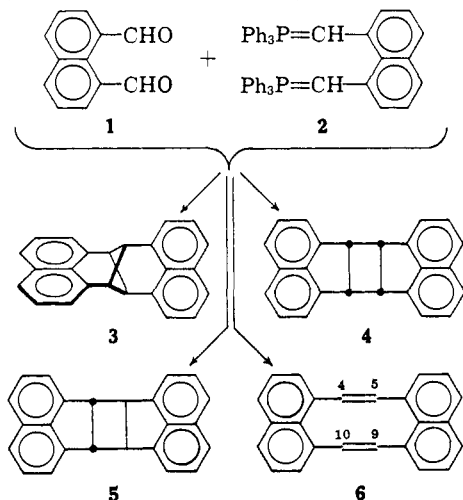


A Dinaphth[10]annulene¹

Sir:

[10]Annulene (cyclodecapentaene) is a compound of considerable interest, since it is the next higher homolog of benzene containing $(4n + 2)$ π electrons, but it may be destabilized through steric or strain effects.² We now report the synthesis of 1,2,3:6,7,8-di(1',8'-naphthyl)-[10]annulene(6), an annelated derivative of [10]annulene.³

Wittig reaction of 1,8-naphthalenedicarboxaldehyde (1)⁴ and the bis(ylide) 2⁵ in boiling benzene-ether for 3 hr gave a mixture of nine substances, separated by chromatography on alumina. For brevity, only the four isomeric products derived by ring formation are described (in order of elution): (a) 1,3:2,4-di(1',8'-naphthyl)cyclobutane (3), 0.1% yield, colorless crystals,



mp 321–322°; mass spectrum, molecular ion at m/e 304.124 (calcd for $^{12}\text{C}_{24}\text{H}_{16}$: 304.125; $\lambda_{\text{max}}^{\text{cyclohexane}}$ ($>250 \text{ m}\mu$) 263 $\text{m}\mu$ ($\log \epsilon$ 3.74), 273 (3.77), 296 (3.87), 309 (4.28), 323 (4.59), 332 (4.27), and 338 (4.76); nmr spectrum (all at 100 Mcps in CD_2Cl_2 , unless stated otherwise), 12H multiplet at τ 2.2–3.0 (aromatic protons) and 4H singlet at 6.48 (cyclobutane protons)⁶ (the compound was recovered unchanged after attempted hydrogenation in ethyl acetate over platinum, confirming the absence of olefinic bonds; structure 3 is formally derived from 6 by joining C(4)–C(9) and C(5)–C(10)); (b) *cis*-1,2:3,4-di(1',8'-naphthyl)cyclobutane (*cis*-ace-

(1) Unsaturated Macrocyclic Compounds. LIV. For part LIII, see W. H. Okamura and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 5991 (1967).

(2) *Inter al.*, see K. Mislow, *J. Chem. Phys.*, **20**, 1489 (1952).

(3) Derivatives of [2.2]metacyclophane-1,9-diene (which are annelated [10]annulenes) have previously been obtained in solution by irradiation of the corresponding 15,16-dihydropyrenes (V. Boekelheide, *et al.*, *J. Am. Chem. Soc.*, **87**, 130 (1965); **89**, 1695, 1704, 1709 (1967)). 1,6-Bridged [10]annulenes have been synthesized by E. Vogel, *et al.* (*Angew. Chem.*, **76**, 145, 785 (1964); **78**, 754 (1966); *Tetrahedron Letters*, 3613, 3625 (1965)) and by our own group (F. Sondheimer and A. Shani, *J. Am. Chem. Soc.*, **86**, 3168 (1964); A. Shani and F. Sondheimer, *ibid.*, **89**, 6310 (1967)). Very recently, evidence has been obtained that [10]-annulene itself is formed as a very unstable intermediate in the photolysis of *trans*-9,10-dihydronaphthalene at -190° (E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967)).

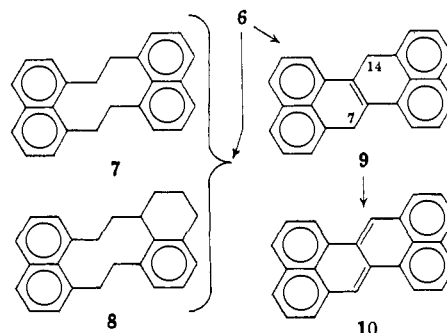
(4) Obtained from the corresponding hydrate (R. Criegee, L. Kraft, and B. Rank, *Ann.*, **507**, 159 (1933); J. K. Stille and R. T. Foster, *J. Org. Chem.*, **28**, 2703 (1963)) by boiling with benzene and removal of water.

(5) (a) E. D. Bergmann and I. Agranat, *ibid.*, **31**, 2407 (1966); (b) H. J. Bestmann, H. Haberlein, H. Wagner, and O. Kratzer, *Chem. Ber.*, **99**, 2848 (1966); (c) R. H. Mitchell and F. Sondheimer, *Tetrahedron*, in press.

(6) By comparison, the nmr spectra of the related substances 4 and 5 showed multiplets at τ 2.6–3.2 and 2.1–2.7, respectively (aromatic protons), as well as singlets at 5.30 and 6.00, respectively (cyclobutane protons).

naphthylene dimer) (4),⁷ 0.07% yield, colorless crystals, mp 230–232° (lit.⁷ mp 232–234°);⁸ (c) *trans*-1,2:3,4-di(1',8'-naphthyl)cyclobutane (*trans*-acenaphthylene dimer) (5),⁷ 0.2% yield, colorless crystals, mp 306–307° (lit.⁷ mp 306–307°)⁸ (both structures 4 and 5 are formally derived from 6 by joining C(4)–C(10) and C(5)–C(9)); (d) 1,2,3:6,7,8-di(1',8'-naphthyl)[10]annulene (6), 2.0% yield, almost colorless needles, mp 175–176° dec (red melt); mass spectrum, molecular ion at m/e 304.127; $\lambda_{\text{max}}^{\text{cyclohexane}}$ 218 $\text{m}\mu$ ($\log \epsilon$ 4.88), 244 (4.56), 274 sh (3.55), 289 sh (3.48), 302 sh (3.61), 341 sh (4.18), and 367 (4.34); $\nu_{\text{max}}^{\text{KBr}}$ (1100–650 cm^{-1} region) 1033 (vw), 1026 (vw), 968 (vw), 905 (w), 872 (w), 851 (vw), 828 (s), 811 (m), 775 (vs), 678 (w), and 666 (vw) cm^{-1} . The nmr spectrum (CD_2Cl_2) showed a 14H multiplet at τ 2.1–3.0, and a 2H multiplet consisting of a singlet at 6.51 (~ 1 H) and a doublet ($J = 7$ cps) at 6.60 (~ 1 H);⁹ in CDCl_3 the 2H multiplet is replaced by a singlet at 6.41 (~ 1 H) and a doublet ($J = 3$ cps) at 6.49 (~ 1 H); in CCl_4 the multiplet is replaced by two singlets at 6.35 and 6.50 (~ 1 H each); in C_6D_6 , by two singlets at 6.73 and 6.82 (~ 1 H each). At present, the nmr spectra cannot be interpreted, and it is not known whether the 2H high-field bands are due to two olefinic protons or to two naphthalene protons shielded by the neighboring π -electron system¹⁰

Catalytic hydrogenation of 6 in ethyl acetate over platinum for 6 hr, followed by chromatography on alumina, gave 40% of the dinaphthalene 7 and 12% of the naphthalenetetralin 8. Substance 7 formed almost colorless leaflets, mp 196–197°; mass spectrum, molecular ion at m/e 308.154 (calcd for $^{12}\text{C}_{24}\text{H}_{20}$: 308.156); $\lambda_{\text{max}}^{\text{cyclohexane}}$ 225 $\text{m}\mu$ ($\log \epsilon$ 4.79), 244 (4.58), 255 (4.51), 274 (4.01), 292 (4.10), 305 (4.27), 327 sh (4.16), 341 (4.34), 353 (4.28), 358 (4.30), and 368 (3.81); nmr spectrum, 12H multiplet at τ 1.6–3.0 (aromatic protons) and 8H complex bands at 5.1–8.1 (aliphatic protons). Substance 8 formed almost colorless needles, mp $\sim 225^\circ$ dec; mass spectrum, molecular ion at m/e 312.186 (calcd for $^{12}\text{C}_{24}\text{H}_{24}$: 312.188); $\lambda_{\text{max}}^{\text{cyclohexane}}$ 228



$\text{m}\mu$ ($\log \epsilon$ 4.57), 266 (4.73), 276 (4.98), 292 (4.30), 305 (4.37), 319 (4.14), 334 (4.14), 355 (3.66), 370 (3.48), and 374 (3.61); nmr spectrum, 9H multiplet at τ 0.9–3.0 (aromatic protons) and 15H complex bands at 5.8–8.4 (aliphatic protons). Both the ultraviolet¹¹ and

(7) K. Dziewonski and R. Rapalski, *Ber.*, **45**, 2491 (1912); K. Dziewonski and C. Paschalski, *ibid.*, **46**, 1986 (1913); J. D. Dunitz and L. Weissman, *Acta Cryst.*, **2**, 62 (1949); F. Gerson and B. Weidmann, *Helv. Chim. Acta*, **49**, 1837 (1966).

(8) The substance was identified by direct comparison with an authentic sample.⁷

(9) The spectrum at -70° was essentially unchanged.

(10) *Inter al.*, see D. J. Wilson, V. Boekelheide, and R. W. Griffin, *J. Am. Chem. Soc.*, **82**, 6302 (1960).

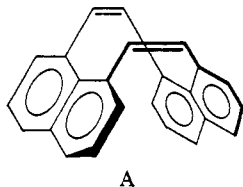
(11) By contrast, the ultraviolet spectra of the corresponding 14-membered ring compounds are normal.^{5b}

nmr spectra¹⁰ of **7** and **8** are unusual, presumably due to steric effects in the ten-membered ring.

Solutions of **6** (pentane, chloroform, benzene, etc.) gradually became red. The change was found to involve initial isomerization to 7,14-dihydrozethrene (**9**),¹² which in the presence of air is then oxidized to zethrene (**10**).¹³ The same changes occurred also in the solid state, most rapidly by pyrolysis; the crystals quickly became pink on the surface even on standing at room temperature, but could be stored with little decomposition at -15° in the dark for several weeks. In preparative experiments, **9** (yellow needles, mp $232-234^{\circ}$ dec) was obtained in over 90% yield from **6** by allowing an unstoppered solution in CD_2Cl_2 (nmr sample) to stand at room temperature without protection from diffuse daylight for 5–60 min,¹⁴ or in ~50% yield by pyrolysis of the solid in air at 200° for 1 min. Substance **10** (red-violet needles, mp $262-263^{\circ}$) was obtained in 30% yield from **6** by allowing an unstoppered solution in CDCl_3 (nmr sample) to stand for 10 days, or in 40% yield by pyrolysis of the solid at 200° for 15 min. Structures **9** and **10** (supported by the nmr and mass spectra) are based on the correspondence of the melting points and the detailed ultraviolet spectra with the reported data.^{12,13}

Reaction of **6** with bromine or chlorine did not result in simple addition, but gave derivatives of zethrine (**10**).

The structure of **6** follows unequivocally from the above-described properties and reactions. We tentatively assign the *cis,cis* configuration **A** to the compound, in view of the presence of only a very weak infrared band (at 968 cm^{-1}) in the $1000-920\text{-cm}^{-1}$ region.¹⁵ We hope that more definite stereochemical information will be provided by an X-ray crystallographic



analysis, which is now being carried out by Mrs. O. Kennard and co-workers.

The properties of **6** indicate that it is a nonplanar molecule and that it does not represent an annelated delocalized ten- π -electron system.

(12) E. Clar, "Aromatische Kohlenwasserstoffe," Vol. 2, Springer-Verlag, Berlin, 1952, p 387.

(13) E. Clar, K. F. Lang, and H. Schulz-Kiesow, *Chem. Ber.*, **88**, 1520 (1955); see also C. A. Coulson and C. M. Moser, *J. Chem. Soc.*, 1341 (1953); C. A. Coulson, C. M. Moser, and M. P. Barnett, *ibid.*, 3108 (1954).

(14) The time required for the formation of **9** (which precipitated directly) was found to vary, and we believe that the reaction is radical initiated.

(15) By comparison, medium or strong infrared bands at $\sim 960\text{ cm}^{-1}$ are shown by *trans*-stilbene and *trans*-1,2-bis(α -naphthyl)ethylene,¹⁶ as well as by some related macrocyclic compounds containing *trans*-stilbene groupings.¹⁷

(16) Prepared according to G. Drefahl, D. Lorenz, and G. Schnitt, *J. Prakt. Chem.*, **23**, 143 (1964).

(17) *Inter al.*, see E. D. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 4281 (1953); C. E. Griffen, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, **27**, 1627 (1962); H. A. Staab, F. Graf, and B. Junge, *Tetrahedron Letters*, 743 (1966).

(18) Recipient of a Science Research Council Research Studentship,

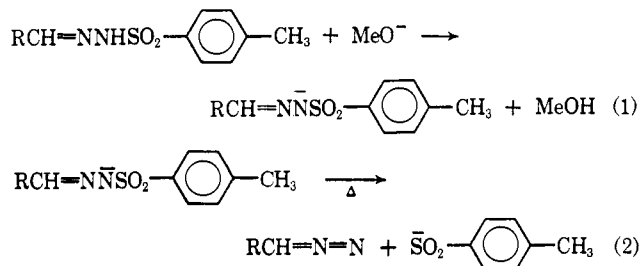
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The Effect of Solvent on the Course of the Bamford-Stevens Reaction^{1,2a}

Sir:

Tosylhydrazone anions of aliphatic and aromatic aldehydes and ketones undergo thermal decomposition to give diazoalkanes *via* α elimination (eq 1 and 2).² The fate of the diazoalkane intermediates as determined by product analysis was found to be mainly dependent upon the nature of the solvent in that in aprotic media such as diethyl Carbitol and diglyme diazoalkanes



thermally decompose with loss of nitrogen, giving carbenes,^{2b,3} while in protic solvents such as ethylene glycol and diethylene glycol competitive protonation of the diazoalkanes occurs, leading to diazonium and/or carbanion ions.^{3,4}

The term "protic" has been poorly defined with regard to these reactions.⁵ A study was initiated in order to obtain further information concerning the relative "protonicity," *i.e.*, proton donor ability, of various representative hydroxylic solvents in these reactions. In addition it was anticipated that base-catalyzed decomposition of several aliphatic tosylhydrazones in these solvents would yield quantitative information regarding the *extent* of competitive carbenic and cationic processes.

2-Methylpropanal and 2,2-dimethylpropanal tosylhydrazones were chosen for study since decomposition in aprotic media gives large amounts of methylcyclopropane and 1,1-dimethylcyclopropane *via* their respective carbenes.³ However, in protic solvents conversion to cyclopropane is markedly reduced as a result of diazonium ion formation with concomitant increase in Wagner-Meerwein rearrangement products.^{3,4}

It has now been found that "protonicity" of solvents is a function of their (a) relative acidity ($\text{p}K_a$ or K_e) [K_e is an acidity scale inversely related to $\text{p}K_a$], and (b) "proton equivalence" (PE), defined herein as milliequivalents of hydroxyl per gram of solvent.

The effects of the solvents can be followed by observing the amounts of methylcyclopropane and 1- and 2-butenes⁷ formed *via* decomposition of 2-methylpropanal tosylhydrazone (I) anion. For example, methylcyclo-

(1) Financial support from the National Science Foundation is gratefully acknowledged.

(2) (a) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); (b) W. Kirmse "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964.

(3) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

(4) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959).

(5) Cf. J. W. Wilt, C. A. Schneider, H. F. Dabele, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966).

(6) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952); P. Ballinger and F. A. Long, *ibid.*, **82**, 795 (1960); H. Shigematsu, Y. Nishikawa, and Y. Ishii, *Kogyo Kagaku Zasshi*, **65**, 945 (1962). K_e , rather than $\text{p}K_a$, is employed since K_e (not $\text{p}K_a$) has been determined for a large number of alcohols and glycols.

(7) The Wagner-Meerwein rearrangement products. Cf. A. T. Jurewicz and L. Friedman, *J. Am. Chem. Soc.*, **89**, 149 (1967).