$ = 3 Hz), respectively, rather than being split by each other as would be expected for structures **3a** or **4**.

Dimerization of 3-methyl-1*H*-indene with phosphoric acid under corresponding conditions gave a dimer as a light yellow viscous oil, bp 162–166 °C (0.8 mm), n^{25}_D 1.6088, having an NMR spectrum (in carbon tetrachloride) consistent with the corresponding structure **2b** (rather than **3b**) since there is no vinyl proton peak and the 2,3-dihydroindenyl methyl peak appears as a singlet at δ 1.52. The indenyl methyl absorption at δ 1.66 appears as a triplet ($J \approx 1.7$ Hz), however, apparently being involved in five-bond zigzag long range coupling[7] with the indenyl methylene group, whose absorption at δ 3.24 appears as an incompletely resolved quartet ($J \approx 1.7$, $W_{1/2}$ = 5.5 Hz).

The lower melting solidified form of diindene was markedly triboluminescent;[8] when broken, struck, or scratched vigorously it emitted flashes of blue light. The higher melting recrystallized form (white needles) was not triboluminescent under the same conditions. The surface of solidified diindene turns yellow on contact with air, apparently the result of autoxidation which can be retarded by storage in a brown bottle

0022-3263/79/1944-1358$01.00/0