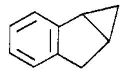
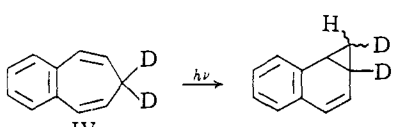
it was necessary to know the nmr chemical shifts of the aliphatic (and vinyl) protons of II. The assignments have been made previously[8] and we have confirmed this by spin decoupling along with the observation that one of the cyclopropyl CH$_2$ protons shows a coupling constant of ~8 Hz with the vicinal protons (the other coupling constants being 3–4 Hz), which means it must be *cis* to these hydrogens,[9] and therefore *exo*. In addition the nmr spectrum of the CH$_2$ group is very similar to that of V.[2] The *endo*-cyclopropyl CH$_2$ hydrogen appears at τ 10.4 ppm, the *exo*-cyclopropyl CH$_2$ hydrogen at 8.6 ppm, the benzylic cyclopropyl hydrogen at 7.7 ppm, the remaining, allylic, cyclopropyl hydrogen at 8.2 ppm, the vinyl hydrogens at 3.8 ppm, and the aromatic hydrogens at 2.9 ppm.

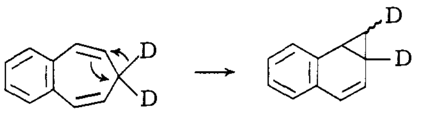

V

With these assignments the product of the photolysis of IV was shown to be VI, with 50% of the deuterium *endo* and 50% *exo* on the methylene group of the three-membered ring. Vogel[8] has demonstrated that flipping of the three-membered ring occurs with an activation energy of 19.4 kcal/mole, which means that at 0 to −5° the half-life of this reaction might be long enough to observe differences in the deuterium *exo*:*endo* ratio if a stereospecific hydrogen shift mechanism obtains. The photolysis at this temperature (including work-up) gave the same 50:50 mixture of *exo*- and *endo*-deuterium and thus the reaction is either nonspecific or the ring is still flipping too fast at this temperature.

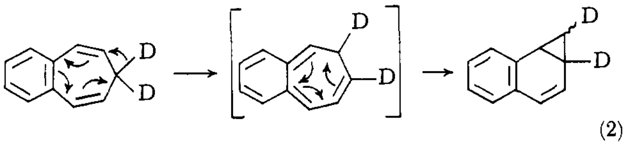


IV VI

The deuterium-labeling experiment thus conclusively proves that a hydrogen shift mechanism is operative. Two mechanisms, which are subtly different, can now be postulated. They are (1) hydrogen shift with concurrent formation of a three-membered ring or (2) hydrogen shift with formation of a product with a rearranged π system followed by rapid valence tautomerization of the first-formed tropilidene to a norcaradiene.

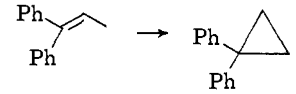


(1)

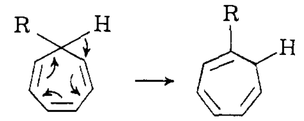


(2)

There is one authentic analogy for the first mechanism in the literature[10] and that involves the rearrangement of 1,1-diphenyl-1-propene (VII) to 1,1-diphenylcyclopropane (VIII), among other products. There are a number of analogies for the second mechanism in the 7-substituted tropilidene series.[11] Photorearrangement of many compounds of this type gives, among the products, the tropilidene having undergone a 1,2-hydrogen shift, presumably by the following mechanism.



VII VIII



One cannot, however, rule out a mechanism analogous to (1) for these rearrangements.

It should also be pointed out that the photochemistry of I differs markedly from the closely related compound *o*-divinylbenzene, which gives V upon irradiation.[2,12] The difference may be due to one or both of two factors. First, the rigidity of I precludes (except perhaps as reactive intermediates) conformations allowed for *o*-divinylbenzene; second, hydrogen shift in the latter compound is of course impossible. One therefore does not known which of these reactions would be the most favorable for a compound having no restrictions on any of these pathways.

The following communication describes the photochemical reorganization of 1,2-benzotropilidene and its relationship to the 3,4-benzotropilidene rearrangement.[13]

---

[8] E. Vogel, D. Wendish, and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, 3, 442 (1964).

[9] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1966, p 695.

[10] G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Pettersen, and C. S. Irving, *Tetrahedron Letters*, 2951 (1965).

[11] See, *e.g.*, G. J. Fonken, "Organic Photochemistry," Vol. 1, Marcel Dekker, Inc., New York, N. Y., 1967, pp 231–232; T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Letters*, 3581 (1967).

[12] J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, **89**, 695 (1967).

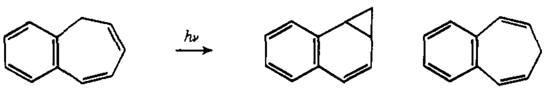
[13] M. Pomerantz and G. W. Gruber, *ibid.*, **89**, 6799 (1967).

Martin Pomerantz, Gerald W. Gruber
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106
Received September 26, 1967

The Photochemical Reorganization of 1,2-Benzotropilidene

Sir:

1,2-Benzotropilidene (I) has been shown to rearrange photochemically (100-w G.E. mercury lamp; Pyrex filter) to benzonorcaradiene (II), the same product one obtains from the photochemical reorganization of 3,4-benzotropilidene (III).[1] In addition, one sees the results of further photorearrangement of II, as indicated in the previous paper.[1] With the knowledge that both I and III give the same product (II) on irradiation, the first questions to be answered are: is there a photoequilibrium between I and III (by, presumably, a 1,3-hydrogen shift) and is only one of these rearranging



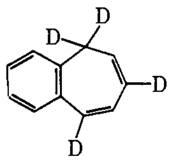
I II III

---

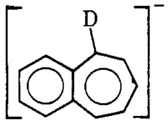
[1] M. Pomerantz and G. W. Gruber, *J. Am. Chem. Soc.*, **89**, 6798 (1967).

photochemically? By irradiating each to partial completion and using nmr analysis (I has a doublet at τ 7.02 ppm and III has a triplet at τ 7.55 ppm), it could be shown that, within experimental error, I was not producing significant quantities of III and III likewise was not giving any measurable amounts of I. Thus a photostationary state is ruled out.

Our preparation of I did not involve any of the published procedures[2-4] but rather was the exclusive (thermodynamically most stable) product formed by equilibrating 3,4-benzotropilidene with the strong base system KO-*t*-Bu–HO-*t*-Bu–DMSO. If this equilibration was conducted using deuterated *t*-butyl alcohol and hexadeuterated dimethyl sulfoxide the product was 3,5,7,7-tetradeuterio-1,2-benzotropilidene (IV). The structure proof of IV was based on the observation that its nmr spectrum showed three broad singlets, the aromatic and two vinyl absorptions, with an integrated intensity of 4:1:1. The CH_2 region showed a trace (~3%) of protium, thus confirming the presence of a CD_2 group. If there is a CD_2 group there must have been more than one exchange and it must have gone, at some time, through the symmetrical (except for the deuteron) anion V. This could then deuterate at either benzylic position and therefore in the product there must be a deuteron at position 3. Since the two vinyl protons appeared as singlets and not an AB quartet the last deuteron must be at position 5, between the two hydrogens.

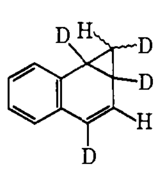


IV



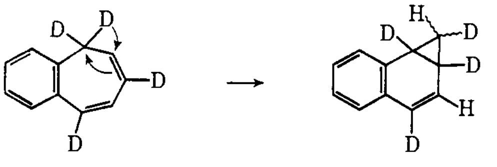
V

The photolysis of IV, even at 0 to −5°, gave VI, containing a 50:50 mixture of *endo*- and *exo*-protium at the cyclopropylmethylene group. Once again, as with 3,4-benzotropilidene, the reaction involves a hydrogen shift and the protium *exo*:*endo* ratio of 50:50 can be accounted for by either indiscriminant, nonspecific hydrogen migration or rapid ring flipping in VI, as discussed in the previous paper.[1]

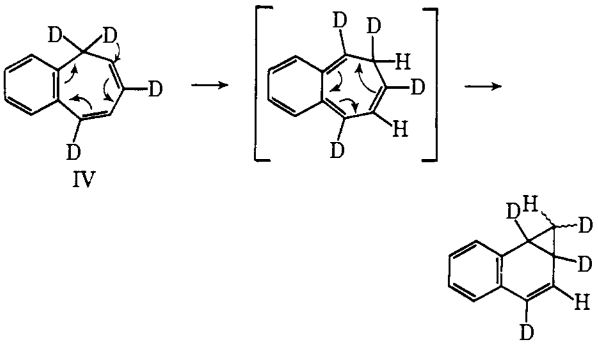


VI

Once again there are two possible mechanisms: (1) hydrogen shift with concurrent three-membered ring formation, and (2) hydrogen shift with reorganization of the π system followed by valence tautomerization to the product, as depicted below. Analogies for these mechanisms have already been cited in the previous paper.[1]

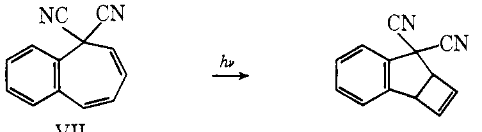


IV VI (1)



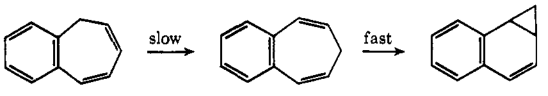
IV VI (2)

Ciganek[5] has recently shown that a related system, 7,7-dicyano-1,2-benzotropilidene (VII), photochemically rearranges to the tricyclic system VIII. The difference in photochemical behavior between I and VII is not surprising when one realizes that 7,7-dicyanotropilidene is completely different in its reactivity and photochemistry from tropilidene[5] and, in addition, the possibility for hydrogen migration is precluded in this system.

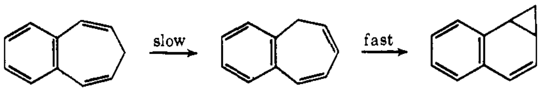


VII VIII

An important question which still remains unanswered is: is either I or III going photochemically to the other in a very inefficient process followed by a high quantum yield photochemical rearrangement to the product? That is, does one of the following reactions (3 or 4) occur? Reaction 4 can be ruled out by the product of the rearrangement of 7,7-dideuterio-3,4-benzotropilidene (IX). The following equations show that two possible dideuteriobenzonorcaradienes (X and XI) should be formed but only one, XI, is indeed formed (assuming a 1,3-hydrogen shift mechanism for formation of the 1,2-benzotropilidene). With the available data reaction 3 must still remain a possibility.



(3)



(4)

A comparison of the reaction course taken by I and that taken by the open-chain system, 1-phenyl-1,3-butadiene, indicates considerable differences. We have

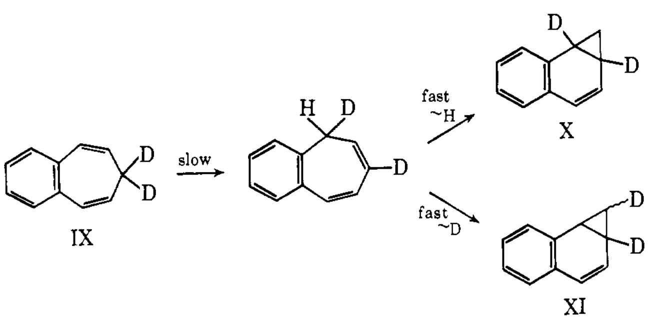
---

(2) Some 1,2-benzotropilidene was also prepared by pyrolysis of benzonorcaradiene.[3]

(3) E. Müller, H. Fricke, and H. Kessler, *Tetrahedron Letters*, 1525 (1964).

(4) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

(5) E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1458 (1967).



shown previously that not only does *trans*-1-phenyl-1,3-butadiene go to a photostationary mixture containing the *cis* and *trans* isomers but longer photolysis time results in electrocyclic ring closure to 3-phenylcyclobutene.[6] The difference may arise as a result of different conformations allowed in I and not in the phenylbutadiene or as a result of the hydrogen shift being the preferred pathway when feasible.

[6] M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966).

Martin Pomerantz, Gerald W. Gruber
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106

Received September 26, 1967

Pseudo-Rotation in *o*-Isopropylphenylbis(*p,p'*-bitolyl)phosphorane[1]

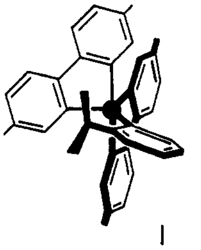
Sir:

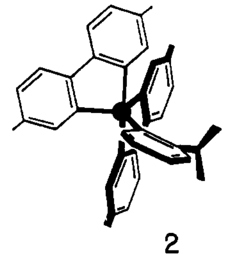
The facile intramolecular interchange of aryl groups between the axial and equatorial positions of pentaarylphosphoranes provides an important example of the stereochemical flexibility which characterizes a variety of pentacoordinate compounds.[2,3] The mechanism of this interchange is generally believed to be that originally suggested by Berry for phosphorus pentafluoride, in which the transition state for the pseudorotation of one ground-state trigonal bipyramid into another is a tetragonal pyramid.[4] However, other less symmetrical mechanisms for axial–equatorial exchange seem possible, particularly for compounds containing bulky or chelating ligands.[3] We wish to report the results of an nmr study of pseudo-rotation in *o*-isopropylphenylbis(*p,p'*-bitolyl)phosphorane (**1**), which support the applicability of the Berry mechanism to this more complicated system.

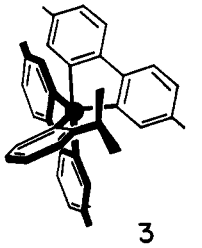
Compound **1** was prepared by the tosylimine procedure developed by Wittig and coworkers.[2,5] Its spectrum at 33° in bromobenzene solution consists of three lines at δ 2.60 (3 H), 2.52 (3 H), and 2.46 (6 H) for the bitolyl methyl protons,[6] and two doublets ($J = 6.6$ Hz) at δ 0.98 and 1.82 for the isopropyl methyl protons. On warming the sample to 130°, the bitolyl methyl signals collapse to a single line,[7] and the isopropyl resonances to a sharp doublet.

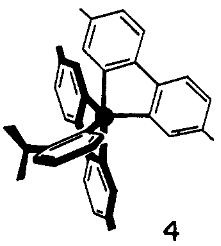
The magnetic nonequivalence of the four bitolyl methyl groups is consistent with the expected[8] trigonal bipyramidal structure **1**, with the restriction that rotation of the *o*-isopropylphenyl group (*e.g.*, **1** → **2**) is slow on the nmr time scale. The magnetic nonequivalence of the diastereomeric isopropyl methyl groups reflects their proximity to the chiral environment provided by the bis(*p,p'*-bitolyl)phosphorus center. This latter type of nonequivalence can be averaged only by reversing the sense of the chirality of the molecule (**1** → **3** or **4**); simple rotation of the *o*-isopropylphenyl group (**1** → **2**) leaves it unchanged.[9] Thus the lines shapes of the bitolyl methyl peaks in the exchange-broadened region provide a measure of the rate of interchange of axial and equatorial positions of **1**; the shapes of the isopropyl resonances provide an independent measure of the rate of interconversion of enantiomers. Comparison of these two rates provides a delicate probe with which to examine details of the pseudo-rotation process.

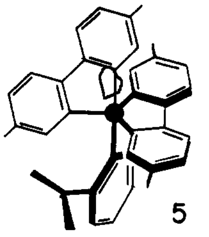
We have carried out kinetic analyses of the temperature dependence of the isopropyl and bitolyl methyl line shapes using standard techniques[10] and find that


1


2


3


4


5

---

[1] Supported in part by the U. S. Army Research Office (Durham), Grant ARO-D-31-124-G691, and by Eli Lilly and Co.

[2] G. Wittig, *Bull. Soc. Chim. France*, 1162 (1966).

[3] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); E. L. Muetterties, *Inorg. Chem.*, **6**, 635 (1967).

[4] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960). An infrared and Raman study of PF_5 has recently indicated that fluorine interchange does *not* take place along normal vibrational modes of the molecule: L. C. Hoskins and R. C. Lord, *ibid.*, **46**, 2402 (1967).

[5] D. Hellwinkel, *Ber.*, **99**, 3628, 3642, 3660 (1966). This work provides convincing evidence that the rate of racemization of optically active bis(biphenyl)phenylphosphoranes is too large to be amenable to polarimetric measurement.

[6] In nitrobenzene solution four lines are clearly resolved.

[7] Hellwinkel has reported similar observations: D. Hellwinkel, *Angew. Chem. Intern. Ed. Engl.*, **5**, 725 (1966); see also D. G. Gorenstein and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 2762 (1967).

[8] Good precedent for this structure is provided by an X-ray examination of bis(biphenyl)phenylantimony: J. Weiss, unpublished results quoted in ref 2; see also P. J. Wheatley, *J. Chem. Soc.* 2206 (1964); W. C. Hamilton S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, **87**, 127 (1965), for related structures.

[9] For examples of magnetic nonequivalence in dissymmetric systems, see W. L. Meyer and R. B. Meyer, *ibid.*, **85**, 2170 (1963); F. A. L Anet, A. J. R. Bourn, and Y. S. Lin, *ibid.*, **86**, 3576 (1964).

[10] R. Kubo, *Nuovo Cimento Suppl.*, **6**, 1063 (1957); R. A. Sack, *Mol. Phys.*, **1**, 163 (1958); C. S. Johnson, Jr., *Advan. Magnetic Resonance* **1**, 33 (1965).