even by strong nucleophiles, such as lithium aluminum hydride and potassium hydroxide, dramatically illustrates the effect of angle strain on displacements at silicon.[14] It now seems clear, as was postulated in our original communication,[1] that the effects at strained bridgehead or strained monocyclic silicon can be accommodated by having an intermediate or transition state in which an apical-equatorial geometry obtains for two nonreacting groups forming a strained angle with the silicon. This leads to *retention* of configuration as the favored stereochemistry *even in the present case in which* (contrasting sharply with the bridgehead case) *inversion of configuration is also possible*, but, nevertheless, does not occur.[15]

Acknowledgment. Support of this work by a grant from National Science Foundation is gratefully acknowledged. We also thank L. Arlie Ulland for originally calling our attention to the reported synthesis of the ring system of compound II.

[14] For a recent review of dramatic rate effects at phosphorus produced by angle strain, see M. J. Gallagher and I. D. Jenkins, *Top. Stereochem.*, 3, 70 (1968). See also, F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968).

[15] Presented in part as a plenary lecture at the Third International Symposium on Organosilicon Chemistry, Aug 23, 1972.

David N. Roark, Leo H. Sommer*
Department of Chemistry, University of California
Davis, California 95616

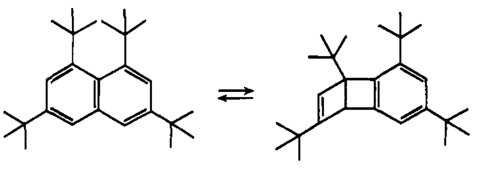
Received October 21, 1972

Photoisomerization of *peri*-Di-*tert*-butylnaphthalenes

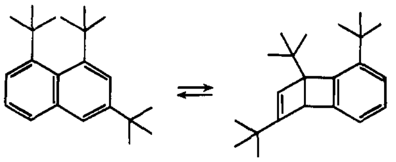
Sir:

The initial preparation of a benzene valence isomer was accomplished by a photoisomerization reaction in 1962.[1] Since that original impetus, there have been published many photochemical and synthetic studies on benzene valence isomers.[2] In the naphthalene series, there have been two cycloaddition type syntheses of a Dewar isomer[3] and one construction of a benzvalene isomer *via* carbenoid insertion.[4] We here report the first photoisomerizations of intact naphthalenes to their Dewar isomers.[5]

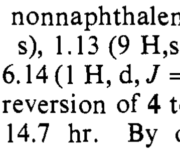
The tetra-*tert*-butylnaphthalene (1) upon irradiation with a Hanovia, 450-W high-pressure lamp with a Pyrex filter, in cyclohexane or hexane, affords a photostationary state in which isomer 2 is present in 94% yield. The photoproduct was isolated from the yellow solution by first removing the solvent at room temperature, then by rapid chromatography through neutral alumina (activity 2). The solid product was recrystallized from warm methanol, affording material in the melting range 54–78°, *m/e* 352, whose uv showed no naphthalenic absorption. *Anal.* Found: C, 88.4; H, 11.4. The product was further characterized by its nmr [(CCl_4) δ 1.00 (9 H, s), 1.13 (9 H, s), 1.30 (9 H, s), 1.38 (9 H, s), 3.91 (1 H, d, J = 1.5 Hz), 6.10 (1 H, d, J = 1.5 Hz), 6.89 (1 H, d, J = 1.5 Hz), 7.08 (1 H, d, J = 1.5 Hz)], its uv [max (hexane) 273 nm (log ϵ 2.83), 282 (2.82)], and its thermal reversion to 1 (thus ruling out any more deep-seated photoisomerization). Rate constants for this reversion were determined to be $1.07 \pm 0.06 \times 10^{-5}$ sec^{-1} at 50° ($t_{1/2}$ 18.3 hr), $5.8 \pm 0.20 \times 10^{-5}$ sec^{-1} at 65° ($t_{1/2}$ 3.35 hr), and $2.6 \pm 0.1 \times 10^{-4}$ sec^{-1} at 80° ($t_{1/2}$ 0.75 hr). These values may be compared to half-lives of 4.0 hr at 38° for the parent Dewar naphthalene,[3a] 1.5 hr at 70° for the tetramethyl case,[3b] and 2.9 hr at 150° for hexamethyl(Dewar benzene).[6] From our data, Arrhenius activation parameters of $E_a = 24.0 \pm 1.0$ kcal/mol and log $A = 11.3 \pm 0.8$ can be derived. We note the small log A (negative entropy of activation) compared to most literature values for Dewar benzene ring openings.[7] An explanation based on the restricted rotation of *tert*-butyl groups observed in the product,[8] requiring constraints on the rotational freedom of the Dewar isomer in order that it might proceed along the reaction coordinate to the transition state, will be presented in our full paper. The tri-*tert*-butylnaphthalene (3) was photolyzed to afford Dewar isomer 4 (colorless oil, *m/e* 296; isolation, *vide supra*) which was characterized by its nonnaphthalenic uv and by nmr (CCl_4): δ 1.00 (9 H s), 1.13 (9 H,s), 1.38 (9 H s), 3.97 (1 H, d, J = 1.5 Hz), 6.14 (1 H, d, J = 1.5 Hz), 6.67–7.17 (3 H, m). Thermal reversion of 4 to 3 occurred at 50° with a half-life of 14.7 hr. By our nmr analytical method, the isomer 5 could not be detected. One interpretation of this result is that it is evidence for buttressing effects between the *m*-*tert*-butyl groups.[9,10] It is clear from an examination of models that if small re-



1 2



3 4



5

---

[1] E. E. van Tamelen and S. P. Pappas, *J. Amer. Chem. Soc.*, 84, 3789 (1962).

[2] E. E. van Tamelen, *Accounts Chem. Res.*, 5, 186 (1972).

[3] (a) R. N. McDonald, D. G. Frickey, and G. M. Muschik, *J. Org. Chem.*, 37, 1304 (1972); (b) D. T. Carty, *Tetrahedron Lett.*, 4753 (1969).

[4] T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, 93, 3782 (1971).

[5] Irradiations of simple naphthalenes result in dimer formation: *cf.*, P. J. Collin, D. B. Roberts, G. Sugowdz, D. Wells, and W. H. F. Sasse, *Tetrahedron Lett.*, 321 (1972).

[6] J. F. M. Oth, *Recl. Trav. Chim. Pays-Bas*, 87, 1185 (1968).

[7] (a) P. Cadman, E. Ratajczak, and A. F. Trotman-Dickinson, *J. Chem. Soc. A*, 2109 (1970); (b) H. C. Volgen and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, 86, 830 (1967); these investigators report activation parameters differing significantly from those given by Oth in ref 6; (c) R. Breslow, J. Napierski, and A. H. Schmidt, *J. Amer. Chem. Soc.*, 94, 5906 (1972).

[8] J. E. Anderson, R. W. Franck, and W. L. Mandella, *ibid.*, 94, 4608 (1972).

[9] E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *ibid.*, 89, 5389 (1967). The discrepancy in $\Delta\Delta H$ isomerism between *m*- and *p*-di-*tert*-butylbenzene (1 kcal mol) with respect to *o*-di-*tert*-butylbenzene may be due to this buttressing.

[10] H. C. Brown and B. Kanmer, *ibid.*, 75, 3865 (1953).

pulsions exist in **3**, they would be removed through formation of **4**.[11]

---

(11) The hypothesis that an electronic substituent effect is the controlling factor in stabilizing the localization occurring in the observed pathway is not attractive. If one can transfer evidence from esr data for the electron distribution in the first excited state, it is clear that β positions in naphthalenes and in benzocyclobutenes have very little spin density to be stabilized or destabilized by substituents such as *tert*-butyl; see R. D. Rieke, S. E. Bales, P. M. Hudnall, and C. F. Meares, *J. Amer. Chem. Soc.*, **93**, 697 (1971), for benzocyclobutene esr data and I. Goldberg and B. M. Peake, manuscript to be published for *tert*-butylnaphthalene esr data.

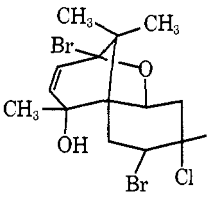
(12) Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for Grant 5150-D4 in support of R. W. F. We also acknowledge the National Cancer Institute for Grant 11,421-07 for support of W. L. M. We are grateful to Professor N. O. Smith for detailed discussions on the error analysis of our kinetic data. A part of this research has been presented by J. E. Anderson, R. W. Franck, and W. L. Mandella, 3rd Northeast Regional Meeting of the American Chemical Society, Abstracts, p 182.

William L. Mandella, Richard W. Franck*[12]
Department of Chemistry, Fordham University
Bronx, New York 10458
Received July 14, 1972

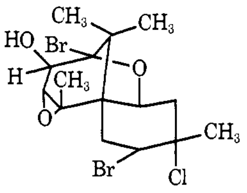
Marine Natural Products. IV. Prepacifenol, a Halogenated Epoxy Sesquiterpene and Precursor to Pacifenol from the Red Alga, *Laurencia filiformis*[1]

Sir:

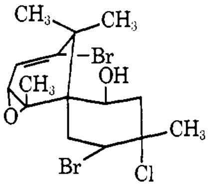
Recently we described the isolation of pacifenol (**1**)[2] and johnstonol[1] (**2**) from *L. pacifica* and *L. johnstonii*, respectively. Marine algae of the genus *Laurencia* were first noted for producing terpenoids containing bromine.[3,4] In addition, the isolation of **1** and **2**, which contain both bromine and chlorine as well as an unusual tricyclic ring structure, makes this genus an important one for the study of marine natural products.



1



2



3

In the course of further work on this interesting group of algae, we have isolated the probable precursor of pacifenol, prepacifenol (**3**). Accordingly, hexane extraction of *L. filiformis* followed by evaporation of the hexane and recrystallization of the partly crystalline residue from hexane gave prepacifenol (**3**) (yield, 0.3% dry plant): $C_{15}H_{21}O_2Br_2Cl$; *m/e* $M^+ = 430, 428, 426$; high resolution $M^+ - H_2O$ *m/e* = 409.9477 (calcd for $C_{15}H_{19}O^{79}Br^{81}Br^{35}Cl$, 409.9472). The nmr spectrum (100 MHz, $CDCl_3$) of **3** indicated at δ 1.88 (s), 1.63 (s), 1.42 (s), and 1.24 (s) four methyl groups, at 2.4 (m) four methylene protons, at 3.02 (d, $J = 3$ Hz) one α-epoxy proton, at 4.72 (four lines, X of ABX) one proton α to bromine, at 4.41 (four lines) one proton α to hydroxyl, and at 6.25 (d, $J = 3$ Hz) one vinyl proton. That prepacifenol was an alcohol was indicated by infrared absorption at 3.5 μ coupled with the disappearance of a one-proton nmr signal (d, $J = 5$ Hz) at δ 1.50 after a D_2O exchange experiment. On analysis of these data for prepacifenol, in particular comparison of its nmr spectrum with the nmr spectra of **1** and **2**, structure **3** was proposed for prepacifenol. Confirmation of this structure was provided in convincing fashion by the conversion of **3** to **1** in almost quantitative yield upon treatment with *p*-toluenesulfonic acid in benzene. The pacifenol so produced was identical with that previously isolated from *L. pacifica*. The conversion of **3** to **1** also occurred on heating **3** to its melting point. Depending upon the rate of heating, **3** melts from 109 to 126°, solidifies, and remelts at 147°. Thin layer chromatography of the residue shows complete conversion to **1**. The cyclization also occurs in high yield under conditions of chromatography upon neutral alumina.

Our original isolation procedure for **1** from *L. pacifica* involved the use of silica gel chromatography and therefore it was possible that pacifenol was an artifact.[2] Indeed, chromatography of prepacifenol on silica gel resulted in quantitative conversion of pacifenol. We conducted a new extraction of *L. pacifica* using the procedure described above which led to the exclusive isolation of prepacifenol. The new extraction gave only prepacifenol and no pacifenol. Thus, our report that pacifenol is present as a natural product in *L. pacifica* is incorrect. However, pacifenol does exist as a natural product in *L. tasmanica*. Extraction of this alga using the new procedure led to pacifenol (0.25% of dry plant) as the major compound.

Acknowledgment. One of us (J. J. S.) wishes to express his gratitude to the Australian National University for a Research Fellowship (1971–1972) and to Professor A. J. Birch, Research School of Chemistry, Australian National University, for the hospitality of his laboratory where this work was carried out. We are grateful to Dr. H. B. S. Womersley, University of Adelaide, for identification of the algae.

---

(1) For paper III of this series see: J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *Tetrahedron Lett.*, 195 (1972).

(2) J. J. Sims, W. Fenical, R. M. Wing, and P. Radlick, *J. Amer. Chem. Soc.*, **93**, 3774 (1971).

(3) T. Irie, M. Suzuki, E. Kurosawa, and T. Masamune, *Tetrahedron*, **26**, 3271 (1970); M. Suzuki, E. Kurosawa, and T. Irie, *Tetrahedron Lett.*, 4995 (1970), and previous papers cited within.

(4) S. Itô, K. Eudo, T. Yoshida, and M. Kodama, *Chem. Commun.*, 186 (1967).

(5) Fellow of the Alfred P. Sloan Foundation.

James J. Sims,* William Fenical
Department of Plant Pathology, University of California
Riverside, California 92502

Richard M. Wing, Phillip Radlick[5]
Department of Chemistry, University of California
Riverside, California 92502
Received September 15, 1972

Short-Lived Intermediates. IV. Adamantene[1]

Sir:

The recent syntheses of bicyclo[3.3.2]non-1-ene[2] have generated considerable interest in the synthesis and

---

(1) Part III: J. E. Gano, *Chem. Commun.*, 1491 (1971).

(2) (a) J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967); (b) J. A. Marshall and H. Faubl, *ibid.*, **89**, 5965 (1967).