

Expectedly, the proportions of these isomers increased with the input of added heat to the system. To achieve maximum sensitivity in product composition analysis, recourse was made to a combination of vpc⁶ and quantitative infrared techniques.⁷

Control experiments performed under precisely identical conditions showed that rearrangement to the 1,3-dimethyl isomer occurs to a small degree from both 7 and 9 at 465° (Table II). The levels of these isomeriza-

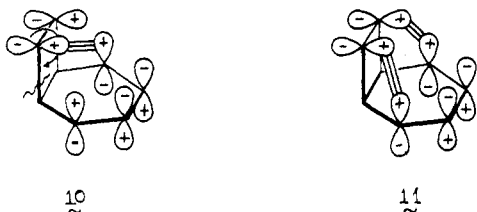
Table II. Control Experiment Data for 7, 8, and 9

Hydrocarbon	Temp, °C	Pressure, mm	Recovery, % ^a	1,2- (9), %	1,3- (8), %	1,4- (7), %	1,5- (4), %
7	435	18	75			100	
	450	18	68	4	5	83	8
	465	18	60	6	19	61	14
8	480	18	83		100		
	525	18	49	8	27	51	14
	395	18	71	100			
9	435	18	70	95		5	
	450	18	63	91		9	
	465	18	58	84	3	11	2

^a Values relate to purified (vpc) hydrocarbon mixture.

tions are such, however, that they could easily account for the amount of 8 which obtains during thermolysis of 4 and consequently becloud the possibility of assaying the direct 4 → 8 conversion, if operative.⁸

Notwithstanding, the thermal behavior of 4 is consistent only with an overall predominance of the Diels-Alder mechanism.⁹ Detailed analysis of the reactivity patterns of 7-9 is similarly reconcilable with a marked preference of these systems for pathway i. Perhaps the concerted [1,5] migration alternative is disfavored because of the orbital symmetry requirement that the sp²-hybridized cyclobutene carbon migrate with retention rather than "opposite-face" bonding through the antisymmetric p orbitals as in 10. This imposition



(6) Our most satisfactory vpc results were achieved with a 0.125 in. × 20 ft 5% PMPE 6-ring on Chromosorb G column operating at 40°. Under these conditions, quantitative assay of the 1,2- ($t_{ret} = 9.58$ hr), 1,5- ($t_{ret} = 10.66$ hr), and 1,3-/1,4- ($t_{ret} = 8.83$ hr) ratio was possible.

(7) The four isomerically pure cyclooctatetraenes exhibit selected fingerprint infrared absorptions which are mutually exclusive of each other; 1,2-, 646, 710, and 857 cm⁻¹; 1,3-, 600, 708, and 828 cm⁻¹; 1,4-, 655, 701, and 844 cm⁻¹; 1,5-, 627, 722, and 891 cm⁻¹. To obtain the ratio of 1,3- to 1,4-dimethyl compounds in the pyrolysate, the relative intensities of the 708 (ϵ 210) and 701 cm⁻¹ (ϵ 182) bands were determined.

(8) In contrast to the data of Table II, the original product composition ratios for pyrolysis of 7 and 9 are now considered of low accuracy because of too great reliance on pmr spectroscopy as the method of analysis. We have since found pmr methods to be quantitatively unreliable for this series of hydrocarbons.

(9) We have considered, and subsequently discounted, the possibility that the pair of 1,5-sigmatropic rearrangements available to 5 and 6 are so energetically imbalanced as to give only 4 (degenerate reaction and consequently unobservable) to the exclusion of 8. Rather, the transition states of the processes in question are assumed to bear a close quantitative resemblance.

forces the potential migratory carbon to maintain an ungainly spatial relationship to the migration terminus, a factor not present in the competing [π 4_s + π 2_s] transition state (11).¹⁰

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(10) Nonconcerted diradical alternatives to these mechanisms are less attractive explanations of our findings since they lack electronic allowedness and a maximum of contiguous bonding.

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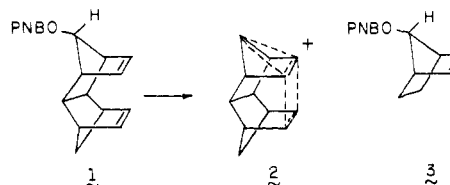
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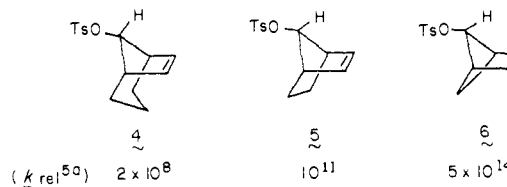
Kinetic Evidence Attesting to the Absence of Enhanced Anchimeric Assistance during Solvolytic Generation of Unsymmetrical (2 + 2 + 0) Laticyclic Cations

Sir:

Remarkably little attention has been given to ionic systems endowed with laticyclic topologies comprised of more than two ribbons¹ despite the extensive structural variations possible and inherent novelty of such species. In the first and only example known to us, Allred and Hinshaw examined the solvolysis of *p*-nitrobenzoate 1 and concluded on the basis of rate constant comparisons that this π -orbital arrangement furnished perhaps the largest driving force to ionization yet discovered.² Enhanced ionic stabilization was presumed and attributed to extended charge delocalization epitomized by nonclassical ion 2. However, the dearth of experimental data on relevant model compounds other than *anti*-7-norbornenyl derivative 3 re-



quires this theoretical interpretation to be less than unambiguous. Because π participation seems to be a sensitive function of puckering of the 5-ring in the bicyclo[*x*.2.1] series, e.g., 4-6,^{3,4} comparable effects by more



subtle strain influences could be anticipated but remained untested. We now wish to report convincing evidence which shows that the enhanced solvolytic reactivity of 1 need not be attributed to laticyclic stabilization arising from involvement of the more remote

(1) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

(2) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 1293 (1968).

(3) B. A. Hess, Jr., *J. Amer. Chem. Soc.*, **91**, 5657 (1969).

(4) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969).

(5) (a) 7-Norbornenyl tosylate, $k_{rel} = 1$; (b) *anti*-7-norbornenyl tosylate, $k_{rel} = 10^{11.1}$.

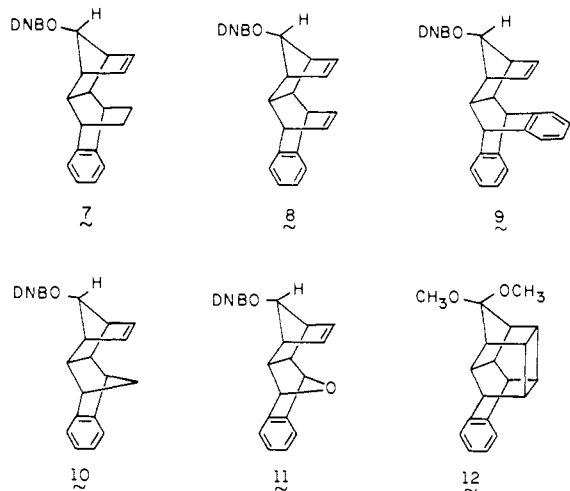
Table I. Kinetic Data for Solvolysis in 80% (v:v) Aqueous Acetone

Compd	Temp, °C ^a	k , sec ⁻¹	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu	100° k_{rel}	114° k_{rel}
7	85.00	$(1.13 \pm 0.10) \times 10^{-5}$	27.3 ± 0.6	-5.2 ± 1.9	2.3	2.3
	99.95	$(5.63 \pm 0.60) \times 10^{-5}$				
	112.00	$(1.79 \pm 0.19) \times 10^{-4}$				
	114 ^b	2.19×10^{-4}				
8	86.00	$(1.13 \pm 0.09) \times 10^{-5}$	27.3 ± 0.5	-5.5 ± 1.4	2.1	2.1
	100.00	$(5.05 \pm 0.28) \times 10^{-5}$				
	114 ^b	1.95×10^{-4}				
	116.00	$(2.33 \pm 0.13) \times 10^{-4}$				
9	114.00	$(2.32 \pm 0.25) \times 10^{-4}$	28.0 ± 2.2	-5.2 ± 5.8	1.0	1.0
10	84.80	$(4.27 \pm 0.30) \times 10^{-5}$				
10	99.90	$(2.41 \pm 0.26) \times 10^{-5}$	27.1 ± 0.6	-8.9 ± 1.7	0.5	0.5
	113.70	$(8.69 \pm 0.35) \times 10^{-5}$				
	114 ^b	9.27×10^{-5}				
11	100.00	$(1.24 \pm 0.04) \times 10^{-5}$	27.1 ± 0.6	-8.9 ± 1.7	0.5	0.5
	114 ^b	4.79×10^{-5}				
	114.75	$(5.05 \pm 0.15) \times 10^{-5}$				
	126.03	$(1.44 \pm 0.10) \times 10^{-4}$				
1-ODNB	100 ^c	3×10^{-5}			1.2	
3-ODNB	100 ^d	1.52×10^{-7}			0.006	

^a All temperatures $\pm 0.1^\circ$ or better. ^b Extrapolated or interpolated from the activation parameters. ^c Value obtained by assuming solvent change identical in magnitude with that found for **3** (see footnote *d*) and employing the relationship $k_{ODNB}/k_{OPNB} = 6$ [P. v. R. Schleyer and G. W. Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966), footnote *i* of Table I]. ^d Value obtained by transforming the rate constant of **3-OPNB** in 60% aqueous dioxane and 70% aqueous acetone [M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967)] to 80% aqueous acetone by means of the relevant *Y* values for these media and correction for the ODNB leaving group as in footnote *c*.

etheno bridge as in **2**. This is not to say that ion **2** completely lacks extended delocalization⁶ but only that anchimeric assistance above that available from customary homoaromatic interaction generated in the *anti*-7-norbornenyl part structure is not demonstrable in kinetic terms.

3,5-Dinitrobenzoate **8** was prepared by Diels-Alder condensation of benzobarrelene with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, dechlorination of the adduct with sodium shot and *tert*-butyl alcohol in anhydrous tetrahydrofuran, and deketalization in 3 *M* aqueous perchloric acid, followed by stereospecific lithium aluminum hydride reduction and reaction with 3,5-dinitrobenzoyl chloride in pyridine.⁷ Stereochemical assignment to the cycloadduct was founded initially on analogy⁸ and confirmed by acetone-sensitized photolysis of the dechlorinated ketal to **12** in 97%



(6) Appropriate pmr and cmr studies in superacid media might serve to clarify this issue.

(7) All new compounds gave satisfactory elemental analyses and structures were verified by spectral techniques.

(8) R. McCulloch, A. R. Dye, and D. Wege, *Tetrahedron Lett.*, 5163 (1969); D. Wege, *ibid.*, 2337 (1971).

yield. Hydrogenation of the first-formed adduct over 5% Pd-C led to selective reduction of the nonchlorinated double bond and eventually to ester **7**. The remaining esters **9-11** were similarly synthesized, and their overall stereochemistry was ascertained by appropriate Eu(DPM)₃ shift data obtained on the penultimate alcohols.

Solvolyses were carried out with 0.002-0.005 *M* solutions of the dinitrobenzoates in 80% aqueous acetone at several temperatures, except for **9** which, because of its insolubility in this medium at lower temperatures, was studied only at 114.0°. The reactions were followed by titration of the resultant 3,5-dinitrobenzoic acid and exhibited clean first-order behavior. The rates are given in Table I together with extrapolated results for **1-ODNB** and **3-ODNB**. Product analyses revealed that alcohol of identical stereochemistry was formed exclusively in each instance. When **7** was heated in unbuffered methanol at 175° for 3 days, 7-OMe was obtained (81% isolated) admixed with minor amounts of 7-OH and methyl 3,5-dinitrobenzoate. These findings denote that alkyl-oxygen cleavage operates and that formation of new σ bonds as a result of possible π -electron stabilization does not gain importance. From this viewpoint, **7-11** parallel closely the behavior of both **1** and **3**.

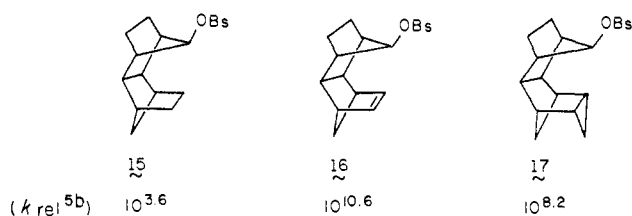
Within the limits of the kinetic measurements, all of the dinitrobenzoates solvolyze some 10^2 times more rapidly than **3-ODNB**. Thus, laticyclic interaction, if operative, must be a minor factor in the overall stabilization of developing cations **1+**, **8+**, and **9+** by comparison to dominant homoaromatic delocalization.⁹ Quantitative assessment of the contributions of various other factors to these rate accelerations is difficult to

(9) It has been recognized previously from theoretical¹ and experimental vantage points¹⁰ that molecules containing two ribbons having the potential for laticyclic interaction possess also homoaromatic components which exert the dominant influence. The present examples seem to agree with this generalization.

(10) M. V. Moncur and J. B. Grutzner, *J. Amer. Chem. Soc.*, **95**, 6449 (1973); M. Goldstein and S. Natowsky, *ibid.*, **95**, 6451 (1973).

make at this time. We note, however, that **7**, **8**, and **9** share the common feature of slightly enhanced (two- to fivefold) reactivity over the group consisting of **1**–**ODNB**, **10**, and **11**. In every case, the additional bicyclic moiety is endo fused (at C₄,C₅) to the 7-substituted norbornenyl framework, but methano bridging as in the latter series increases the angle separating the remaining two-carbon bridges in this appendage.¹¹ Diminution in intrabridge nonbonded interactions may possibly ensue.^{12,13}

Accordingly, the present situation differs in a significant way from the behavior of somewhat related doubly bridged laticyclic systems such as **15**–**17**^{14–16}

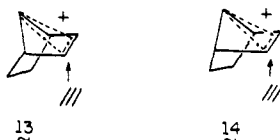


where remote stabilizing influences are convincingly manifested in kinetic acceleration. One is led to conclude that abrupt changes in electron-deficiency demand markedly affect the need for laticyclic interaction, so much so that the additional π bridge in cations possessing (2 + 2 + 0) topology contributes little to anchimeric assistance.¹⁷

(11) M. J. Goldstein, S. Natowsky, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **56**, 294 (1973).

(12) Factors other than steric compression which may contribute to the enhanced rates of ionization include differences in the field and orbital electronegativity inductive effects for oxa, methylene, etheno, and ethano bridges and differences in the geometries of the 7-norbornenyl moieties in the more highly bridged systems.

(13) When apprised of our results, L. M. Loew and R. Hoffmann initiated an EH search of possible interactions which might arise upon approach of an acetylene molecule to the underside of "normal" and "bent" 7-norbornenyl cations as in **13** and **14**, respectively. Their



calculations have revealed that even at intra- π distances as small as 3 Å, no meaningful interaction is generated in either model (private communication).

(14) S. Winstein and R. L. Hansen, *J. Amer. Chem. Soc.*, **82**, 6206 (1960).

(15) S. Winstein and R. L. Hansen, *Tetrahedron Lett.*, **4** (1960).

(16) M. A. Battiste, J. Haywood-Farmer, H. Malkus, P. Seidl, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2144 (1970).

(17) Research supported in part by grants from the National Science Foundation and Chevron Research Co. whom we thank.

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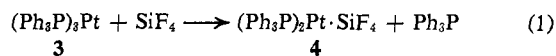
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Some Chemistry of Silicon Tetrafluoride with Transition Complexes in Glass Vessels

Sir:

The close correspondence between the activation parameters for addition of triphenylphosphine and of silicon hydrides to the reactive intermediate hydrido-carbonylbis(triphenylphosphine)iridium(I) (**1**) led to the hypothesis that the primary interaction between the

addend and the Ir^I, on the approach to the transition state, was a π acceptance of electrons by the former from the latter.¹ An obvious test of the validity of this hypothesis would be the demonstration of coordinate bond formation between a π -acid possessing no lone pairs and a π -basic metal. To explore the possibility of such bond formation, a study of the reaction of SiF₄ with hydridocarbonyltris(triphenylphosphine)iridium(I) (**2**) was undertaken. Encouragement to continue this approach was provided by a report that SiF₄ formed a coordination complex with a bis(triphenylphosphine)platinum(0) moiety, by displacement of triphenylphosphine from tris(triphenylphosphine)platinum(0) (**3**) (eq 1).² Such a reaction would be



difficult to rationalize on grounds other than that Pt⁰ behaves more as a π -base than as a σ -acid.

Reaction of **2** with a slight excess of SiF₄ in benzene at room temperature gave a pale yellow, coarse crystalline precipitate, **5**, over a period of several hours. After recrystallization from benzene, **5** gave strong bands in the infrared at 875, 780, 477, and 445 cm⁻¹ (KBr disk), due to Si–F modes. The compound also gave a singlet at ϕ 136.4 due to ¹⁹F resonance, in methylene chloride solution. These physical parameters were indistinguishable from those reported for **4**.² They are also in accord with values reported for SiF₅⁻ salts.^{3–5} The similarity of the infrared spectrum of **5** in the $\nu_{\text{Ir-H}}$ (2100 s, 2140 sh cm⁻¹) and $\nu_{\text{C-O}}$ (2000 cm⁻¹) regions to the spectra of the dihydride resulting from addition of silicon hydrides to **2**⁶ was striking. The presence of the 1,2-dihydrido-3,4,5-tris(triphenylphosphine)carbonyliridium(III) cation (**6**) in **5** was confirmed by observation of its 60-MHz pmr spectrum at high field in methylene chloride [H(1), τ 20.5; H(2), τ 22.2; $J_{\text{H-H}} = 4$ Hz; $J_{\text{H1-P3,5}} = 20$ Hz; $J_{\text{H2-P4}} = 100$ Hz; $J_{\text{H1-P4}} = 20$ Hz].⁷ After establishment of the presence of the latter cation in **5**, it became virtually certain that the silicon was present as SiF₅⁻.

The compound **5** consistently gave a sharp resonance due to free benzene in its pmr spectrum. That this benzene was present as benzene of crystallization was suggested by the fact that the crystals melted sharply at 92°, resolidified, and decomposed without further melting at 170°. After melting, the crystals lost weight and the features in the infrared and pmr spectra due to benzene of crystallization disappeared. Chemical analysis, weight loss, and pmr integral measurements all suggested the presence of roughly three molecules of free benzene per iridium. Although **5** consistently gave good C, H, and P analyses for the pentafluorosilicate of **6**, the Si and F analyses were always poor.

Since no successful structure determination for SiF₅⁻

(1) J. F. Harrod, C. A. Smith, and Khin Aye Than, *J. Amer. Chem. Soc.*, **94**, 8321 (1972).

(2) T. R. Durkin and E. P. Schram, *Inorg. Chem.*, **11**, 1048 (1972).

(3) H. C. Clark, K. R. Dixon, and J. G. Nicolson, *Inorg. Chem.*, **8**, 450 (1969).

(4) I. Wharf and M. Onyszczuk, *Can. J. Chem.*, **48**, 2250 (1970).

(5) H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, **90**, 2259 (1968).

(6) J. F. Harrod, D. F. R. Gilson, and R. Charles, *Can. J. Chem.*, **47**, 2205 (1969).

(7) D. Commereuc, I. Douek, and G. Wilkinson, *J. Chem. Soc. A*, 1771 (1970); L. Malatesta, G. Caglio, and M. Angoletta, *J. Chem. Soc.*, 6974 (1965); L. Vaska, *Chem. Commun.*, 614 (1966); M. S. Fraser and W. H. Baddeley, *J. Organometal. Chem.*, **36**, 377 (1972).