

spectroscopic⁷ and combustion analysis as well as by the reduction of isolated intermediates.

The exclusive formation of product **3** in the low temperature reduction indicates a mechanistic characteristic of interest, that is, either a carbene (probably not carbenoid) species is involved or a Fritsch–Buttenberg–Wiechell rearrangement may be operating in the rearrangement process. In the former process, carbanion **11**, which is formed by the stepwise two-electron reduction⁸ of **1**, must be the precursor and this undergoes elimination of Cl^- to generate cyclopropylidene **12**, kinetically favored at lower temperatures. Carbene **12**, instead of giving a highly strained allenic structure as the usual behavior of cyclopropylidenes, undergoes aryl shift to give cyclopropene **13**, which, in turn, easily isomerizes into methylenecyclopropane derivative **14** by base catalysis.⁹ The structure of **3**, however, does not exclude the possibility of a methyl shift in **12** although it seems less favorable. Mechanistic possibility of the latter process (F–B–W rearrangement) may

(7) **4**: nmr 7.79 (6 H, s), 7.81 (6 H, s), 7.88 (3 H, s), 8.08 (3 H, bs), 8.13 (3 H, s), 8.21 (3 H, bs); P^+ (m/e) 334; mp 217°. **5**: nmr (all singlet) 3 H at 7.80, 7.91, 7.98, and 8.04, 6 H at 7.83 and 8.43; P^+ 334; mp 187°. **6**: nmr (all singlet) 6 H at 7.86, 7.90, 8.44, and 8.79, 2 H at 8.14; P^+ 336. **7**: nmr 3.81 (H, m, $J = 1.4$ Hz), 4.13 (H, m, $J = 1.5$ Hz), 7.84 (6 H, s), 7.85 (6 H, s), 8.14 (3 H, d, $J = 1.4$ Hz), 8.17 (3 H, d, $J = 1.5$ Hz), 8.43 (6 H, s); P^+ 266; λ_{max} (cyclohexane) 233 nm ($\log \epsilon$ 4.30), 330 (1.46); mp 104°. **8**: nmr 3.86 (H, m, $J = 1.6$ Hz), 4.53 (H, q, $J = 7$ Hz), 7.73 (3 H, s), 7.76 (6 H, s), 7.78 (3 H, s), 7.91 (3 H, d, $J = 1.6$ Hz), 8.09 (3 H, bs, $J = 2.5$ Hz), 8.32 (3 H, bs, $J = 2.5$ Hz), 8.54 (3 H, d, $J = 7$ Hz); P^+ 266; λ_{max} 223 (4.33), 278 (3.67). **9**: nmr singlet (6 H) at 7.67, 7.83, 8.74, and 8.84, 2 H at 7.80 and 9.78; P^+ 268.

(8) (a) D. B. Ledrie, R. L. Thorne, and G. Weiss, *J. Org. Chem.*, **36**, 2186 (1971); (b) J. Jacobus and D. Pensak, *Chem. Commun.*, 401 (1969).

(9) G. Schroeder, *Chem. Ber.*, **96**, 3178 (1963).

also exist. For example, sodium naphthalene reduction of the adduct obtained by the addition of dichlorocarbene to 1,2,3,4-tetramethylnaphthalene did not give a similar product as **3** but ring opened products even at -78° . However, referring to the less covalent character of the sodium–carbon bond and the configuration of the anionic center,¹⁰ this process seems less plausible. More evidence for carbene intermediate was offered by the sodium naphthalene reduction of 7,7-dichloro-1,6-dimethylnorcaradiene,¹¹ in which the formation of hydrocarbons C_9H_{14} and $\text{C}_{18}\text{H}_{28}$ was confirmed.

The ring-opening process¹² predominating at 25° apparently requires higher activation energy than ring retention. Actually, however, the energy can be lowered by the release of strain of the tricyclic system **11**. Formation of a stable carbanion, **15**, which is more stable than the alternative, **15a**, may also be another cause of lowering energy if the opening of two rings is concerted. Carbanion **15**, thus formed, behaves as a precursor of carbene **16**, which undergoes β -bond migration of either aryl or methyl to give **4** or **5**, respectively.

(10) In F–B–W-type rearrangement, the leaving halide group should be oriented trans to the migrating aryl moiety (see Kirmse "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, p 103), that is, anion **11** should have syn configuration which seems less likely; see also footnote 12.

(11) Unpublished results.

(12) According to the Woodward–Hoffmann rule, only anti anion **11** can give rise to ring opened products having cis olefinic bonds. Syn anion, which may be a minor portion, if any, may therefore operate in the proton abstraction to give **6** and **9**. The predominant population of the anti anion would be due to charge repulsion between the electron-rich aryl ring and carbanion orbital.

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Thermal Rearrangement of 3,4-Bis(trimethylsiloxy)-endo-tricyclo[4.2.1.0^{2,5}]nona-3,7-diene and the C_9H_{10} Rearrangements Controversy

Sir:

At temperatures between 350 and 450° (<2 sec contact time) in a conventional Vycor flow system, the title compound (**1**)¹ is quantitatively isomerized to 4,5-bis(trimethylsiloxy)-cis-8,9-dihydroindene (**2**). At 325° , the rearrangement proceeds to approximately half completion and no other intermediates or products are detected by pmr examination of the crude pyrolysate. Compound **2** is characterized by its uv spectrum² ($\lambda_{\text{max}}^{\text{cyclohexane}}$ 281 nm (ϵ 4400)), ir spectrum ($\nu_{\text{C}=\text{C}}^{\text{neat}}$ 1590, 1660 cm^{-1}), mass spectrum (M^+ 294), and pmr spectrum (see Figure 1).

Owing to the complexity of the pmr spectrum, de-

(1) H. Bode, *Chem. Ber.*, **70**, 1167 (1937), describes the diester which can be converted by the method of J. J. Bloomfield, *Tetrahedron Lett.*, 587 (1968), to **1**: 66% yield; bp $94-95^\circ$ (0.5 mm); M^+ 294; nmr spectrum (CCl_4 , 60 MHz) δ 0.16 (s, two OSiMe_3), 1.44 and 1.87 (broadened AB, CH_2 bridge, $J_{\text{AB}} = 8.0$ Hz), 2.38 to 2.70 (m, four bridgehead H's), 5.68 (t, two olefinic H's, $J \approx 1$ Hz). Dr. R. D. Miller in a private communication has confirmed the endo configuration by spectral comparison with both isomers; cf. R. D. Miller and D. Dolce, *Tetrahedron Lett.* 4541 (1972). All new compounds had satisfactory microanalyses.

(2) T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **85**, 2852 (1963), report $\lambda_{\text{max}}^{\text{EtOH}}$ at 262 (ϵ 3710) and 271 nm (ϵ 3240) for cis-8,9-dihydroindene and $J_{\text{AB}} = 12$ Hz for the bridgehead protons (whereas $J_{\text{AB}} = 20$ Hz for the trans isomer).

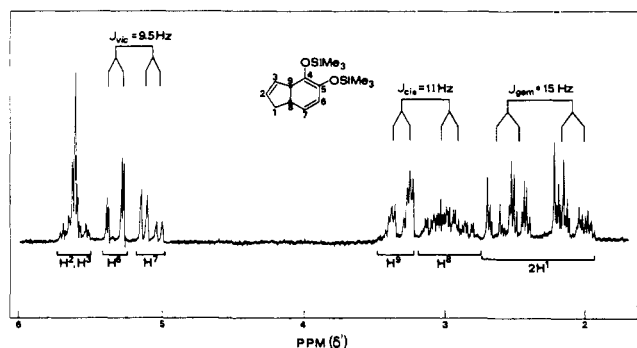
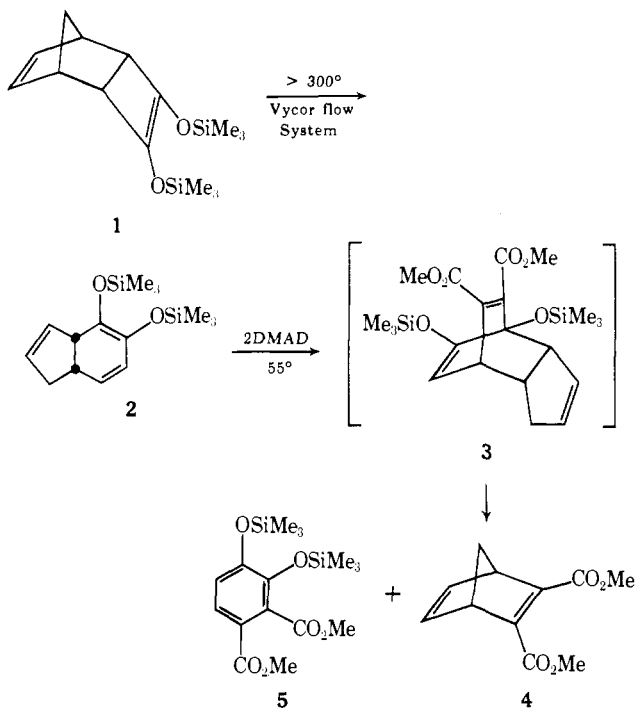


Figure 1. A 90-MHz (CCl_4) pmr spectrum of the nuclear protons of **2** relative to the OSiMe_3 protons at 0 Hz.

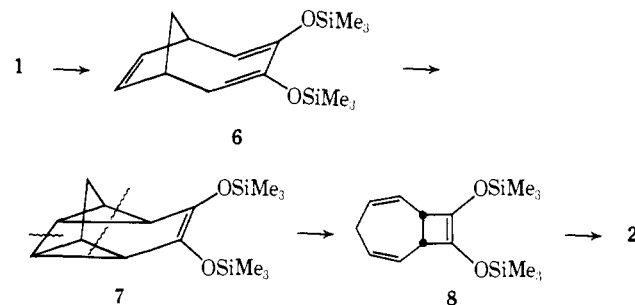


coupling experiments were required to establish the *cis* configuration at the bridgehead ($J_{\text{cis}} \approx 11$ Hz),² and the positioning of the five-ring double bond as pictured. Irradiation at the centers of the H^6 , H^7 , and $\text{H}^6\text{-H}^7$ frequencies caused collapse of the H^8 multiplet and irradiation at the $\text{H}^2\text{-H}^3$ frequency caused collapse of the H^9 multiplet. The additional fine structure in H^8 is apparently a result of coupling with the adjacent CH_2 . The relative chemical shifts are as expected. These assignments were confirmed by further extensive decoupling experiments (including INDOR) on the tetracyanoethylene adduct of **2** (mp 132–135°).

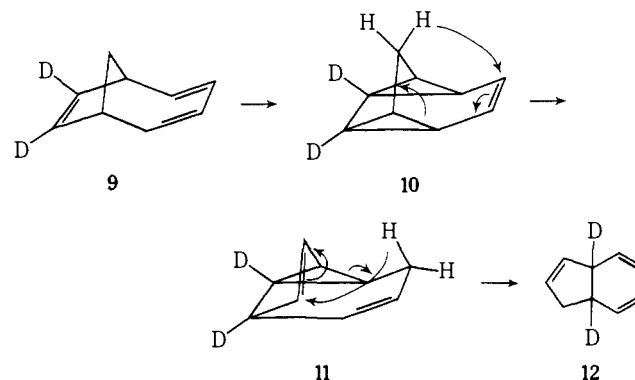
Compound **2** was readily converted by dimethyl acetylenedicarboxylate (DMAD) to its Diels–Alder adduct (**3**), which underwent a very facile Diels–Alder retrogression under the conditions of addition, ultimately yielding the cyclopentadiene adduct of a second molar equivalent of DMAD (**4**) and the unsymmetrical 3,4-bis(trimethylsiloxy)phthalic acid dimethyl ester (**5**).³ This result established the substitution pattern for the trimethylsiloxy groups as pictured in **2**.

(3) Compound **5** has bp 122° (0.07 mm), M^+ 370, and pmr spectrum (CCl_4 , 60 MHz) δ 0.16 and 0.26 (two singlets for OSiMe_3 's), 3.68 and 3.70 (two singlets for CO_2Me 's), and 6.58 and 7.27 (AB system for ring H^1 's, $J_{\text{ab}} = 8.0$ Hz).

Based on some related skeletal rearrangements that occur or are postulated to occur in this temperature range (*i.e.*, corresponding to steps $1 \rightarrow 6$,⁴ $6 \rightarrow 7$,^{5,6} and $8 \rightarrow 2$,⁷) and a hypothetical concerted σ_{2s} , σ_{2b} , σ_{2a} cleavage for $7 \rightarrow 8$, the following plausible rearrangement scheme emerges.



Interestingly, all other rearrangement schemes (mostly concerted) devised thus far for the C_9H_{10} energy surface^{4–7} predict a product isomer having the same skeleton as **2** but with the 4,5-bis(trimethylsiloxy) substituents at the 5,6- or 6,7-positions. The most closely analogous scheme appears to be suggested in ref 6 to account for the major path leading to the interesting D-labeling pattern found in the dihydroindene (**12**) resulting from rearrangement of **9**. Note



that it is only the rearrangement of the postulated intermediate (**7**) and that of its postulated hydrocarbon counterpart (**10**)⁶ where the divergence of mechanism appears to occur. Perhaps the trimethylsiloxy substituents in **7** are blocking the migration of the hydrogen atom as proposed for the hydrocarbon case (*i.e.*, step $10 \rightarrow 11$)⁶ and in this way altering the remaining reaction path.

Whatever the cause, the results reported here indicate a fundamental dichotomy between the hydrocarbon and the bis(trimethylsiloxy) substituted cases under consideration so that neither is of predictive value with regard to the other. Thus, it would seem that progress in elucidation of substituent effects in valence isomerizations should be brought abreast of the progress gained in understanding the rearrangements of the pure hydrocarbons.

(4) H. M. Frey, J. Metcalfe, and J. M. Brown, *J. Chem. Soc. B*, 1586 (1970).

(5) T. S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5868 (1967).

(6) J. A. Berson, R. B. Boettcher, and J. J. Vollmer, *J. Amer. Chem. Soc.*, **93**, 1540 (1971), and references cited therein.

(7) A. G. Anastassiou and R. C. Griffith, *J. Amer. Chem. Soc.*, **93**, 3083 (1971).

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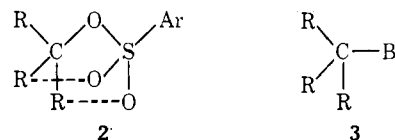
Received August 24, 1973

A Remarkably Large Solvolytic Rate Enhancement Due to Relief of Ground State Leaving Group Strain¹

Sir:

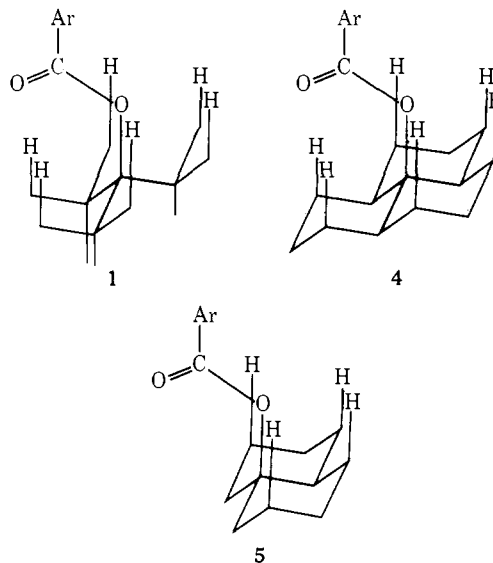
In the past, the significance of ground state steric strain specific to different leaving groups, if considered at all, has often been dismissed as an important contributor to solvolytic rate accelerations.²⁻⁵ Thus, explanations for the large increase in tosylate-bromide ratios in going from primary to tertiary substrates have stressed effects which influence transition state energies;⁶ steric effects were discounted.^{6a,7} The greatly enhanced solvolytic reactivities of highly branched tertiary *p*-nitrobenzoates,^{3,8} such as tri-*tert*-butylcarbinyl-OPNB (**1**-OPNB),⁹ have been attributed to relief of ground state repulsive nonbonded interaction among the alkyl groups during ionization (B strain).^{8,9a} The possibility that rate enhancement by relief of leaving group strain (F strain)^{9b} may be quite large apparently has not been appreciated until recently.³

In contrast, Schleyer, *et al.*, have pointed out that tertiary tosylates (**2**) suffer from 1,5-nonbonded interactions not present in the corresponding bromides (**3**).^{4,5} Relief of ground state tosylate strain during ionization may be the major factor contributing to the large OTs-Br ratios in tertiary systems and may be important in secondary substrates as well.^{4,5} We now



report unambiguous evidence that relief of similar 1,5- (and 1,6-)nonbonded interactions in congested tertiary *p*-nitrobenzoates can contribute as much as 10³ to 10⁴ acceleration to solvolytic reactivity.

We postulate a remarkably large ground state leaving group effect to explain the 2860-fold solvolytic rate enhancement at 25° of *trans,trans,trans*-perhydro-9b-phenanyl-OPNB (**4**-OPNB) relative to *trans*-9-decalyl-OPNB (**5**-OPNB).^{1a} **4**-OPNB but not **5**-OPNB suffers



(1) Based in part on the Ph.D. Theses of (a) W. C. Dickason, Purdue University; *Diss. Abstr.*, 2559-B (1970); (b) R. C. Bingham, Princeton University, 1970; *Diss. Abstr.*, 7178-B (1971).

(2) Exceptions include: (a) effects of the halogen on the rates of solvolysis of tertiary halides (H. C. Brown and A. Stern, *J. Amer. Chem. Soc.*, **72**, 5068 (1950)); (b) effects of the size of leaving group on the direction of bimolecular elimination (H. C. Brown and R. L. Klimisch, *ibid.*, **88**, 1425 (1966); R. A. Bartsch, *J. Org. Chem.*, **35**, 1023 (1970), and references cited therein); (c) relative solvolysis rates of cyclopropyl derivatives (W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 133 (1972), also see ref 3-5).

(3) J. E. Dubois and J. S. Lomas, *Tetrahedron Lett.*, 1791 (1973).

(4) (a) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2538 (1970); (b) J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *ibid.*, **92**, 2542 (1970).

(5) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).

(6) (a) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965); (b) *Tetrahedron Lett.*, 4393 (1967); (c) G. M. Fraser and H. M. R. Hoffmann, *J. Chem. Soc. B*, 265 (1967); (d) H. M. R. Hoffmann and G. M. Fraser, *ibid.*, 425 (1967); (e) R. G. Pearson and J. Songstad, *J. Org. Chem.*, **32**, 2899 (1967); (f) D. D. Roberts and J. G. Traynham, *ibid.*, **32**, 3177 (1967); (g) J. W. S. Trahanovsky and M. P. Doyle, *Chem. Commun.*, 1021 (1967); (h) A. F. Cockerill, *Tetrahedron Lett.*, 4913 (1969); (i) C. H. DePuy and C. A. Bishop, *J. Amer. Chem. Soc.*, **82**, 2532 (1960).

(7) Similarly, M. L. Sinnott and M. C. Whiting, *J. Chem. Soc. B*, 965 (1971), "eliminated" differential steric effects as a contributing factor to erratic tosylate-picrate leaving group ratios.

(8) (a) P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, **77**, 2806 (1955); (b) P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968). This paper does point out that "the more reactive [ester] has the greater steric hindrance around the leaving group," but this observation is not further developed.

(9) (a) H. C. Brown and R. S. Fletcher, *J. Amer. Chem. Soc.*, **71**, 1845 (1949); H. C. Brown, *Science*, **103**, 385 (1946); (b) H. C. Brown, M. D. Taylor, M. Gerstein, and H. Bartholomay, *J. Amer. Chem. Soc.*, **66**, 431 (1944); **69**, 1332 (1947).

from unavoidable repulsive interactions involving (depending on the conformation of the *p*-nitrobenzoate group) the carbonyl oxygen, the carbonyl carbon, and/or the aryl group. These special 1,5- and 1,6-type interactions will not be present in the corresponding chlorides **4**-Cl and **5**-Cl.

In systems not suffering from such 1,5- and 1,6-nonbonded interactions, quantitative conformational analysis can be used to predict reactivities with reasonable success.^{5,10} In the present degree of refinement of this approach, the leaving group is not considered explicitly. The ground state energies are approximated by the parent hydrocarbon and transition state free energies by the carbocation. The difference in these calculated energies, $\Delta H(\text{calcd})$, is a reactivity index; for **4**, $\Delta H(\text{calcd})$ is 8.6 kcal/mol. On the basis of eq 1,⁵ the

$$-\log k_{\text{Cl}, 80\% \text{EtOH}, 70^\circ} = 0.32\Delta H(\text{calcd}) + 2.15 \quad (1)$$

predicted rate for **4**-Cl is $4.9 \times 10^{-5} \text{ sec}^{-1}$ at 70° in 80% ethanol,^{1b} a value which is one-twelfth that found experimentally for **5**-Cl (Table I).

The major discrepancy between this prediction and the experimental *p*-nitrobenzoate data (at 70° in 80% acetone, **4**-OPNB/**5**-OPNB = 466), prompted us to synthesize **4**-Cl. This was accomplished from **4**-OH by hydrochlorination in pentane in the presence of anhydrous FeCl₃ at -78°. **4**-Cl, mp 83.5-84.5°, which had consistent microanalysis and spectra data, gave

(10) J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 4628 (1972), and references cited therein.