Table I. Protodetritiation of 9-Trifluoromethylfluorene-9-*t*

[I-t], *N*	[NaOMe], *N*	Temp, °C	$10^4 k_1$, sec^{-1}	$10^3 k_2$,[a] l. mole^{-1} sec^{-1}
0.00421	0.143	−31.5 ± 0.3	20.9 ± 0.3	14.6 ± 0.2.
0.00421	0.262	−31.0 ± 0.1	44.2 ± 0.6	16.9 ± 0.2
0.00427	0.145	−45.3 ± 0.4	4.55 ± 0.02	3.13 ± 0.11
0.00427	0.266	−45.0 ± 0.1	9.02 ± 0.10	3.39 ± 0.37
		45		9700[b]

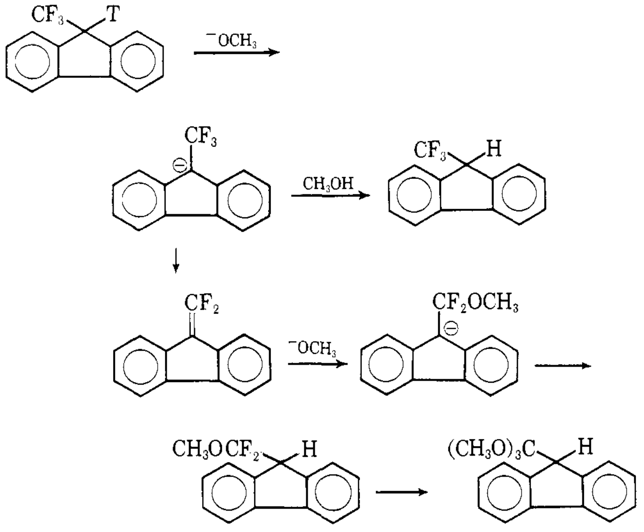
[a] At the reaction temperature; that is, k_2 is corrected for solvent contraction from room temperature. [b] Extrapolated from data at lower temperatures.

Table II. Protodetritiation of 9-Substituted Fluorenes in Methanolic Sodium Methoxide at 45°

9-Substituent, Y	k_{rel}[a]	p*K*[b] YCOOH
H	1.00	. . .
CH_3	0.26	4.76
CH_3CH_2	0.18	4.88
$CH_2C_6H_5$	0.72	4.31
CH_2OCH_3	12.9	3.57[c]
CF_3	2 × 10^4	−0.26, + 0.23

[a] k_2 for fluorene-9-*t* is (43.2 ± 1.5) × 10^{-5} l. mole^{-1} sec^{-1}. We are indebted to R. A. MacQuarrie, R. I. Sadayasu, J. S. Wright, and Dr. T. L. Kruger for individual kinetic runs. [b] J. F. King in "Technique of Organic Chemistry," Vol. XI, Part 1, K. W. Bentley, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 317. [c] E. J. King, *J. Am. Chem. Soc.*, **82**, 3575 (1960).

its inclusion would not alter the conclusions. A line drawn through the hydrocarbon substituents passes rather close to the point for the trifluoromethyl substituent. Because of the reactivity differences long extrapolations are required. The methoxymethyl group deviates significantly from the line, but this value is the result of a single kinetic run. The present conclusion does not change significantly if we draw the best line to include the methoxymethyl group. Because of the importance of the correlation line in defining the magnitude of inductive effects in the exchange reactions of 9-substituted fluorenes, we expect to define it more precisely with additional compounds and measurements. Nevertheless, the present data suffice to establish that the trifluoromethyl group does not produce reactivity significantly in excess of that expected from inductive effects alone. In particular, there is no room in these results for any significant contribution from C–F anionic hyperconjugation.



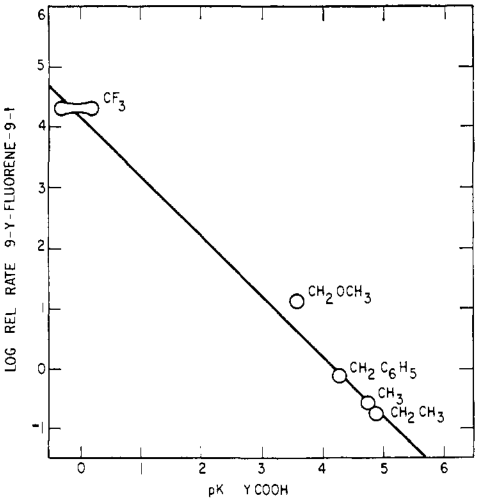


Figure 1. Comparison of kinetic acidities of 9-substituted fluorenes with the acidities of the corresponding substituted acetic acids.

This study and that of the preceding paper[1] are independent and involve different assumptions and logic, but lead to the same conclusion; taken together they provide compelling evidence for the absence of fluorine hyperconjugation as a significant stabilizing phenomenon in fluoroalkyl anions.

Acknowledgment. This research was supported in part by a Petroleum Research Fund grant and by Grant No. GM-12855 of the National Institutes of Health, U. S. Public Health Service.

(4) National Institutes of Health Postdoctoral Fellow, 1965–1966.

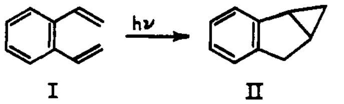
A. Streitwieser, Jr., Alan P. Marchand,[4] A. H. Pudjaatmaka
Department of Chemistry, University of California
Berkeley, California 94720

Received September 14, 1966

Photochemical Rearrangement of *o*-Divinylbenzene

Sir:

As a result of our interest in $C_{10}H_{10}$ compounds containing an aromatic ring fused to a system containing a small ring[1] we decided to examine a possible route to one or more of these by a photochemical rearrangement of *o*-divinylbenzene (I). When a solution of I, pre-



I II

---

(1) M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966).

pared by the method of Wittig,[2] in pentane was irradiated (100-w G.E. mercury lamp, H100-A4/T; Pyrex filter) for 10 hr, a 3–5% yield of benzobicyclo[3.1.0]hex-2-ene (II) was obtained, along with a trace of another product having a comparable glpc retention time and higher molecular weight products. Benzobicyclo[3.1.0]hex-2-ene (II) was identified by comparison to the known material synthesized by the method of Goodman and Eastman.[3]

In order to elucidate the mechanism of this transformation we looked at the rearrangement of *o*-divinylbenzene-d_4 (III) containing the deuterium atoms at the terminal methylene positions. The synthesis of this compound, containing 93% of four deuterium atoms, as determined by nmr spectroscopy, was carried out by treating triphenylphosphinemethylene-d_2 with *o*-phthalicdicarboxaldehyde in pentane–ether solution. The deuterated Wittig reagent was prepared from trideuteriomethyltriphenylphosphonium bromide and *t*-butyllithium in pentane–ether solution.[4] The deuterated phosphonium salt could be conveniently made by dissolving methyltriphenylphosphonium bromide in a 22-fold molar excess of D_2O, adding a small amount of NaOD in D_2O, warming to 50° for 1 hr, and removing the H_2O–D_2O with a rotary evaporator. Two additional exchanges with an 18-fold molar excess of D_2O finally gave, after drying the salt in vacuum, the deuterated phosphonium salt. Except for the observation that the nmr peaks due to the $-CH_3$ had vanished, no quantitative determination of the extent of deuteration of this salt was made. If one assumes no exchange in the Wittig reaction the salt was at least 93% deuterated. The yield of III was approximately 2%.

Location of the deuterium atoms in the product (II) requires assignment of the various bands in the nmr spectrum (Figure 1). By employing spin decoupling it could be shown that the peaks centered at τ 7.0 are due to the benzylic hydrogens H_5 and H_6 since they are coupled to only one other hydrogen, H_3, which appears at τ 8.3. Of the remaining three sets of peaks, at τ 7.8, 9.1, and 10.0, assignable to H_1, H_2, and H_4, the lowest field one must be the benzylic hydrogen, H_4. Thus, the cyclopropyl CH_2 group appears at the high-field positions of τ 9.1 and 10.0, as expected.[5]

The product of the photochemical rearrangement of III was shown by nmr spectroscopy to be IV. That is, all of the deuterium (± *ca.* 5%) in the product appeared at the methylene groups (IV) and none at H_3 or H_4 (V). Thus, as is indicated in Chart I, the mechanism for the reaction cannot involve hydrogen migration. The two other pathways shown in the chart are only schematic and are in no way meant to present the details of the mechanism. They differ only in the order of steps leading to VI and might represent the same concerted step.

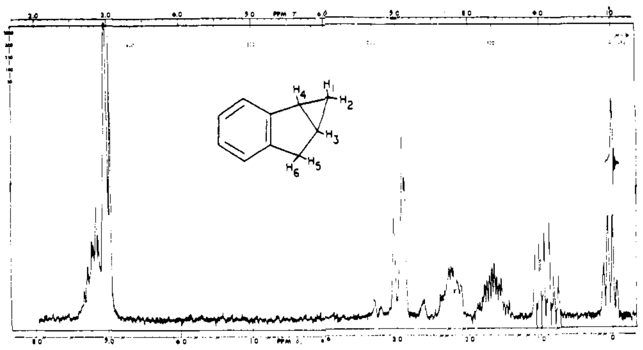
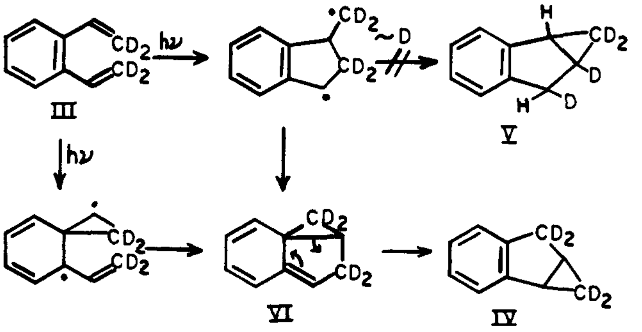
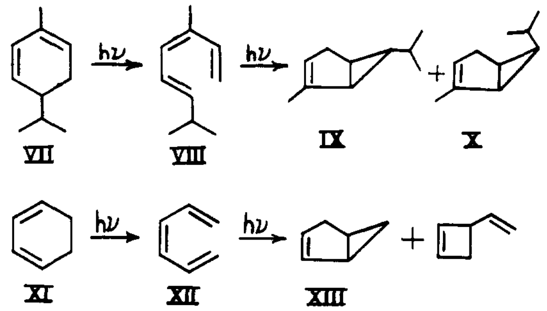


Figure 1. Nmr spectrum of benzobicyclo[3.1.0]hex-2-ene (neat; TMS external standard).

There are in the literature[7] a number of examples of this type of rearrangement of open-chain trienes: vitamin D_2 to suprasterol-II, α-phellandrene (VII) to IX and X, apparently *via* the triene VIII, and 1,3-cyclohexadiene (XI), probably *via* XII, to bicyclo[3.1.0]hex-2-ene (XIII). These first two reactions are most simply rationalized by assuming a reaction pathway not involving a hydrogen shift. The products, in all three cases, are those analogous to the intermediate VI.

Chart I





It would not necessarily have been predictable *a priori* that the photochemical rearrangement of *o*-divinylbenzene should proceed through VI since this involves loss of the benzene resonance energy. The energy initially absorbed by the molecule, however, is more than enough to compensate for this. The hydrogen shift mechanism, to give V, does not involve this loss of resonance energy. Once VI is formed it should rapidly rearrange, by a vinylcyclopropane–cyclopentene rearrangement, to the product, IV, as a

---

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

(3) A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964); A. L. Goodman, Ph.D. Thesis, Stanford University, Stanford, Calif., 1963.

(4) See A. Maercker, *Org. Reactions*, **14**, 270 (1965), for an excellent review of the Wittig reaction and general experimental procedures.

(5) Since *cis*-cyclopropane coupling constants are apparently larger than *trans* ones[6] the peak at τ 9.1, which shows coupling to H_3 and H_4 with a coupling constant of about 7–8 Hz, can therefore be ascribed to H_2 and that at τ 10.0 to H_1.

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

(7) W. G. Dauben and P. Baumann, *Tetrahedron Letters*, 565 (1961); J. Meinwald, A. Eckell, and K. L. Erickson, *J. Am. Chem. Soc.*, **87**, 3532 (1965); J. Meinwald and P. H. Mazzocchi, *ibid.*, **88**, 2850 (1966).

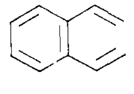
result of a gain in resonance energy and some loss of strain energy.

Martin Pomerantz
Department of Chemistry, Case Institute of Technology
Cleveland, Ohio 44106
Received November 29, 1966

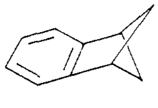
Photoisomerization of *o*-Divinylbenzene[1]

Sir:

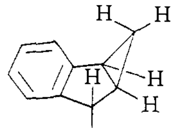
Research on the photochemistry of 1,3,5-hexatrienes[2] has led us to study the photochemistry of *o*-divinylbenzene (I), a related system in which the central double bond is replaced by a benzene ring. We expected as one possible photoreaction of I a head-to-tail cycloaddition between the two vinyl groups to give benzobicyclo[2.1.1]hexene (II), a nucleus which was unknown until most recently.[3,4]



I



II

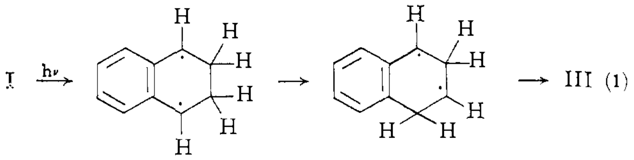


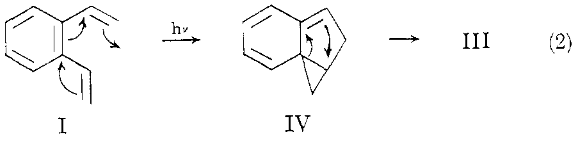
III

Irradiation of a 0.2% ethereal solution of I with a 450-w Hanovia high-pressure mercury lamp, through a Corex filter, proceeded with the appearance of a single, volatile product as determined by glpc analysis. In a typical experiment using 2.0 g of I, the starting material was completely consumed after 4.5 hr of irradiation, and a 30% yield of the volatile product (estimated by glpc) had formed. Distillation of the reaction mixture afforded a pure sample of this material, which was established to be 1,1a,6,6a-tetrahydrocycloprop[*a*]indene (III),[5] rather than II, on the basis of the following evidence.

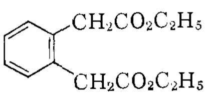
The infrared spectrum of III showed absorption maxima at 3030 (m), 2900 (w), 1600 (w), 1475 (s), 805 (m), 790 (m), 758 (s), and 720 (s) cm^{-1}. In its nmr spectrum, III showed complex mutliplets centered at τ 10.0 (*endo* cyclopropyl proton), 9.1 (*exo* cyclopropyl proton), 8.3 and 7.8 (homobenzylic and benzylic bridgehead protons), 7.1 (benzylic methylene protons), and 3.1 (aromatic protons), in a ratio of 1:1:1:1:2:4.[6] These spectra, clearly excluding structure II, were found to be identical with those of authentic III, synthesized previously by Goodman and Eastman.[7]

An interesting feature of this photoisomerization is the necessity of either a hydrogen atom migration, such as that shown in eq 1, or a carbon skeleton rearrangement. An attractive version of the latter might be based on the initial cyclization of I to IV, closely analogous to one mode of 1,3,5-hexatriene cyclization,[2] followed by a vinylcyclopropane–cyclopentene rearrangement which restores the aromatic ring (see eq 2). Deuterium tracer studies described below have now excluded mechanism 1 and similar hydrogen atom rearrangements, but are in accord with expectations based on mechanism 2.

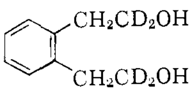




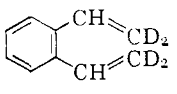
Reduction of ethyl *o*-phenylenediacetate (V) with lithium aluminum deuteride gave diol VI, which was dehydrated over potassium hydroxide at 180–200° (60 mm)[8] to give $\beta,\beta,\beta',\beta'$-tetradeuterio-*o*-divinylbenzene (VII) in 47% over-all yield. The mass spectrum of VII showed its parent peak at *m/e* 134 and indicated that the product was at least 97% d_4 labeled. The nmr spectrum of VII showed no discernable β-proton absorption.



V

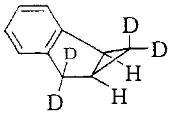


VI



VII

Irradiation of VII, carried out as described above, gave deuterated 1,1a,6,6a-tetrahydrocycloprop[*a*]indene, isolated in 29% yield by careful distillation. The nmr spectrum of this product showed *only* aromatic absorption at τ 3.1 and the two bridgehead protons in their previously observed positions as an AB quartet ($J \cong 7$ cps). This spectral evidence establishes unambiguously the labeling pattern shown in formula VIII, as required by mechanism 2. Deuterium or hydrogen atom rearrangements are excluded.



VIII

Further experiments have indicated that similar isomerizations occur with *o*-divinylbenzene derivatives bearing substituents on the olefinic carbon atoms, and we are now engaged in a more detailed investigation of these novel reactions.

Jerrold Meinwald, Paul H. Mazzocchi[9]
Department of Chemistry, Cornell University
Ithaca, New York 14850
Received December 6, 1966

---

(1) The partial support of this research by National Science Foundation Research Grant GP-4128 is acknowledged with pleasure.

(2) For leading references and a review of this area of photochemistry see J. Meinwald and P. H. Mazzocchi, *J. Am. Chem. Soc.*, **88**, 2850 (1966); H. Prinzbach, H. Hagemann, J. Hartenstein, and R. Kitzing, *Chem. Ber.*, **98**, 2201 (1965).

(3) H. Tanida and Y. Hata, *J. Am. Chem. Soc.*, **88**, 4289 (1966).

(4) M. Pomerantz, *ibid.*, **88**, 5349 (1966).

(5) A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

(6) These assignments were made on the basis of chemical shifts and coupling constants; *cf.* W. G. Danben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964).

(7) We wish to thank Professor Eastman for providing us with the infrared and nmr spectra of authentic III.

(8) J. O. Halford and B. Weissmann, *J. Org. Chem.*, **17**, 1646 (1952).

(9) National Institutes of Health Postdoctoral Fellow, 1965–1967.