salt gave white insoluble silver tetraphenylborate and the crude yellow-brown immonium fluoroborate which, combined with a second crop from the mother liquors on repetition of the separation sequence, provided an 80% yield of N-methyl-2,4,6-cycloheptatrienylidenimmonium fluoroborate (**2e**), pale yellow micaceous crystals, mp 79–80° (*i*-PrOH), structure confirmation by ultraviolet, visible, and nmr spectra (Table I). (*Anal.* Found: C, 46.42; H, 4.87; N, 6.77; B, 5.22; F, 36.72.)

Table I

Immonium fluoroborate	R_1	R_2	λ_{max} (MeCN), mμ	τ (MeCN), area^a
2d	H	H	234^b (315 sh), 324	2.35 (scm)^c
2e	H	CH_3	239^b (324 sh), 331	2.35 (scm, 6 H);^{c} 6.77, 6.87 (d) or 6.82 (s)^d (3 H)
2c	H	C_7H_7	240, 330	2.35 (scm, 6 H);^{c} 3.15 (t), 3.56 (q), 4.42 (q), 6.00^e (t) (7 H)
2b	CH_3	CH_3	241, 335^f	2.35 (scm, 6 H);^{c} 6.47 (s, 6 H)

^{a} TMS internal reference. Allowance made for very broad (τ 1–2 width) absorptions of N–H protons in the region of ring protons. ^{b} Centers of finely structured band. ^{c} Approximate center of strongly coupled multiplet (scm). ^{d} Time average of doublet ($J \simeq 5.5$ cps) seen on N–H proton exchange. ^{e} C-7 proton absorption shifted τ 1.5 to lower field by adjacent positive charge. ^{f} ϵ_{max} 15,000.

Tropenylidenimmonium ions (**2b,d,e**) are devoid of detectable basicity as their uv and nmr spectra are unchanged even in concentrated sulfuric acid solvent. Conjugate tropenylidenimine bases are formed readily on deprotonation of primary and secondary immonium ions (**2d,c**) by trimethylamine (MeCN), tropenylidenimine (λ_{max} (MeCN) 231, 297 mμ), and N-tropenyltropenylidenimine (λ_{max} (MeCN) 232, 295 mμ) and are fairly stable in low concentrations but readily polymerized in concentrated solutions.

Limited data available preclude accurate evaluation of the relative importance of immonium (**2′**) and amine (**2″**) canonical structures in the hybrid. Hydrolysis of N,N-dimethyltropenylidenimmonium fluoroborate (**2b**) to tropone occurs rapidly in aqueous sodium carbonate and slowly in aqueous sodium bicarbonate and is undectable for several hours in pure water, in sharp contrast to immediate hydrolysis of diphenylmethylidenimmonium chloride[11a,b] (pK_a = 6.82)[11c] in cold water to benzophenone. These facts suggest an appreciable contribution of the charge-migrated amine structure (**2″**) to the resonance hybrid (**2′** ↔ **2″**) and presumably more than the estimated 16% contribution[12a] of the charge-separated structure to the tropone hybrid (pK_a = −1.02).[12b,13]

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[11] (a) A. Hantzsch and F. Kraft, *Ber.*, **24**, 3516 (1891); (b) C. Moureu and G. Mignonac, *Ann. Chim.* (Paris) [9] **14**, 320 (1891); (c) J. B. Culbertson, *J. Am. Chem. Soc.*, 73, 4818 (1951); *cf.* pK_a-(cyclohexylidenimmonium ion) = 9.15 (M. Brězina and P. Zuman, *Chem. Listy*, 47, 975 (1953)).

[12] (a) H. Hosoya, J. Tanaka and S. Nagakura, *Tetrahedron*, **18**, 859 (1962); (b) H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Japan*, **39**, 1414 (1966).

[13] Partial support by the U. S. Army Research Office (Durham) and the National Science Foundation and technical assistance by Allen R. Banks are gratefully acknowledged.

[14] Visiting Professor, University of California at Los Angeles, spring quarter, 1967.

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Phenonium *vs.* Open Ions in Solvolyses of 3-Phenyl-2-butyl Tosylate and Its *p*-Nitro Derivative[1]

Sir:

This paper reports the dramatic differences in solvolytic behavior between the optically active stereomers of 3-phenyl-2-butyl tosylate (I-OTs) and those of the *p*-nitro derivative II-OTs. The nitro group is far removed from the reaction site and should seriously depress the tendency of phenyl to act as a neighboring group. Because of the identical structures of the two systems aside from the remote *para* substituent, II-OTs serves as a splendid stereochemical and kinetic model for open-chain behavior in the 3-phenyl-2-butyl system.

Nitration of the acid phthalate of optically pure L-*threo*-I-OH[2] gave product, hydrolysis of which gave L-*threo*-II-OH,[3] $[\alpha]^{25}\text{D}$ 39.2° (*c* 3, ethanol). Similarly, L-*erythro*-II-OH was prepared,[3] $[\alpha]^{25}\text{D}$ 15.6° (*c* 3, ethanol), from 94% optically pure L-*erythro*-I-OH.[2] Oxidation[4] of the optically pure L-*threo*-II-OH and the 94% optically pure L-*erythro*-II-OH samples under neutral conditions gave L-3-(*p*-nitrophenyl)-2-butanone[3] of rotations $[\alpha]^{25}\text{D}$ −192 ± 2° (*c* 1, chloroform) and −181 ± 2° (*c* 1, chloroform), respectively. Acetolysis at 100° of optically pure L-*threo*-II-OTs gave a 13% yield of secondary acetate (7% *threo* and 93% *erythro* by nmr analysis) and 68% olefin. Hydrolysis of the acetate and oxidation[4] of the alcohol to ketone gave material, $[\alpha]^{25}\text{D}$ −184 ± 2° (*c* 1, chloroform), or 4 ± 2% racemized. In formolysis at 50°, an 11% yield of secondary formate (30% *threo* and 70% *erythro*) and a 72% yield of olefin were formed. Hydrolysis of the formate and oxidation[4] of the alcohol gave ketone, $[\alpha]^{25}\text{D}$ −143 ± 2° (*c* 1, chloroform), or 25 ± 2% racemized. In acetolysis at 100°, 94% optically pure L-*erythro*-II-OTs gave a 9% yield of secondary acetate (10% *erythro*, 90% *threo*) and 57% olefin. Conversion of the acetate to the ketone gave $[\alpha]^{25}\text{D}$ −182 ± 2° (*c* 1, chloroform), or no detectable racemization. In formolysis of 94% optically pure L-*erythro*-II-OTs at 50°, a 9% yield of secondary formate (37% *erythro*, 63% *threo*) and 59% olefin was obtained. Conversion of the formate to ketone gave $[\alpha]^{25}\text{D}$ −183 ± 2° (*c* 1, chloroform), no detectable racemization. These results indicate that the racemized portion of ketone ultimately obtained from L-*threo*-II-OTs acetolysis arose

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[1] This research was sponsored by the U. S. Army Research Office, Durham, N. C. The authors extend their thanks.

[2] (a) D. J. Cram, *J. Am. Chem. Soc.*, 71, 3863 (1949); (b) D. J. Cram, *ibid.*, 74, 2129 (1952).

[3] All new compounds gave carbon and hydrogen analyses within 0.3% of theory.

[4] K. E. Pitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 5670 (1965).

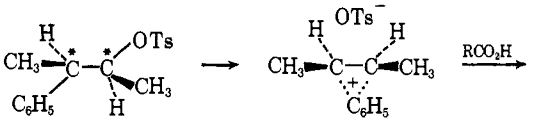
from the 7% *threo*-acetate, which must have been 60 ± 30% racemic. Likewise, the racemized portion of ketone from L-*threo*-II-OTs formolysis came from the 30% *threo*-formate, which must have been 84 ± 7% racemic. Control experiments demonstrated that all products once formed persisted.

The effect of the nitro group on the stereochemical course of these reactions is best visualized through comparison of values for I-OTs and II-OTs of k_r/k_i, the rate constant of ionization processes leading to tosylate or carboxylate esters of *retained* configuration over rate constant for processes leading to similar products of *inverted* configuration. The value of k_r/k_i for (+)-L-*threo*-I-OTs racemization and acetolysis was calculated as being k_α/k_t[5] × (yield of *threo*-I-OAc/yield of *erythro*-IOAc),[6] or $4.4(^{94}/_{6}) = 69$. In formolysis the factor was $k_r/k_i \sim 1.2(^{99}/_{0.01}) \sim 10^4$. In both solvents phenyl migrated 50%. Smith's[7] elegant label-scrambling results coupled with our product data[6] indicate that for tosylate scrambling and acetolysis, L-*erythro*-I-OT gave $k_r/k_i \sim 4.2(^{98}/_{2}) \sim 206$. Thus the values of $(k_r/k_i)_{\mathrm{AcOH}}{}^{75°}$ for *threo*-*p*-H, *threo*-*p*-NO_2, *erythro*-*p*-H, and *erythro*-*p*-NO_2, are 69, 0.078, 206, and 0.11, respectively. The values of $(k_r/k_i)_{\mathrm{HCO_2H}}{}^{50°}$ for the same four compounds are 10^4, 0.44, . . ., and 0.59, respectively.

The titrimetric and polarimetric first-order rate constants (k_α and k_t, respectively)[5] for II-OTs are as follows. The L-*threo* isomer in acetolysis gave: at 74.98°, $k_t = (1.46 \pm 0.04) \times 10^{-6}\ \mathrm{sec}^{-1}$; at 100.66°, $k_t = (2.78 \pm 0.02) \times 10^{-5}\ \mathrm{sec}^{-1}$; at 75.25°, $k_\alpha = (1.68 \pm 0.02) \times 10^{-6}\ \mathrm{sec}^{-1}$; at 100.52°, $k_\alpha = (3.08 \pm 0.05) \times 10^{-5}\ \mathrm{sec}^{-1}$. Thus, $k_\alpha/k_t = 1.1$ at both temperatures. The L-*erythro* isomer in acetolysis gave: at 74.98°, $k_t = (1.72 \pm 0.05) \times 10^{-6}\ \mathrm{sec}^{-1}$; at 100.66°, $k_t = (3.26 \pm 0.04) \times 10^{-5}\ \mathrm{sec}^{-1}$. The L-*threo* isomer in formolysis gave: at 49.85°, $k_\alpha = (1.39 \pm 0.02) \times 10^{-5}\ \mathrm{sec}^{-1}$; at 65.40°, $k_\alpha = (8.92 \pm 0.10) \times 10^{-5}\ \mathrm{sec}^{-1}$. The rate ratios for ionization of the *p*-H and *p*-NO_2 compounds extrapolated to the same temperatures are $(k_\alpha{}^{\mathrm{H}}/k_\alpha{}^{\mathrm{NO_2}})_{\mathrm{AcOH}}{}^{50°} = 190$; $(k_\alpha{}^{\mathrm{H}}/k_\alpha{}^{\mathrm{NO_2}})_{\mathrm{HCO_2H}}{}^{25°} = 560$.

An order of magnitude estimate of the inductive effect of the nitro group on ionization rate was made through comparison of the rates of acetolysis of 2-phenylethyl tosylate[8] (only 5.5% isotopic scrambling accompanies acetolysis)[9] and of 2-(*p*-nitrophenyl)ethyl tosylate at 100.50° [$k_t = (1.95 \pm 0.02) \times 10^{-6}\ \mathrm{sec}^{-1}$]. For that fraction of the rate not involving phenyl participation (89% in the parent and 100% in the nitro compound), $k^{\mathrm{H}}/k^{\mathrm{NO_2}} \sim 1.5$. From the ionization rates and product data of material arising without phenyl migration in *threo*-I-OTs and *threo*-II-OTs, k_s, the rate constants for production of acetate without phenyl assistance, can be calculated, and $k_s{}^{\mathrm{H}}/k_s{}^{\mathrm{NO_2}} \sim 4.4$. As expected, the inductive effect of the *p*-nitro group in the secondary system is somewhat larger than in the primary system, but still makes only a negligible contribution to the rate enhancement factors of 190 and 560 observed for *p*-H as compared to *p*-NO_2. Correction for this inductive effect leaves factors of about 43 and 128 for rate enhancement due to phenyl participation in ionization.

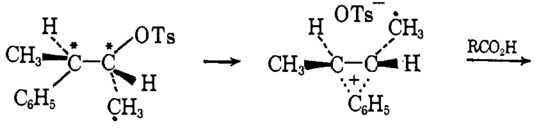
Solvolyses rates of I-OTs isomers and 2-butyl tosylate are close to one another.[5] Without taking into account the inductive effect of phenyl, or the fact that I-OTs *ionizes* faster than it solvolyzes, Brown, *et al.*,[10] questioned the phenonium ion interpretation (see formulation) on the basis of the above near-equality of rates. They explain the stereochemical results of the I-OTs system with five assumptions. (1) Ionization occurs to give open ion pairs only when phenyl and tosyl are *trans* for steric reasons, the tosyl group swelling as it ionizes. (2) The ion pair is unsolvated from the back because of the blocking effect of the phenyl in its resting state. (3) The phenyl migrates back and forth faster than rotation occurs about the central C–C bond, and faster than solvent attacks the ion pair. Solvent is blocked from the back by migrating phenyl (windshield wiper effect). (4) Rotation about the central C–C bond in the ion pair is slowed because of the steric necessity of phenyl and the tosylate anion remaining *trans* to one another. (5) Capture of the ion pair occurs from the front because of the blocking ability of the phenyl at the back and because of solvation of the anion.



L-*threo*-I-OTs

cis-phenonium tosylate ion pair

racemic tosylate and carboxylic esters



L-*erythro*-I-OTs

trans-phenonium tosylate ion pair

scrambled optically active tosylate, and carboxylic esters

Our *p*-H and *p*-NO_2 systems are stereochemically identical. Assumptions 1, 2, 4, and 5 apply equally well to our *p*-H and *p*-NO_2 systems. The nitro group slows down the rate of aryl migration, and hence assumption 3 might not apply to the *p*-NO_2 system. Now the question arises as to whether a phenyl that migrates is different sterically than a *p*-nitrophenyl that does not. The two should be the same, since little of an open ion-pair's lifetime is spent in the transition state for migration. Clearly, the aryl groups in the starting materials present the same steric inhibition to solvation from the back in transition states leading to open ion pairs,

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[5] This is the ratio of rate constant for racemization to that for appearance of *p*-toluenesulfonic acid: S. Winstein and K. Schrieber, *J. Am. Chem. Soc.*, **74**, 2165 (1952).

[6] Small computational errors were made in the original paper,[2b] and these are corrected here. These corrections in no way change the argument.

[7] W. B. Smith and M. Showalter, *J. Am. Chem. Soc.*, **86**, 4136 (1964).

[8] S. Winstein, C. R. Lindegran, H. Marshall, and L. L. Ingraham, *ibid.*, **75**, 147 (1953).

[9] (a) C. C. Lee, G. D. Slater, and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1417 (1957); (b) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); (c) W. H. Saunders, S. Asperger, and D. H. Edison, *J. Am. Chem. Soc.*, **80**, 2421 (1958).

[10] H. C. Brown, K. J. Morgan, and F. J. Chlocysek, *ibid.*, **87**, 2137 (1965).

whether they be solvated carbonium tosylate or oxonium tosylate ion pairs. Thus, the Brown model predicts similar k_r/k_i ratios for the *p*-H and *p*-NO$_2$ systems. Furthermore, since the Brown model excludes aryl participation in ionization, the only difference in ionization rates the model predicts must be due to the small inductive effect.

The Brown model is incompatible with the results on both stereochemical and kinetic grounds. Instead of k_r/k_i values being similar for the *p*-H and *p*-NO$_2$ systems, they differ by factors of 800–1800 in acetic acid and by a factor of 23,000 for the *threo* isomer in formic acid. Instead of the rates of ionization for the *p*-H and *p*-NO$_2$ systems differing by factors of 1.5–4.3, they differ by factors of 190–560. In contrast, these results are completely consistent with the original interpretation[2] in which aryl and solvent compete with one another for participating at the back of secondary carbon in ionization. In the *p*-H system, phenyl assists in ionization, producing a rate enhancement, and channels the reaction through a phenonium ion to produce ester of retained configuration. In the *p*-NO$_2$ system, the nitro group depresses the ability of neighboring phenyl to assist in ionization, thereby reducing the rate, and this leaves solvent to assist in the ionization from the back, producing inversion. Thus, the remote theoretical difficulties with the phenonium ion imagined by Brown[10] have been swept away with the broom of experimental fact.

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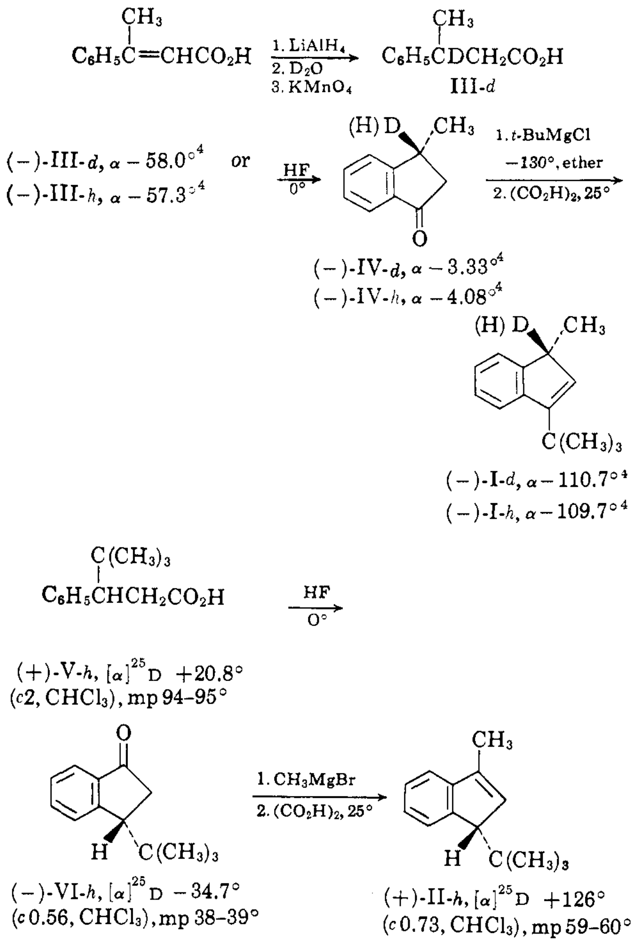
Factors That Control 1,3-Asymmetric Induction and Intramolecularity in Base-Catalyzed 1,3-Proton Transfer in an Indene System[1]

Sir:

As part of our investigation of the mechanism of base-catalyzed proton transfers of carbon acids, we envisioned 1,3-dialkylindenes as systems that would allow study with a variety of weak bases of the stereochemical and isotopic changes that accompany 1,3-proton (allylic proton) transfers.[2] The key intermediate, (+)-I-*h*, had been synthesized when the first 1,3-asymmetric induction result of Bergson, *et al.*, appeared.[3a] After survey, we selected reaction I → II[3b,c] as most ideally suited for investigation.

Preparation of compounds (−)-I-*h* and (−)-I-*d* (0.99 atom of deuterium per molecule, mass spectrometry, ±0.5%) of maximum rotation is formulated.[4] Synthesis of deuterated 3-phenyl-1-butanol paralleled that of its protonated analog.[5] Acid V[6] was resolved to maximum rotation through its brucine salt (methanol–ethanol). Indene (+)-II-*h* was separated from the 10% exocyclic isomer by vpc on a 17% silicone nitrile on 60–80 Firebrick column. The configuration and maximum rotation of (−)-III-*h* were previously determined,[7] and optically pure (−)-III-*h*(*d*) gave optically pure (−)-I-*h*(*d*). Acid (+)-V-*h*, ketone (−)-VI-*h*, and indene (+)-II-*h* did not change melting point or rotation on recrystallization, and the melting point of the corresponding racemates were widely different (*e.g.*, (±)-II-*h*, mp 33–34°). Hence, (+)-II-*h* is at maximum rotation. Optical rotatory dispersion curves (Cary 60 spectropolarimeter) of (−)-I-*h* and (+)-II-*h* in cyclohexane (*c* 0.03–0.0012) were almost mirror images of one another. Indene (−)-I-*h* exhibited negative Cotton effect with maximum (−) rotations occurring at 298 mμ (Φ 4620°), 287 (Φ 4080°), and 228 (Φ 23,100°), and Φ = 0 at 224 mμ. Indene (+)-II-*h* gave a positive Cotton effect with maximum (+) rotations at 298 mμ (Φ 2850°), 200 (Φ 1470°), and 224 (Φ 32,700°), and Φ = 0 at 215 mμ. Ketones (−)-IV-*h* and (−)-VI-*h* also gave optical rotatory dispersion curves that were roughly mirror images of one another. Thus, (−)-I-*h* and (+)-II-*h* possess opposite configurations.



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[1] This research was supported in part by the U. S. Army Research Office, Durham, N. C., and in part by the Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant No. AF-AFOSR-124-65.

[2] (a) D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, **84**, 4358 (1962); (b) D. J. Cram and R. T. Uyeda, *ibid.*, **86**, 5466 (1964); (c) D. J. Cram, F. Willey, H. P. Fischer, and D. A. Scott, *ibid.*, **86**, 5370 (1964); (d) D. J. Cram, F. Willey, H. P. Fischer, H. M. Relles, and D. A. Scott, *ibid.*, **88**, 2759 (1966); (e) D. H. Hunter and D. J. Cram, *ibid.*, **88**, 5765 (1966); (f) D. J. Cram and L. Gosser, *ibid.*, **86**, 2950 (1964); (g) D. J. Cram and L. Gosser, *ibid.*, **86**, 5445 (1964); (h) D. J. Cram and L. Gosser, *ibid.*, **86**, 5457 (1964); (i) R. D. Guthrie, W. Meister, and D. J. Cram, *ibid.*, **89**, 5288 (1967); (j) W. T. Ford, E. W. Graham, and D. J. Cram, *ibid.*, **89**, 4661 (1967).

[3] (a) G. Bergson and A. Weidler, *Acta Chem. Scand.*, **17**, 1798 (1963); (b) A. Weidler, *ibid.*, **17**, 2724 (1963); (c) A. Weidler and G. Bergson, *ibid.*, **18**, 1484 (1964); (d) A. Weidler and G. Bergson, *ibid.*, **18**, 1487 (1964); (e) L. Ohlsson, I. Wallmark, and G. Bergson, *ibid.*, **20**, 750 (1966).

[4] All new compounds gave hydrogen and carbon analyses within 0.2% of theory. All deuterated intermediates contained at least 0.99 atom of deuterium, combustion and falling-drop method. All rotations are neat, l = 1 dm, 25°, λ 589 mμ unless otherwise specified.

[5] R. T. Uyeda and D. J. Cram, *J. Org. Chem.*, 30, 2083 (1965).

[6] C. F. Koelsch, *J. Am. Chem. Soc.*, **65**, 1640 (1943).

[7] (a) D. J. Cram, *ibid.*, **74**, 2137 (1952); (b) *ibid.*, **74**, 2149 (1952).