gave only the *threo* hydrocarbon **2**. Since this transformation is well documented[7] as an over-all *syn* addition, it follows that the tetrasubstituted olefin (mp 278–279°) must possess the *E* or *trans* configuration (**5**).

While 1,2-diferrocenyl-1,2-diphenyl-1,2-ethanediol has been suggested as a possible intermediate in the Clemmensen reduction of benzoylferrocene (**6**),[8] its isolation from that reaction has recently been accomplished in this laboratory.[5] As expected the pinacol was produced in two diastereomeric forms (mp 202–204 and 207–209°).

In another example of asymmetric selection brought about by the presence of an optically active solvent, it was found that only the higher melting pinacol is optically active, and therefore must be the *threo* isomer **8**.

Treatment of a solution of benzoylferrocene (**6**) in (+)-(*S*)-1-methoxy-2-methylbutane (**4**) with zinc dust and aqueous hydrochloric acid gave the two diastereomeric pinacols in good yield. Separation was achieved by fractional crystallization: the less soluble isomer (mp 207–209°) was optically active (*threo*-**8**, $[\alpha]^{21}_{546}$ 9.2 ± 1.0° (*c* 1.0, benzene)), while no optical activity could be detected in the more soluble isomer (mp 202–204°, *erythro*-(**7**)).

Thus, the relative stereochemical features of all the relevant compounds involved in the Clemmensen reduction of benzoylferrocene have been rigorously elucidated by novel means.[9]

[7] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 128 ff.

[8] M. D. Rausch and D. L. Admas, *J. Org. Chem.*, **32**, 4144 (1967).

[9] R. W. Murry, R. D. Youssefyeh, and P. R. Story (*J. Amer. Chem. Soc.*, **88**, 3655 (1966)) have assigned the relative configurations to *cis*- and *trans*-2,5-dimethylhexene-3 ozonides by means of kinetic resolution, a process similar in principle to that used in the present work.

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On the Pyramidal Stability of Allylmethylphenylphosphine[1]

Sir:

It has been suggested[2] that the facile racemization[2] of allylmethylphenylphosphine (**1**) relative to methylphenyl-*n*-propylphosphine (**2**) might be attributed to an intramolecular allylic rearrangement.[3] We wish to report that the thermal racemization of **1** is actually somewhat *slower* than that of **2**, and that allylic rearrangements play no significant role in the racemization of **1**.

Optically active (+)-(*R*)-**1**, prepared by hexachlorodisilane reduction[4] of (+)-(*R*)-allymethylphenylphosphine oxide,[5] undergoes racemization in benzene with first-order kinetics:[6] $k_{\text{rac}} \times 10^5$ (sec^{-1}) = 1.69 (130°), 7.48 (145°), and 28.0 (160°), whence E_a = 32.2 kcal/mol and log A = 12.8. In decalin (*cis*:*trans* = 2:1) at 130°, **1** racemizes with $k_{\text{rac}} = 1.44 \times 10^{-5}$ sec^{-1}, compared to $k_{\text{rac}} = 3.34 \times 10^{-5}$ sec^{-1} for the racemization of **2** under identical conditions.[7]

That an allylic rearrangement is not implicated in the racemization of **1** was demonstrated by the observation that the pmr spectrum of the labeled compound,[8] **1**-α-d_2, suffered no perceptible change when solutions in C_6D_6 were heated[6] for prolonged periods of time at temperatures up to 150°. At 175°, a slow exchange of protons at the α- and γ-allylic positions (τ 7.6–7.8 and 4.95–5.36, respectively) was noted, accompanied by slight decomposition. The half-life for exchange at 175°, *ca.* 50 hr, is about 300 times the half-life for racemization at the same temperature, *ca.* 10 min. The allylic rearrangement, whatever its mechanism, is therefore too slow[9] to account for the racemization, which must occur by pyramidal inversion.

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[1] We are grateful to the Air Force Office of Scientific Research for support of this research under Grant No. AF-AFOSR-1188-B.

[2] L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Lett.*, 161 (1961).

[3] For a related rearrangement, see T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Amer. Chem. Soc.*, 88, 3832 (1966).

[4] K. Naumann, G. Zon, and K. Mislow, *ibid.*, 91, 2788 (1969).

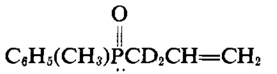
[5] A. W. Herriott and K. Mislow, *Tetrahedron Lett.*, 3013 (1968).

[6] The phosphine **1** is extraordinarily susceptible to decomposition in air, and *all* measurements must be performed under rigorous exclusion of oxygen.

[7] This value is in good agreement with the rate constant, k_{rac} = 3.78×10^{-5} sec^{-1}, previously reported for the racemization of **2** in decalin at 130° (L. Horner and H. Winkler, *Tetrahedron Lett.*, 461 (1964)).

[8] Reaction of methylphenylbromophosphine with allyl-γ-d_2 alcohol, followed by rearrangement[5] of the allyl-γ-d_2 methylphenylphosphinite (i) at 100°, gave a phosphine oxide (ii), reduction of which with hexachlorodisilane[4] afforded the specifically deuterated phosphine (**1**-α-d_2).

$C_6H_5(CH_3)POCH_2CH{=}CD_2$
i


$C_6H_5(CH_3)P(=O)CD_2CH{=}CH_2$
ii

$C_6H_5(CH_3)PCD_2CH{=}CH_2$
1-α-d_2

[9] In a related observation, M. P. Savage and S. Trippett, *J. Chem. Soc., C*, 1998 (1967), found that in the absence of catalysts diphenyl-(1-phenylallyl)phosphine does not rearrange to cinnamyldiphenylphosphine on heating at 220° for 15 hr.

[10] National Science Foundation Trainee, 1968–1969.

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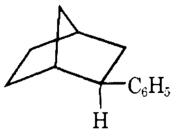
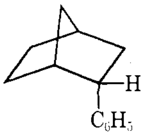
Stabilization *via* Carbon–Carbon Hyperconjugation

Sir:

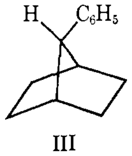
Investigation of the aluminum chloride catalyzed benzoylation of the phenylnorbornanes I–IV has revealed some significant findings. These results will be discussed in terms of (a) the general importance of differential solvent effects in stabilization of a charge developed either at or adjacent to an aromatic ring, (b) the importance of C–C hyperconjugation where the C–C bond(s) involved contain an "abnormal" high degree of p character.



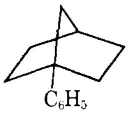
I



II



III



IV

Table I. Reaction of Benzoyl Chloride–Aluminum Chloride with Aromatic Hydrocarbons at 0.100 M^a Complex Concentration

Aromatic	$k_2 \times 10^3$ l. mol^{-1} sec^{-1}	Isomer distribution % *o*	% *m*	% *p*	*para* $(p_f)^b$ partial rate factor
t-Butylbenzene[c]	0.462	0	5.4	94.6	398
Isopropylbenzene[c]	0.606	3.1	4.0	92.9	519
Ethylbenzene[c]	0.660	3.6	3.4	93.0	563
Toluene	0.80 ± 0.01[d]	8.4	1.4	90.2	633
7-Phenylnorbornane (III)	1.00 ± 0.01	1.3	4.8	93.9	822
endo-2-Phenylnorbornane (II)	1.27 ± 0.10	2.3	3.8	93.9	1040
exo-2-Phenylnorbornane (I)	1.94 ± 0.12	1.8	2.3	95.9	1630
1-Phenylnorbornane (IV)	2.10 ± 0.01	0.1	2.5	97.4	1790

[a] All reactions followed to at least 60% and each exhibited close coherence to second-order kinetics. Yields checked for I and IV were >95% (quantitative within experimental uncertainty). [b] Partial rate factor for substitution on a single position of benzene is 1. [c] H. C. Brown and G. Marino, *J. Am. Chem. Soc.*, **81**, 5611 (1959). [d] Toluene, 0.763×10^{-3} l. mol^{-1} sec^{-1}; see footnote *c* and F. R. Jensen, G. Marino, and H. C. Brown, *ibid.*, **81**, 3303 (1959).

It is known that numerous reactions of alkyl-substituted benzenes in which a positive charge is developed at a position adjacent to the alkyl group exhibit the order of reactivity[1] Me > Et > *i*-Pr > *t*-Bu. This enhanced ability of alkyl groups as compared to hydrogen has been explained in terms of a special type of conjugation known as hyperconjugation.[1] For simple alkyl groups theoretical[2] and experimental[3] evidence has been presented that C–C hyperconjugation is less important than C–H hyperconjugation. Some have argued against this hypothesis and postulated that the rate sequence Me > Et > *i*-Pr > *t*-Bu is due to steric hindrance of solvation.[4]

In the norbornylbenzenes, I–IV, the alkyl substituents are more bulky than the simple alkyl substituents, Me, Et, *i*-Pr, or *t*-Bu. *A priori*, it is reasonable to expect compounds I–IV to undergo electrophilic substitution slower than isopropylbenzene under the same conditions if differential solvent effects are operative. However, the data in Table I indicate that the rates of benzoylation of I–IV are all greater than isopropylbenzene, in fact, greater than even toluene. Clearly differential solvent effects, although they may be operative, are not the dominant factor influencing the rate of reaction of the simple alkyl- as compared to the norbornyl-substituted compounds.

Either (a) solvent effects are not important in either system or (b) a differential solvent effect is ordering the rates for the alkylbenzenes but the same solvent effect is obscured by some rate-enhancing factor in the phenylnorbornane system. Whichever standpoint is accepted, the unusual reactivity of the norbornylbenzenes is indicative of some important rate-enhancing factor not present in the simple alkylbenzenes.

On the basis of reactivity order Me > Et > *i*-Pr > *t*-Bu, one expects toluene to benzoylate faster than any of the norbornylbenzenes. Surprisingly, the compound exhibiting the fastest rate is 1-phenylnorbornane, which contains no hydrogens α to the ring. *It is suggested that the norbornylbenzenes exhibit C–C hyperconjugation in addition to any C–H hyperconjugation and the C–C hyperconjugation in the norbornylbenzenes is comparable to the C–H hyperconjugation in toluene.*

The importance of C–C hyperconjugation relative to C–H hyperconjugation is seen in the solvolysis of various *t*-cumyl chlorides.[5] The cyclopropane substituent in 4-cyclopropyl-*t*-cumyl chloride increases the rate of solvolysis by a factor of 157 over *t*-cumyl chloride. The 4-*i*-Pr substituent gives a factor of 17.8 increase. In 4-cyclopropyl-*t*-cumyl chloride, the cyclopropane ring is free to align parallel to the developing p orbital of the carbonium ion in order to have optimum stabilization *via* C–C hyperconjugation (Figure 1a).

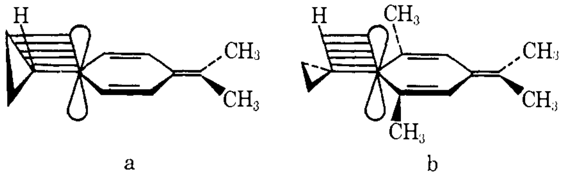


Figure 1.

However, when the cyclopropane ring is forced into a conformation where only the cyclopropane C–H bond is aligned properly for hyperconjugation, as in 3,3-dimethyl-4-cyclopropyl-*t*-cumly chloride, the contribution of the cyclopropane group is only a factor of 9 (Figure 1b). These data indicate stabilization *via* C–C hyperconjugation through the p-rich ring bonds of cyclopropane[6] is more stabilizing than C–H hyperconjugation exhibited by the *i*-Pr group. The C–H bonds in cyclopropane possess an abnormally high degree of s character[5] and their C–H hyperconjugation capacity is therefore reduced relative to the C–H hyperconjugation of *i*-Pr. In any compressed ring systems, the internal C–C bonds are expected to gain p character over the normal sp^3 hybrid.[5] This has been seen for cyclopropane and should also be the case for the norbornyl ring system.[7] The proposed increased contribution of C–C hyperconjugation is thus a result of increased p character in the C–C ring bonds of the norbornyl substituent.

---

(1) R. W. Taft, Jr., and I. C. Lewis, *Tetrahedron*, **5**, 210 (1959); E. Berliner, *ibid.*, **5**, 202 (1959); J. W. Baker, "Hyperconjugation," Oxford University Press, New York, N. Y., 1952; J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

(2) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.*, **63**, 41 (1941); S. Ehrenson, *ibid.*, **86**, 847 (1964).

(3) E. Berliner and F. J. Bondjus, *ibid.*, **70**, 854 (1948).

(4) W. M. Schubert, J. M. Craven, R. G. Minton, and R. B. Murphy, *Tetrahedron*, **5**, 194 (1959); M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962.

(5) H. C. Brown and J. D. Cleveland, *J. Am. Chem. Soc.*, 88, 2051 (1966).

(6) K. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964; C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1951; C. S. Foote, *Tetrahedron Letters*, 579 (1963).

(7) Traylor, *et al.*, have reported 28% s character in the C$_1$–H of norbornane through $J_{^{13}\mathrm{C-H}}$ measurement: R. A. Alden, J. Kraut, and T. G. Traylor, *J. Am. Chem. Soc.*, **90**, 74 (1968). This excess in s character is expected to be reflected in an increase of p character in the internal C–C bonds. See also J. F. Chaing, C. F. Wilcox, and S. H. Buner, *J. Am. Chem. Soc.*, **90**, 3149 (1968); M. Randic and D. Stefanovic, *J. Chem. Soc.*, *B*, 423 (1968).

A consideration of inductive effects is also pertinent. Higher degree of s character in a bond is reflected in a higher electronegativity.[8] Since the norbornyl C–H bonds presumably possess more than 25% s character, the hybridization effect results in a greater electron-withdrawing capacity relative to *i*-Pr. However, the norbornyl ring system may possess special bulk and steric factors which also contribute to the over-all inductive effect. At present, there are insufficient data to evaluate such contributions.[9]

The rates of benzoylation for a number of cycloalkylbenzenes are also under investigation. The amount of p character in the C–C bonds of various cycloalkanes is known or can be calculated from bond angles and $J_{^{13}C-H}$ values.[6] It is hoped that some meaningful correlation between rates of electrophilic substitution and C–C bond p character exists.

The present work has indicated C–C hyperconjugation should be considered as a primary factor in stabilizing carbonium ions when the C–C bond(s) involved are expected to possess more than 75% p character and this is anticipated to be a general phenomenon. The importance of differential solvent effects is not manifested in the present work (*vide supra*).

exo-2-Phenylnorbornane[10] (I), 7-phenylnorbornane[11] (III), and 1-phenylnorbornane[12] (IV) were all prepared by previously reported methods. Hydrogenation of 2-phenyl-2-norbornene[12] in ethyl acetate with 10% Pd–C catalyst afforded *endo*-2-phenylnorbornane (II). All compounds were shown to be homogeneous by gas chromatographic examination and displayed nmr spectra in agreement with indicated structures. Purification of ethylene dichloride,[13] aluminum chloride,[14] and benzoyl chloride[14] for kinetic measurements has been described previously. Preparation of solutions and kinetic measurements employed are described in previous work.[13,15]

Acknowledgment. This work was supported by the National Science Foundation under Grant GP 6350X.

(8) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 60 (1947); A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947); A. D. Walsh, *J. Chem. Soc.*, 398 (1948).

(9) Synthesis and determination of pK_a values of a number of norbornyl-substituted benzoic acids are under investigation to clarify this point.

(10) L. Schmerling, U. S. Patent 2,480,267 (1949).

(11) P. R. Story and S. R. Fahenholtz, *J. Org. Chem.*, **28**, 1716 (1963).

(12) D. C. Kleinfelter and P. von R. Schleyer, *ibid.*, **26**, 3741 (1961).

(13) See Table I, footnote *d*.

(14) H. C. Brown and F. R. Jensen, *J. Am. Chem. Soc.*, **80**, 2291, 2296 (1958).

(15) H. C. Brown, B. Bolto, and F. R. Jensen, *J. Org. Chem.*, **23**, 414, 417 (1958).

(16) National Institutes of Health Predoctoral Fellow, 1968–1969.

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Received May 6, 1969

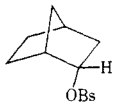
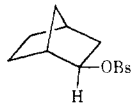
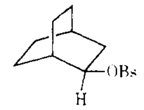
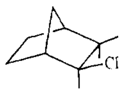
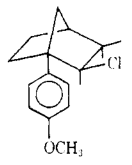
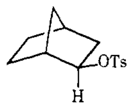
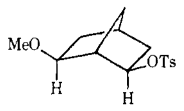
Carbon–Carbon Hyperconjugation in the Norbornyl Cation[1]

Sir:

In the preceding paper[2] it was proposed that increased hyperconjugative stabilization due to the presence of excess p character in C–C bonds in the norbornyl ring is responsible for the observed abnormally high rate of Friedel–Crafts benzoylation of the norbornylbenzenes. It is now suggested that the "extra" hyperconjugative ability of the strained C–C bonds in the norbornyl system is responsible, at least in part, for the rate acceleration observed in the formation of the *exo*-2-norbornyl cation. It is also suggested that accelerated rates of carbonium ion formation will be observed whenever the developing p bond has the proper geometry to undergo hyperconjugative stabilization by a (compressed) strained ring system.

A comparison of the solvolysis rates of the 2-bicyclo[2.2.2]octyl arenesulfonate III and the *endo*- and *exo*-norbornyl arenesulfonates I and II probably provides the best evidence for rate enhancement in the *exo*-norbornyl compound (Table I). The norbornyl system contains considerably more internal strain than the bicyclo[2.2.2]octyl system and this strain is expected to be considerably increased in forming the cations. Nevertheless, the 2-*exo*-norbornyl reacts faster than the 2-bicyclo[2.2.2]octyl compound, and this suggests the presence of a special stabilizing factor in the formation of the 2-*exo*-norbornyl cation. Although considerable evidence has been presented by Brown and coworkers[3] indicating the *exo*-2-norbornyl cation is classical, the existence of a factor producing rate acceleration appears to be present.

Table I. Relative Acetolysis Rates at 25°

			
	I	II	III
k_{rel}^{a}	1	350	36
			
k_{rel}^{b}	1	0.6	
			
k_{rel}^{c}	1	0.014	

[a] See ref 6. [b] H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **86**, 5003 (1964). [c] P. J. Stang and P. von R. Schleyer, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, p 192.

In the preceding paper,[2] *exo*-2-norbornylbenzene was reported to undergo acylation 4.2 times faster than *t*-butylbenzene (>90% *para* substitution). This increased rate of reaction was attributed to increased (C–C) hyperconjugative stabilization in the norbornyl system because of the greater amount of p character in norbornyl C–C bonds and the observed stabilization is equivalent to about 850 cal/mol. The developing posi-

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(1) Refers to the cation developed from heterolysis of the appropriate 2-norbornyl derivatives.

(2) See F. R. Jensen and B. E. Smart, *J. Am. Chem. Soc.*, **91**, 5686 (1969).

(3) (a) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962; (b) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966); M. Rei and H. C. Brown, *J. Am. Chem. Soc.*, 88, 5335 (1966).