ment with Li–$C_2H_2NH_2$ at −78°,[11a] was converted to acetal **12b** (95%) [nmr δ 5.2 (2, m); *m/e* M+ 428, 205 (31%), 109 (97%), 95 (100%)]. The experimental sequence acetal → aldehyde → terminal epoxide, as described elsewhere,[11b] was applied here, providing (55% overall from **12b**) epoxide **5** [nmr δ 2.70 (1, t, J = 6 Hz), 1.20 and 1.17 (6, s,); *m/e* M+ 426.385010 (calcd 426.385986)], unquestionably a *ca.* 50:50 mixture of racemates differing stereochemically at C-3(*). Alternatively and more expeditiously, similar reductive coupling of bromide **10b** with *trans,trans*-farnesyl phenyl thioether furnished (53%) the expected bicyclic tetraene (**5**, with Δ^2 double bond instead of 2,3-epoxide) [nmr δ 5.1 (3, m); *m/e* M+ 410, 205 (46%), 109 (100%), 95 (82%)], which was terminally oxidized[12] (55%) to epoxide **5**.

Stannic chloride–CH_3NO_2 at 0° for 2 hr effected transformation of epoxide **5** to *dl*-δ-amyrin (8%, based on the consumption of one of the two epoxide racemates) (mp 185–188°), isolated and purified by multiple elution tlc[13] and indistinguishable by mass spectra, nmr, and vpc from δ-amyrin produced by acid isomerization of β-amyrin benzoate.[14] Resolution of *dl*-δ-amyrin was accomplished by means of the (*R*)-α-methoxy α-trifluoromethylphenylacetate (MTPA),[15] which, after three crystallizations from $CHCl_3$–MeOH (1:10), yielded ester (mp 233–234.5°), identical (mmp 232.5–234.5°) with the MTPA ester of authentic δ-amyrin (mp 233–234.5°). (−)-δ-Amyrin was regenerated from the ester by $LiAlH_4$ reduction. In view of the prior conversion of δ-amyrin from natural sources to δ-amyrene,[14] and the transformation of the latter to β-amyrin,[3b] the δ-amyrin synthesis described herein also constitutes a formal synthesis of β-amyrin (**3**). Finally, the laboratory production of **2** also embraces germanicol (**4**), since the latter is isolated as the predominant product when δ-amyrin in *t*-BuOH–H_2O (10:1) is photolyzed in the presence of *p*-xylene (quartz tube at 2537 Å in Rayonet reactor) for 48 hr at 30°[16] under nitrogen, followed by preparative vpc.[17]

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(16) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969), and references cited therein.

(17) Elemental analyses on all intermediates were satisfactory. All nmr spectra were recorded in $CDCl_3$ + 1% TMS.

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Preferential Stabilization of σ-Delocalized Ions by Methyl Substituents Compared to Phenyl Substituents[1,2]

Sir:

The solvolytic rate ratio between a secondary halide or ester and the related α-methyl substituted tertiary derivative is[3,4] 10^5–10^8. The particular value found depends on the leaving group, the solvent, and any special structural features present. Under those conditions leading to the 10^5 value[3] the rate enhancement due to phenyl substitution in place of methyl was found to be 10^8, in approximate conformity to the rule of thumb that "one phenyl is worth two methyls."[5]

Substitution of methyl groups for hydrogen on a cyclopropylcarbinyl residue produces solvolytic rate enhancements that depend on the position of attachment.[6] The pattern of rate response to methyl substitution can be interpreted in terms of transition state charge delocalization corresponding to that calculated for the free cation.[7]

Interestingly, the pattern for phenyl substitution is strikingly different with little or none of the expected rate enhancement for a phenyl in the 2 position.[8] This has been ascribed to the absence of charge,[8a] steric inhibition of resonance,[8b] and to a fortuitiously balanced blend of conjugative stabilization and retarding inductive effect.[9]

In a recent numerical exploration of symmetrical σ-bridged ions using an extended Hückel model[10] a remarkable insensitivity to resonance stabilizing substitutents was noted[11] which provided an alternative explanation for many of the seemingly anomalous results observed in studies of neighboring σ participation.[12] It seemed of interest to determine if this result also provided an explanation for the different response patterns of methyl and phenyl substitution of cyclopropylcarbinyl molecules. Toward this end we report here some new experimental results that probe this question by determining the substituent effect on the homoallylic route to cyclopropylcarbinyl intermediates.

(1) Taken largely from the Ph.D. Dissertation of H. D. Banks, Cornell University, 1970.

(2) Supported, in part, by the National Science Foundation.

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(4) See P. v. R. Schleyer, *et al.*, *J. Amer. Chem. Soc.*, **92**, 2538 (1970), for a detailed discussion and further references.

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(9) K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, 87, 1331 (1965); G. D. Sargent has proposed a fortuitous blend of conjugative stabilization and inductive retardation to explain the lack of stabilization of several proposed nonclassical transition states by phenyl groups, *Quart. Rev., Chem. Soc.*, 20, 301 (1966).

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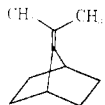
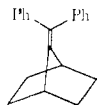
DePuy[13] found that homoallylic endo tosylate I (X = OTs) acetolyzes 270 times faster than the saturated endo tosylate II (X = OTs), which he took as a reference. The rate enhancement was attributed to formation of a σ-delocalized cyclopropylcarbinyl transition state. Consistent with this formulation the acetolysis product was exclusively endo acetate.

In order to explore further the stabilization of the cyclopropylcarbinyl transition state by methyl and phenyl substituents alcohols III (X = OH) and IV (X = OH) were prepared and characterized.[1] Acetolysis of the related tosylates (X = OTs) gave the kinetic results listed in Table I.

Table I. Rates of Acetolysis of Some Bicyclo[2.2.1]heptyl Tosylates (X=OTs)

Compound	T, °C	Rate	Rel rate	ν_c = 0, cm^{-1}
 II	101.0	6.3×10^{-4}		
	25	8.4×10^{-8}	22	1751
 III	125.1	5.32×10^{-4}		
	101.0	5.43×10^{-6}		
	(25.0)	(3.76×10^{-9})	1	1752
 I	50.1	3.32×10^{-4}		
	50.0	3.24×10^{-4}		
	(25.0)	(2.26×10^{-5})	6000	1751
 IV	120.0	9.39×10^{-4}		
	101.0	1.56×10^{-4}		
	(25.0)	(1.25×10^{-8})	3	1756

The 22-fold rate retardation produced by the 7-methylene group agrees precisely with the factor of 18–23[14–17] estimated for a simple inductive effect. The essential identity of the carbonyl stretching frequencies of the ketones corresponding to II and III indicates that internal angle strain effects[18] make an insignificant contribution to the rate ratio.

Using now the tosylate III as reference the acetolysis of tosylate I shows a rate enhancement of 6000. This value agrees well with the ratio of 4500 for the formolysis of 4-methyl-3-pentenyl tosylate to 3-butenyl tosylate[9] and reinforces DePuy's thesis that a σ-delocalized transition state is involved. Still more convincing is the observation that the products from the slow tosylate III were about 90% rearranged, in significant contrast to DePuy's observation of retention of configuration for the products of solvolysis of the rate enhanced tosylate. The formation of rearranged products from III suggests that little neighboring group stabilization exists in III and the products are controlled by steric factors.

Given this internal consistency we were initially surprised to observe that the benzhydrylidene compound, IV, showed almost no rate enhancement. The inductive retardation calculated for IV amounts to a factor of 2.1–2.2,[19] or an expected solvolysis rate relative to III of about 10. When the observed relative rate of IV is corrected upward for angle strain using the Foote–Schleyer recipe[18] the rate ratio is, in fact, close to 10. Isolation of the unaltered tosylate IV after 16% acetolysis excluded rapid addition of solvent to the 7-double bond as an explanation of the low rate. This was confirmed by preparing the *p*-nitrobenzoate of IV and determining its (slow) solvolysis rate in 90% acetone–water, a less acidic solvent in which addition to the double bond is therefore unlikely.

The lack of rate enhancement with IV is particularly striking given that naive application of the "one phenyl equals two methyls" rule would have led to an expected rate enhancement of *ca.* 10^7. Preparation and acetolysis of 4,4-diphenyl-3-butenyl tosylate gave a similar small rate factor,[20] demonstrating the probable generality of the result by excluding steric hindrance arguments peculiar to the norbornyl system.

A portion of the loss of phenyl rate enhancement may be caused by resonance stabilization of the ground state.[9] While the proper estimation of this effect is too complex to analyze here it seems apparent that even after correction the diphenyl compounds are too slow by a factor of at least 10^4. This is not as dramatic as the loss observed for more symmetrical σ-delocalized transition states but its origin may be related. We are continuing our study of this problem.

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(14) From the Taft[15] $\rho\sigma^*$ relationship using σ^* = +0.65 for (CH_2=C<).[16] The lower ratio was obtained using Gassman's[17] ρ of −1.94 based on five 7-substituted *endo*-norbornyl tosylates; the higher ratio based on ρ = 2.09 derived from Gassman's data but with only those (three) compounds with 7 substituents anti to the C-2 position.

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(19) Based on the ρ values described in ref 14. The σ^* for (Ph_2C=CH) was estimated as the difference between the σ^* for vinyl[16] and twice the difference between the σ^* values for vinyl and (PhCH=CH).[15]

(20) Under conditions where the dimethyl analog gave a rate ratio of 4500 the diphenyl compound gave a ratio of only 19 (unpublished work of Mrs. M. Magde).

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On the Lack of Stabilization of σ-Delocalized Cyclopropylcarbinyl Ions by π Participation[1,2]

Sir:

Attention has been drawn to the remarkable lack of stabilization of the transition state from exo norbornyl derivatives by a phenyl substituent at C_1.[3,4] Previous

(1) Taken from the Ph.D. Dissertation of J. N. C. Hsu, Cornell University, 1970.

(2) Supported, in part, by the National Science Foundation.

(3) C. F. Wilcox, Jr., R. G. Jesaitis, and S. Belin, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. ORGN 8.