of the General Electric Company for the obtention of the ^{13}C nmr spectrum.

(8) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient.
(9) National Institutes of Health Predoctoral Fellow.

Barry M. Trost,*[8] Peter J. Whitman[9]
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

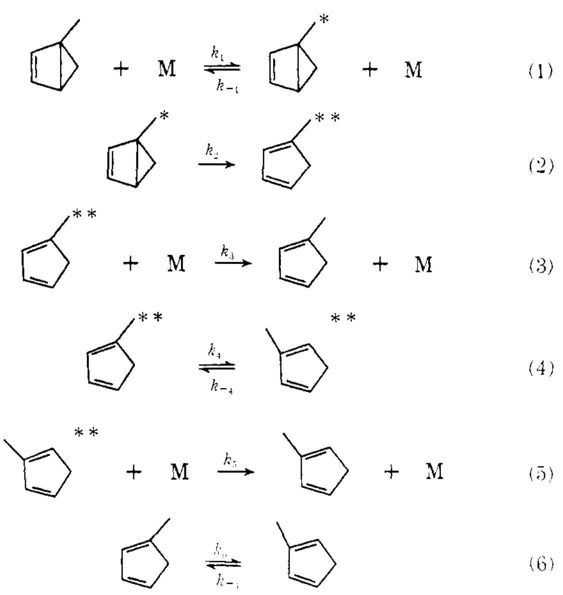
Received August 18, 1972

Hot Molecule Effects in the Thermal Isomerization of Methylbicyclo[2.1.0]pent-2-enes

Sir:

There is a controversy about the mechanism of the isomerization of bicyclo[2.1.0]pent-2-ene to cyclopentadiene. Originally a biradical process was proposed.[1,2] Later experiments[3] with deuterated bicyclopentene and 2-methylbicyclo[2.1.0]pent-2-ene were interpreted as conclusive evidence for the occurrence of an allowed $[_{\sigma}2_s + {}_{\sigma}2_a]$ process. The methyl compound results have not been substantiated and diametrically opposite experimental results have been reported.[4] These two sets of data were obtained in the liquid phase. About this work we merely note in passing that even if the allowed process were of major importance the experimental findings of Baldwin and Andrist[3] of only *one* product are inexplicable on kinetic grounds.

The report of some gas-phase results prompts us to present some RRKM calculations that are pertinent. Briefly, Baldwin and Andrews[5] found that in the gas phase at 50°, 1-methylbicyclo[2.1.0]pent-2-ene isomerizes to both 1-methyl- and 2-methylcyclopentadiene. Similarly, 2-methylbicyclo[2.1.0]pent-2-ene gave both methylcyclopentadienes. Since the interconversion between the cyclopentadienes is appreciably slower at 50° than is the isomerization of the bicyclo[2.1.0]pent-2-enes they conclude that the decomposition of each reactant yields both cyclopentadienes directly. This would be consistent with allowed processes (but would not, incidentally, be subject to the kinetic objections mentioned above). These experimental findings are completely explicable on the basis of the initial formation of only *one* isomer (the one predicted by the biradical mechanism) and are exactly as expected. The scheme is shown below for 1-methylbicyclo[2.1.0]pent-2-ene (eq 1–6). Step 1 represents the collisional activation–deactivation process of a unimolecular reaction and steps 3 and 5 simple collisional deactivation steps. Step 6 is a shorthand form and is applicable to all unimolecular reactions in their high-pressure region. Steps 2 and 4 may be treated by RRKM theory.



Reliable Arrhenius parameters are not available for k_6 and k_{-6}; however, calculations have been carried out using the rate constants reported by Baldwin and Andrews[5] at 50° and assuming an "A" factor for both reactions of 10^{13}. Other calculations used an "A" factor of 10^{12}, deliberately chosen to be unrealistically low, and also a further set used different A factors for k_6 and k_{-6} to increase the possible difference in energy of activation of these reactions. The results are presented in Table I. The values of the ratios of 1- and 2-methylcyclopentadienes (A/B) at various pressures correspond to hypothetical "zero time" reactions. In Table II we report the time evolution of the system.

Table I. Ratio of 1- to 2-Methylcyclopentadiene as a Function of Pressure

	Pressure, Torr				
	1	10	100	1000	10^6
A/B^a	0.937	0.939	0.951	1.07	140
A/B^b	0.938	0.944	1.01	1.639	670
A/B^c	1.647	1.650	1.670	1.870	220

[a] Assuming $\log k_6 = 13 - 26{,}745/\theta$; $\log k_{-6} = 13 - 26{,}967/\theta$. [b] Assuming $\log k_6 = 12 - 25{,}271/\theta$; $\log k_{-6} = 12 - 25{,}493/\theta$. [c] Assuming $\log k_6 = 12.7 - 26{,}299/\theta$; $\log k_{-6} = 13.0 - 26{,}967/\theta$. $\theta = 2.303RT$; $R = 1.987$ cal mol^{-1} K^{-1}.

Table II. Time Evolution of System at 50°

	Time, sec				
	0	500	1000	4000	8000
A/B^a	1.009	1.008	1.006	0.998	0.984
A/B^b	1.639	1.634	1.629	1.593	1.538

[a] At 100 Torr. [b] At 1000 Torr. Data relate to footnote *b* of Table I.

Table I shows that irrespective of the particular choice of Arrhenius parameters the ratio A/B is essentially constant below 100 Torr and does not increase greatly up to 1000 Torr. At very high pressures the ratio of A/B is sufficiently large that little or no 2-methylcyclopentadiene should be formed in the liquid phase in accord with the findings of McLean, *et al.*[4]

The predicted ratio of A/B for runs carried out at around 1 atm pressure is between 1.0 and 1.75 depending on the particular choice of Arrhenius parameters; Baldwin and Andrews[5] obtained 1.6. Within the un-

---

(1) J. I. Brauman and D. M. Golden, *J. Amer. Chem. Soc.*, **90**, 1920 (1968).

(2) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

(3) J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *J. Amer. Chem. Soc.*, **92**, 5249 (1970); J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

(4) S. McLean, D. M. Findlay, and G. I. Dmitrienko, *J. Amer. Chem. Soc.*, **94**, 1380 (1972).

(5) J. E. Baldwin and G. D. Andrews, *ibid.*, **94**, 1775 (1972).

certainties of the data used this agreement must be considered remarkable.

The formation of the "wrong" methylcyclopentadiene arises because step 2 yields a molecule which contains the energy of activation of this step and the large contribution due to the high value of ΔH for this reaction. (This was estimated[6] to be 36 kcal mol^{-1}, but calculations using values of 35 and 36.5 kcal mol^{-1} produced insignificant changes in A/B). The methylcyclopentadiene initially contains more than 63 kcal mol^{-1} of excess energy; the energy of activation for step 4 (and, of course, 6) is about 26 kcal mol^{-1}, so this process takes place very rapidly in the absence of collisional stabilization. Thus, although the interconversion between methylcyclopentadienes (and, similarly, 5-deuteriocyclopentadiene and its isomers) is relatively slow at 50°, because they are produced by what is essentially a process of chemical activation, this interconversion is of considerable importance, under the experimental conditions employed.

The calculated values of A/B depend only on the validity of RRKM theory and the energetics of the reaction; they do not depend on the detailed nature of the transition state. Thus, while the results are *consistent* with a biradical mechanism they do not *require* such a mechanism; the results do, however, require that by whatever process (biradical or concerted), 1-methylcyclopentadiene is formed directly from 1-methylbicyclo[2.1.0]pent-2-ene. The fact that the ratio of A/B is close to the experimental value means that it is probable that the mechanism presented represents the system completely, and hence it is unnecessary to postulate the *direct* formation of any 2-methylcyclopentadiene. Even if a small fraction of the yield of 2-methylcyclopentadiene did arise directly, this could not be determined on the basis of the gas-phase experiments reported, nor indeed from any gas-phase experiments that could be carried out at reasonable pressures.

(6) S. W. Benson and H. E. O'Neal, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. **21** (1970).

M. C. Flowers
Chemistry Department, Southampton University
Southampton, England
H. M. Frey*
Chemistry Department, Reading University
Reading, England

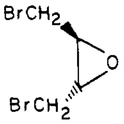
Received May 15, 1972

Spiro[4.4]nonatetraene and Spiro[4.4]nona-1,3,7-triene

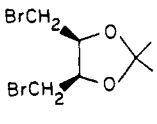
Sir:

Spiro[4.4]nonatetraene (**1**) has been the subject of discussion concerning the overlap of orthogonal ribbons of p orbitals[1] (spiro conjugation) and experimentally accessible examples of planar tetracoordinate carbon.[2] It has also been the subject of at least two attempted syntheses,[3] both of which failed to provide detectable quantities of **1**. Highly substituted derivatives, such as 1,2,3,4-tetramethyl-6,7,8,9-tetrachlorospiro[4.4]nonatetraene, have been prepared[4] but are not useful in testing the relevant bonding theories because of electronic and/or steric perturbations by the substituents. We wish to report direct and simple syntheses of spiro[4.4]nonatetraene and spiro[4.4]nona-1,3,7-triene (**2**).[5]

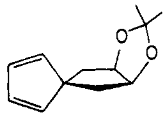
Originally, an efficient route to **2** was sought as a potential pathway to **1**, and cyclopentadiene (**3**) was chosen as an obvious synthon. Treatment of *trans*-2,3-epoxy-1,4-dibromobutane (**4**) with acetone in the presence of stannic chloride produced a mixture of *cis*- and *trans*-2,2-dimethyl-4,5-bis(bromomethyl)dioxolanes (**5a** and **5b**) in the ratio of 10:1, respectively.[6] Condensation of cyclopentadiene with **5a** using excess sodium hydride in tetrahydrofuran gave the spirodioxolane **6** in 50–60% yield (bp 80–84° (3.0 Torr)). Hydrolysis of **6** (dilute hydrochloric acid in aqueous methyl alcohol under conditions of slow distillation) produced the diol **7** which was converted to the bis-*p*-toluenesulfonate ester **8** (mp 124–126°, 40% overall for **6** → **8**). All attempts to convert the diol **7** to spiro[4.4]nonatetraene (**1**) *via* pyrolysis of the diacetate **9** or dixanthate **10** gave low (*ca.* 20%) yields of indene as the only C_9H_8 product. Similarly, attempted base-promoted elimination of *p*-toluenesulfonic acid from **8** failed to produce **1**.



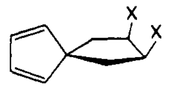
4



5a



6



7, X = OH
8, X = OSO$_2$-*p*-tolyl
9, X = OCOCH$_3$
10, X = OCS$_2$CH$_3$

The reaction of excess sodium iodide with **8** in acetone at 100° in a closed system for 20 hr gave spiro[4.4]nona-1,3,7-triene (**2**) in 70% yield, after short-path distillation. The triene **2** is obviously an attractive precursor of **1**, but all attempts to introduce a substituent such as halide at C-6 failed. For example, reaction of **2** with *N*-bromosuccinimide under the usual conditions for allylic bromination led to indene in 23% yield; no monobromide of **2** was isolated. The failure of the above approaches to **1** is not surprising, considering the reactivity of **1** (see below).

A very simple, low-temperature approach to **1** proved successful. The diacid chloride **11** (bp 57° (1.0 Torr)) of diallylmalonic acid was prepared from the diacid using thionyl chloride in carbon tetrachloride at reflux for 15 hr (88% yield). In methylene chloride solution containing several mole equivalents of nitromethane, the diacid chloride **11** reacted with aluminum

---

(1) (a) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5219 (1967); (c) R. Boschi, A. Dreiding, and E. Heilbronner, *ibid.*, **92**, 123 (1970).

(2) R. Hoffmann, R. W. Alder, and C. F. Wilcox, *ibid.*, **92**, 4992 (1970).

(3) (a) D. J. Cram and B. L. van Dauren, *ibid.*, 77, 3576 (1955); (b) D. Schonleber, *Chem. Ber.*, **102**, 1789 (1969).

(4) (a) E. T. McBee, G. W. Calundann, and T. Hodgins, *J. Org. Chem.*, **31**, 4260 (1966); see also (b) G. Haas and V. Prelog, *Helv. Chim. Acta*, **52**, 1202 (1969).

(5) Spiro[4.4]nona-1,3,7-triene (**2**) is observed as a minor product during condensation of sodium cyclopentadienide with *cis*-1,4-dichlorobut-2-ene: (a) M. F. Semmelhack and J. Foos, unpublished observations; (b) ref 3b.

(6) M. S. Malinovskii, V. G. Dryak, A. G. Yudasina, and N. N. Maksimenko, *Zh. Org. Khim.*, **2**, 2086 (1966).