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Effects of a Remote Double Bond or Cyclopropane Ring on Electrophilic Aromatic Substitution[1]

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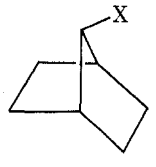
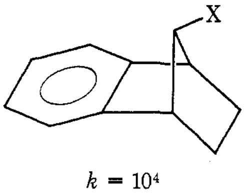
Relative positional reactivities have been determined for nitration of benzonorbornene (1), benzonorbornadiene (2), and the corresponding *exo-* and *endo-*benzotricyclo[3.2.1.0^{2,4}]octenes (3 and 4). For β positions, homoconjugation in 2 and 3 dominates over hyperconjugative effects; for α and ipso positions, inductive effects dominate. A "buttressed fused ortho effect" is proposed to account for the lower α reactivity of 3 than of 4.

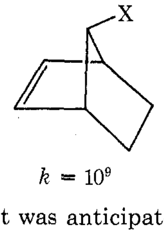
There is continued widespread interest in interactions between electron-deficient centers and remote (i.e., nonconjugated) double bonds, arenes, and cyclopropane rings.^{2} However, little attention has been turned to the effects of a remote double bond or cyclopropane ring on electrophilic substitution reactions of an aromatic ring; experimental approaches to determination of optimum geometries for such interactions have not been reported. Consideration of the literature on remote participation effects facilitated a choice of substrates for this type of study. As summarized recently,^{2a} conformationally mobile molecules thus far have afforded no kinetic evidence of significant contributions from cyclopropane participation. In contrast, fusion of a cyclopropane ring into a rigid framework has produced some of the most dramatic solvolysis rate variations known, as exemplified by the group of compounds formulated below (X = brosylate or *p*-nitrobenzoate).^{3}



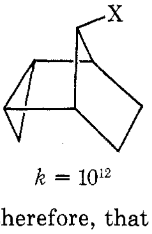
$k_{\mathrm{rel}} = 1.00$



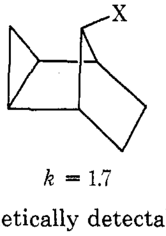
$k = 10^4$



$k = 10^9$

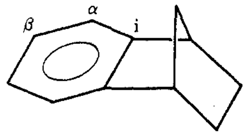


$k = 10^{12}$



$k = 1.7$

It was anticipated, therefore, that kinetically detectable interaction between arene and remote cyclopropane (or double bond) moieties would be found in a study of the series of rigid structures 1–4. Further impetus was given to this work by the discovery^4 that 1 undergoes detectable ($\sim$3%) ipso^5 (i) nitration; thus the influence of remote substituents might be accessible via measured reactivities at each of three distinct arene positions.



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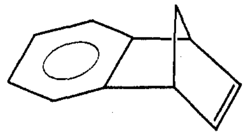

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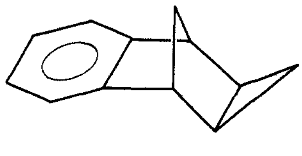

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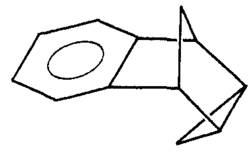

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Results and Discussion

Benzonorbornadiene (2), prepared by established methods,^{6} was converted to 1 by catalytic hydrogenation and to a 95:5 mixture of 3 and 4 by Simmons–Smith cyclopropanation.^{7,8} Pure 3 was obtained by crystallization from the mixture; pure 4 was obtained by chromatography of the enriched mother liquor.

Certain features of the nitration study by Tanida and Muneyuki^9 were adapted to the present work; indan and tetralin were nitrated for comparison purposes, with the latter used as a standard (rel rate = 1.00) for computation of substrate reactivities. Because of the sensitivity of 2, 3, and 4 toward other nitrating agents, nitrations were performed with copper nitrate in acetic anhydride (0 °C). Product mixtures were subjected to VPC analysis; product distributions were checked against artificial mixtures of similar composition. Percentages of nitro compounds (α and β) for 1, indan, and tetralin were nearly identical with those previously re-

Table I. Isomer Ratios and Relative Rates for Nitration of 1. Indan, and Tetralin in Different Media

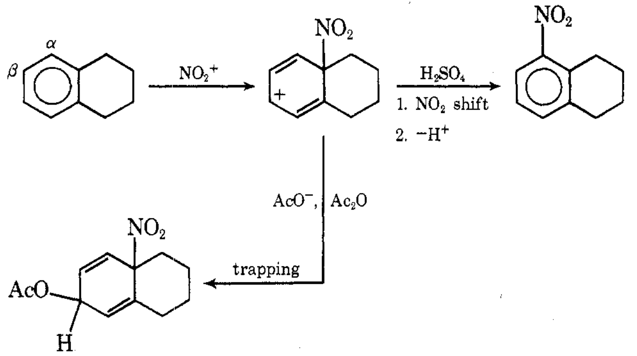
Substrate	α:β Ratio[c]	Rel rate
1[a]	7/93	1.88
1[b]	3/97	3.92
Indan[a]	50/50	1.27
Indan[b]	27/73	1.01
Tetralin[a]	52/48	1.00[d]
Tetralin[b]	37/63	1.00[d]

[a] Reference 9; HNO_3–H_2SO_4, CH_3NO_2, 0 °C. [b] This work; $Cu(NO_3)_2 \cdot 3H_2O$, Ac_2O, 0 °C. [c] In the present work, duplicate nitrations were done for each substrate; distributions were within ± 3% of the average values. Repetitions of work done elsewhere gave equally good agreement. [d] Standard of comparison.

ported[9,10] for nitration in nitric acid–acetic anhydride. To interrelate nitration rates, pairwise competitive nitrations were performed: 1 vs. **2**, **3**, indan, and tetralin; **3** vs. **4**; **4** vs. indan; indan vs. tetralin. Percentages of both isomers of both compounds in each competition were determined and checked as in individual nitrations.

Discussion will center first on those aspects of the present results bearing on attack of the nitrating agent at ipso positions. Tanida and Muneyuki,[9] on nitrating **1**, indan, and tetralin with nitric–sulfuric acid, reported 1 to be about twice as reactive as the other two substrates (Table I). However, nitric–sulfuric acid nitration now is known to allow ipso nitroarenium ions (exemplified by tetralin in Scheme I) to rearrange and deprotonate, falsely enhancing the reactivity of the α position. Nitration in acetic anhydride leads to extensive[11] trapping of these nitroarenium ions (Scheme I); α-nitro derivative then is *not* the ultimate product of normal workup. Because indan and tetralin appear to undergo ca. 50% ipso attack[10,12] whereas 1 gives evidence of only 3% ipso attack,[4] the α reactivities for indan and tetralin, as well as the total substrate reactivities toward *direct* (non-ipso) nitration are inflated in the Tanida–Muneyuki work, relative to the corresponding values for 1. When the ipso effect is taken into account, closer agreement is found between the two studies, although our nitration conditions still appear to afford a more selective nitrating agent.

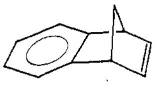
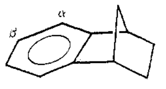
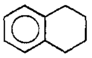
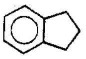
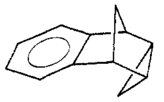
Scheme I



Results of nitration of all substrates in the present study are assembled in Table II. Because no ipso nitration was observed for **2**, **3**, or **4**, ipso partial rate factors have been omitted for all compounds,[13] and the relative rates given are only for non-ipso aromatic nitration. That they are reliable in this regard is indicated by the stability of all nitro derivatives under conditions of nitration and workup.[14]

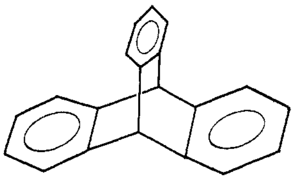
With a few exceptions, the range of relative rates is not large. Interpretation therefore is confined here to salient features, with more extensive discussion available as supplementary material (see paragraph at end of paper).

Table II. Relative Rates[a] and Partial Rate Factors[b] for Nitration[c] of Selected Benzomono-, -bi-, and -tricyclic Compounds

Compd	Structure	Rate[c]	α/β[d]	α_f	β_f
3		6.47	0.2/99.8	0.02	10.2
2		6.28	0.1/99.9[e]	0.01[e]	9.9
1		3.92	2.9/97.1	0.18	6.0
Tetralin		1.00	37/63	0.56	1.00
Indan		1.01	27/73	0.43	1.2
4		0.84	5.8/94.2	0.08	1.2

[a] Relative to tetralin. [b] Relative to the β position of tetralin. [c] Competitive nitration with copper nitrate in acetic anhydride at 0 °C. [d] See footnote *c*, Table I. [e] Approximate value.

The inértness of ipso and α positions in 2–4 (at least 50 times less reactive than the β positions in 2 and 3) is attributed principally to inductive electron withdrawal from these positions. These results are consistent with previous reports of very high preferences for β-nitration in triptycene (**5**),[15] janusene (**6**),[16] and other compounds containing homoconjugated π systems.[15] Precedent for inductive deactivation of an ipso position by a cyclopropyl group is found in the apparently complete preference for ipso attack at C_3 in substrate **7**.[17,18]



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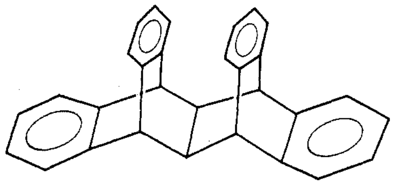

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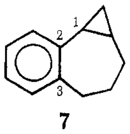

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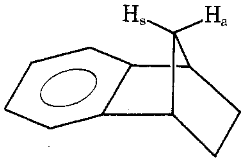
An a priori unexpected feature of Table II is the greater α reactivity of **4** than of **3**. No α-activating effect can be proposed for **4**, relative to **3**; we suggest a deactivating steric factor for **3**. The C_7 syn proten (H_s) in 1 has been held responsible for some of the steric hindrance to α-attack in 1 ("fused ortho effect").[9] Incorporation of an exo (but not an endo) cyclopropane ring into that skeleton (to give **3**) introduces severe nonbonding interaction between H_a and a cyclopropane methylene hydrogen. This interaction should force the methylene bridge (and H_s) closer to the α carbons, generating a "buttressed fused ortho effect" in this case. The viability of



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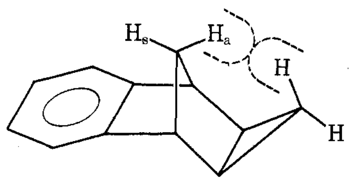


3

this explanation is under study.

Experimental Section

Proton magnetic resonance spectra were obtained with a Varian A-60 or a Varian XL-100; ultraviolet spectra were recorded on a Perkin-Elmer Model 202 or a Cary 118. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E mass spectrometer. Melting and boiling points are uncorrected.

***exo-* and *endo*-Benzo[6,7]tricyclo[3.2.1.0^{2,4}]octane (3 and 4).** These compounds were prepared as a 95:5 mixture from benzonorbornadiene using the Simmons–Smith procedure.[7] Separation of the isomers began with low-temperature crystallization of **3** from pentane until **4** had been enriched to 20–30%. Pure **4** then was obtained by chromatography on silica gel, using pentane as the elutant. Physical properties of **3** and **4** are given below.

3: mp 37 °C (lit.[20] 35–37 °C); bp 40–41 °C (1 mm); ir (neat, NaCl) 3000 (cyclopropyl C–H), 1485, 1438, 1290, 1258, 1240, 1160, 1140, 1085, 1065, 970, 940, 930, 897, 860, 820, 799, 735, 720, and 677 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.1 (m, 4 H, aryl), 3.27 (s, 2 H, H$_1$ and H$_5$), and 1.65–0.68 (m, 6 H, –CH$_2$– and cyclopropyl H's).

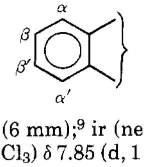
4: bp 38–39 °C (1 mm); ir (neat, NaCl) 2950 (cyclopropyl C–H), 1380, 1150, 1115, 980, 780, 740, 710, and 678 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.05 (s, 4 H, aryl), 3.27 (m, 2 H, bridgehead H's), 2.25 (dt, 1 H, J = 2.0, 8.0 Hz, syn H$_8$), 2.0 (d, 1 H, J = 8.0 Hz, anti H$_8$), 1.63 (m, 2 H, H$_2$ and H$_4$), 0.45 (m, 1 H, anti H$_3$), and −0.70 (overlapping dt, 1 H, J = 2.0, 6.0 Hz, syn H$_3$).

Indan was prepared from distilled indene by hydrogenation over 10% Pd/C in a Parr hydrogenator. Commercial tetralin was passed through a column of alumina and distilled prior to use, as was indan.

General Procedure for Nitration with Copper Nitrate Trihydrate. The hydrocarbon in acetic anhydride was pipetted into a cooled (0 °C in an ice–salt bath) round-bottom flask. Freshly powdered copper nitrate trihydrate was added to the cooled solution, and the reaction was maintained at 0 °C with magnetic stirring for 1–2 h. The mixture was poured onto ice and an equal volume of water was added. Solid sodium bicarbonate was added to the magnetically stirred solution at 0 °C. When no more gas evolution (CO$_2$) was observed, the water layer was extracted three times with half volumes of ether. The combined ether layers were washed once with an equal volume of 5% aqueous sodium bicarbonate and once with an equal volume of water. The solution was dried (MgSO$_4$) and ether was removed on a rotary evaporator. The nitro compounds were isolated by column chromatography on silica gel (60–80 mesh, grade 95%, Fisher S-662, 30:1) using pentane to elute starting material and benzene–pentane (20:80 → 50:50; depending on the compounds) to elute the nitro compounds.

Nitro derivatives of **2**, **3**, indan, and tetralin were separated as described above. Nitro derivatives of **1** and **4** were separated using high-pressure liquid chromatography on Porasil columns.

The physical properties and spectral data of the nitro derivatives of **1–4** are given below, using the nomenclature shown on the partial formula.



α-NO$_2$-**1:** bp 140–141 °C (6 mm);[9] ir (neat, NaCl) 1520 and 1340 cm^{-1} (–NO$_2$); ^{1}H NMR (CDCl$_3$) δ 7.85 (d, 1 H, J = 8.0 Hz, β-H), 7.45 (d, 1 H, J = 8.0 Hz, α'-H), 7.2 (t, 1 H, J = 8.0 Hz, β'-H), 4.25 (m, 1 H, benzyl H near NO$_2$), 3.45 (m, 1 H, other benzyl H), 2.2–1.5 [m, 4 H, –(CH$_2$)$_2$–], and 1.1 (broad s, 2 H, –CH$_2$–); uv λ_{max} (hexane) 275 nm (ϵ 5180) and 302 (1500).

β-NO$_2$-**1:** bp 140–142 °C (6 mm);[9] ir (neat, NaCl) 1520 and 1340 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.05 (d, 1 H, J = 2.0 Hz, α-H), 8.07 (dd, 1 H, J = 2.0, 8.0 Hz, β'-H), 7.42 (d, 1 H, J = 8.0 Hz, α'-H), 3.50 (broad s, 2 H, bridgehead H's), 2.22–1.50 [m, 4 H, –(CH$_2$)$_2$], and 1.18 (m, 2 H, –CH$_2$–); uv λ_{max} (hexane) 271 nm (ϵ 8460).

α-NO$_2$-**2:** this isomer was not positively identified; a small VPC peak of suitable retention time was seen in the mother liquor from crystallization of the β isomer; the α isomer must constitute less than 0.1% of the product mixture.

β-NO$_2$-**2:**[21] mp 38–38.5 °C; ir (KBr) 1520 and 1340 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.98 (d, 1 H, J = 2.0 Hz, α-H), 7.85 (dd, 1 H, J = 2.0, 8.0 Hz, β'-H), 7.28 (d, 1 H, J = 8.0 Hz, α'-H), 6.80 (broad s, 2 H, vinyl H's), 3.95 (m, 2 H, bridgehead H's), and 2.33 (m, 2 H, –CH$_2$–); uv λ_{max} (hexane) 280.5 nm (ϵ 6625); uv λ_{max} (EtOH) 290 nm (ϵ 7900).

α-NO$_2$-**3:** ir (KBr) 1520 and 1340 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.78 (dd, 1 H, J = 2.0, 8.0 Hz, β-H), 7.36 (dd, J = 2.0, 8.0 Hz, α'-H), 7.12 (t, 1 H, J = 8.0 Hz, β'-H), 4.20 (broad s, 1 H, benzyl H near NO$_2$), 3.40 (broad s, 1 H, other benzyl H), and 1.74–0.68 (m, 6 H, –CH$_2$– bridge and cyclopropyl H's); uv λ_{max} (hexane) 259 nm (ϵ 7500); MS *m/e* 201 (M$\cdot^+$, 12.5%).

β-NO$_2$-**3:** mp 79–80 °C; ir (KBr) 1520 and 1340 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.08 (d, 1 H, J = 2.0 Hz α-H), 8.01 (dd, 1 H, J = 2.0, 8.0 Hz, β'-H), 7.35 (d, 1 H, J = 8.0 Hz, α'-H), 3.40 (s, 2 H, H$_1$ and H$_5$), and 1.72–0.63 (m, 6 H, –CH$_2$– bridge and cyclopropyl H's); uv λ_{max} (hexane) 276 nm (ϵ 9050); uv λ_{max} (EtOH) 290 nm; MS *m/e* 201 (M$\cdot^+$, 40.5%).

α-NO$_2$-**4:** ir (neat, NaCl) 1520 and 1340 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.88 (dd, 1 H, J = 2.0, 8.0 Hz, β-H), 7.35 (dd, 1 H, J = 2.0, 8.0 Hz, α'-H), 7.26 (t, 1 H, J = 8.0 Hz, β'-H), 4.29 (m, 1 H, benzyl H near NO$_2$), 3.43 (m, 1 H, other benzyl), 3.34 (td, 1 H, J = 2.0, 8.0 Hz, syn H$_8$), 2.08 (broad d, 1 H, J = 8.0 Hz, anti H$_8$), 2.00–1.72 (m, 2 H, H$_2$ and H$_4$), 0.57 (dt, 1 H, J = 3.0, 6.0 Hz, anti H$_3$), and −0.74 (td, 1 H, J = 3.0, 6.0 Hz, syn H$_3$); uv λ_{max} (hexane) 260 nm (ϵ 3000); MS *m/e* 201 (M$\cdot^+$, 15%).

β-NO$_2$-**4:** ir (neat, NaCl) 1520 and 1340 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.04 (dd, 1 H, J = 2.0, 8.0 Hz, β'-H), 7.91 (d, 1 H, J = 2.0 Hz, α-H), 7.32 (d, 1 H, J = 8.0 Hz, α'-H), 3.43 (broad s, 2 H, H$_1$ and H$_5$), 3.34 (td, 1 H, J = 2.0, 8.0 Hz, syn-H$_8$, 2.08 (broad d, 1 H, J = 8.0 Hz, anti H$_8$), 1.93 (m, 2 H, H$_2$ and H$_4$), 0.57 (m, 1 H, anti H$_3$), and −0.70 (td, 1 H, J = 3.0, 6.0 Hz, syn H$_3$); uv λ_{max} (hexane) 272.5 nm (ϵ 8370); MS *m/e* 201 (M$\cdot^+$, 100%).

The spectral data and physical constants of the nitro isomers of indan and tetralin were identical with those reported in the literature.[12b]

General Procedure for Competitive Nitrations. The distribution of nitro compounds from competitive nitrations was obtained using VPC analysis (10% QF-1 on 60–80 Chromosorb W, 5 ft × 0.125 in. column at 150–220 °C, Aerograph Hy-Fi Model 600-C).

The nitration conditions were identical with those described above. A typical competition was run as follows. The two competing arenes (7.6 mmol each) were dissolved in 10–20 ml of acetic anhydride. To this solution at 0 °C was added 3.8 mmol of freshly powdered copper nitrate trihydrate. The reaction was allowed to proceed for 1–2 h and worked up as for preparative nitrations, except that all nitro compounds were taken off the silica gel column together and weighed. VPC analyses were checked by comparing the results with artificial mixtures of similar composition. Relative reactivities were calculated from the expression derived by Ingold and Shaw.[22]

Registry No.—**1**, 4486-29-7; α-NO$_2$-**1**, 4228-29-9; β-NO$_2$-**1**, 4228-30-2; **2**, 4453-90-1; α-NO$_2$-**2**, 58673-43-1; β-NO$_2$-**2**, 42810-33-3; **3**, 15577-76-1; α-NO$_2$-**3**, 58673-44-2; β-NO$_2$-**3**, 58673-45-3; **4**, 58717-04-7; α-NO$_2$-**4**, 58717-05-8; β-NO$_2$-**4**, 58717-06-9; tetralin, 119-64-2; indan, 496-11-7.

Supplementary Material Available. A more extensive discussion of partial rate factors and appropriate external comparisons (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Preliminary report: M. W. Galley and R. C. Hahn, Abstracts, 168th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 8–13, 1974, No. ORGN-38.

(2) (a) J. Haywood-Farmer, *Chem. Rev.*, **74**, 315 (1974), and references cited therein; (b) G. R. Wenzinger and J. A. Ors, *J. Org. Chem.*, **39**, 2060 (1974); (c) P. E. Schueler and Y. E. Rhodes, *ibid.*, **39**, 2063 (1974); (d) G. Ellen and G. W. Klumpp, *Tetrahedron Lett.*, 3637 (1974).

(3) Values are approximate; see Table X, ref 2a, for data sources, experimental conditions, extrapolations, and related compounds.

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(11) Ipso attack percentages cited here must be regarded as minimum values; even in "trapping" media, nitroarenium ions may be partitioned between

trapping and nitro migration. However, data available so far are consistent with the assumption of essentially complete trapping.

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(13) Ipso partial rate factors in benzo-fused bi- and tricyclic systems currently are under separate study, and will be reported in due course.

(14) Nitrations of **2-4** with copper nitrate–acetic anhydride are not clean; benzonorbornadiene, in particular, gives considerable amounts of products derivable at least in part from reaction of the isolated double bond. Introduction of the nitro group, however, appears to stabilize nitro derivatives toward further electrophilic attack. Side reactions of **2-4** do not affect the data presented.

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(18) A referee has suggested that preferential ipso attack at C_3 in **7** can be explained by cyclopropane stabilization of a Wheland-type transition state, which would invalidate this reaction as a useful precedent for inductive deactivation of an ipso position by cyclopropyl. We note that (a) there is evidence to indicate that the cyclopropane ring in **7** is in nearly the worst possible geometry for conjugative interaction with the benzene π system,[19] and (b) this situation is not greatly improved in the Wheland intermediate (model inspection). Thus, in our view, inductive deactivation by cyclopropyl remains a viable factor in nitration of **7**.

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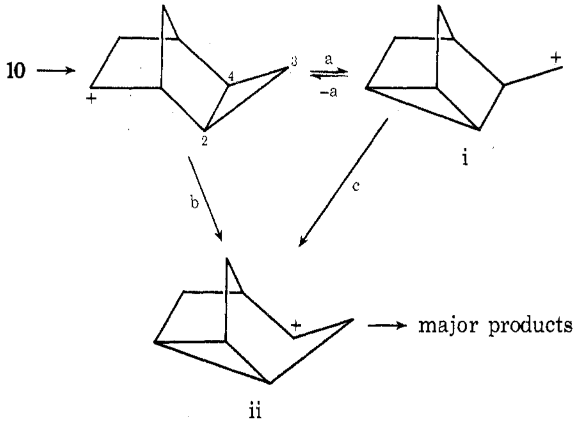
(23) The question of relative magnitudes of 2,3- and 2,4-bond participation has been raised by a referee. Studies[24,25] of a reaction which generates a stereoelectronically similar system (solvolysis of brosylate **10**; see text) can be interpreted as sources of evidence for either mode of participation, depending on whether one regards step b or steps (a + c) as a more facile route to species ii (below). Our preference for step b is based on the facts that i is a primary cation whereas ii is secondary, and cyclopropyl σ-route migration to a C^+ center (step c) is not facile relative to processes involving C–C ring bonds (see comments in ref 25).



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Estimations of van der Waals Strain in Hydrocarbons

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Evaluation of van der Waals strain can in principle be based on enthalpies of formation of appropriate reference compounds. However, experimental enthalpies are available for molecules exhibiting only relatively restricted ranges of crowding. A potentially useful source of further data may be found in relative reaction rates of crowded molecules.

Recent studies have shown encouraging success in calculating steric retardation and steric acceleration.[1-6] These have been based ultimately on calculation of enthalpies of formation of model compounds, and more specifically on calculation of relative differences in strain energy between some model of the reactant system and some model of the transition state.

A wide variety of methods has been proposed for estimating enthalpies of formation of alkanes and cycloalkanes; these are, of course, methods of interpolation and extrapolation from experimental values.[7-17]

We have made a careful evaluation of four representative methods for estimating the strain energy component of alkanes (primarily van der Waals) and have explored the usefulness of two criteria for judging effectiveness: (1) the accuracy with which the method reproduces experimental ΔH_f^0 values, and (2) the accuracy with which it treats relative rates of reactions controlled primarily by steric factors. We conclude that accuracy of reproducing ΔH_f^0 values is at present an insufficient criterion; methods which are expected a priori to give a poor account of strain energy may yield quite good ΔH_f^0 values. The problem lies in three facts: (1) that for alkanes the strain energy component is a small (and variable) fraction of the total ΔH_f^0, (2) that the six or more adjustable constants employed in each method tend to absorb the strain components in nonspecific ways, and (3) that accurate experimental ΔH_f^0 values exist for rather few strained molecules, the available data making relatively modest demands on any method of calculating ΔH_f^0. We have evaluated the Franklin protocol,[15] a simple and relatively effective older method which treats strain effects very roughly, the Allen protocol,[16,17] which reproduces experimental ΔH_f^0 values well, and molecular mechanics using two of the several available good alkane force fields, Allinger 1971[13] and Schleyer 1973.[12] The list we have treated includes most of the alkanes and methyl-substituted alkanes for which accurate experimental ΔH_f^0 values are reported.[9] The results are shown in Figures 1a–c. The standard deviations and correlation coefficients are as follows: Franklin, 0.6, 0.998; Allen, 0.3, 0.999; Schleyer, 0.7, 0.998; Allinger (not shown), 0.4, 0.999. The molecular mechanics data are based on our calculations (a) of steric energies, (b) of statistical mechanical corrections,[18] and (c) of reparameterized group increment values.[5] Each of the four methods does a good job overall in predicting ΔH_f^0 for the reference compounds. The problem may now be presented by reference to Figures 2a–c. These show what happens when a series of considerably more hindered alkanes is treated by the same methods. Each point in Figure 2 is based on a difference, $\Delta\Delta H_f^0 = \Delta H_f^0[RC(CH_3)_3] - \Delta H_f^0[RCH(CH_3)_2]$ for a neoalkane and an isoalkane. Experimental data are available for just a few of the 36–40 alkanes represented in the figure. The log k_{rel} are the Taft E_s values representing steric hindrance;[19] $k_{rel} = k/k_0$ where k is rate of hydrolysis of any ester RCOOEt