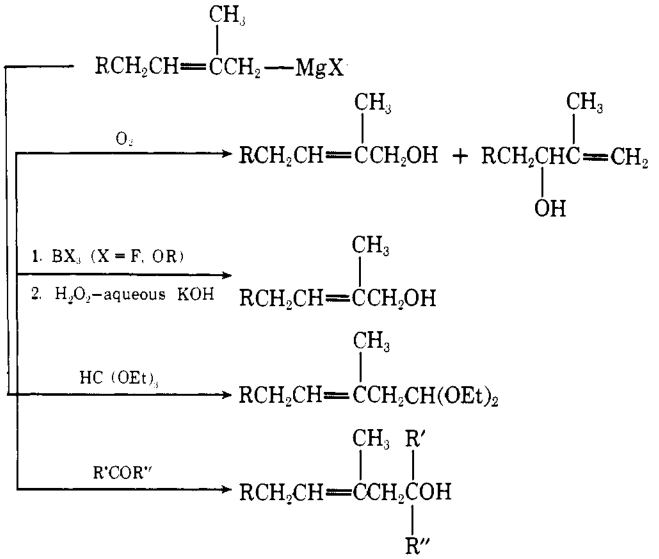
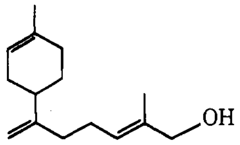
Scheme II



tion. The selectivity requires a particular orientation of an isoprene unit with respect to the Mg-η^1-allyl bond in the transition state and a kinetically controlled attack of the isoprene tail carbon into isomeric form **2** rather than **1**.[4] Apparently attendance of the titanium ion achieves these conditions. The reaction without the titanium compound does not take place under comparable conditions and under forced conditions the allyl Grignards give Wurtz-type reaction products.

The newly formed substituted allyl magnesium compound undergoes usual Grignard reactions (step 2): a few examples are shown in Scheme II. The apparent two-step reaction can be carried out virtually as a one batch process, and the pure products (>90%) were obtained by simple distillation. Concerning the stereochemistry of the double bonds in the products, the trans isomers are predominant in each case (>80%). The utility is demonstrated for synthesis of natural terpenes such as lanceol (**6**), lavandurol (**8**), and damascone (**11**), as well as double bond isomers of geraniol (3,7-dimethyl-3,7-octadien-1-ol) (**7**), geranic acid (3,7-dimethyl-3,7-octadienoic acid) (**9**), citral (3,7-dimethyl-3,7-octadienal) (**10**), and geranylacetone (6,10-dimethyl-6,10-undecadien-2-one) (**12**) (see Table I). Lanceol,[5] for example, was synthesized as follows. A THF solution of 2-(4-methyl-3-cyclohexenyl)allylmagnesium chloride (50 mmol), prepared from 10-chloro-1,8-*p*-methadiene, was treated with isoprene (100 mmol) in the presence of Cp_2TiCl_2 (0.5 mmol) at 60-70°. The reaction mixture was then treated with BF_3OEt_2 (60 mmol) at 5° for 0.5 hr, and subsequently oxidized at 10° with an alkaline hydrogen peroxide solution (50 ml of 3% aqueous NaOH plus 8 ml 30% H_2O_2). After usual work-up, *cis*- and *trans*-lanceol (1:4) were obtained as a yellow oil. The stereoisomers were separated by preparative GLC and identified by spectral analysis including mass spectrometry.[5]



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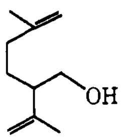

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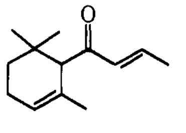
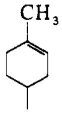


11

Table I. Terpenoid Synthesis Using the Isoprene Insertion[a]

R_3 in $CH_2{=}C(R_3)CH_2MgX$	Reagent for step 2	Product (% yield)[b]
	1. BF_3OEt_2	**6** (52)[c]
	2. H_2O_2–aqueous NaOH	**7** (60), **8** (10)
CH_3–	CH_2O	**7** (60), **8** (10)
CH_3–	CO_2	**9** (80)
CH_3–	$HC(OEt)_3$	**10** (55)
CH_3–	1. $CH_3CH{=}CHCHO$	
	2. CrO_3–acetone	**11** (40)
	3. H_2SO_4–AcOH	
CH_3–	$CH_2{=}CHCOCH_3$[d]	**12** (30)

[a] The isoprene reaction was generally carried out using a mole ratio of the allyl Grignard reagent (the entry at the extreme left)/isoprene/Cp_2TiCl_2 = 100/150/1 at 60° for 10 hr. [b] The isolated yield based on the allyl Grignard reagent. [c] The organoboron compound being the intermediate, secondary alcohol was not formed. [d] Two mole percent of CuCl was used.

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(3) (a) K. Tamao, K. Sumitani, and M. Kumada, *J. Am. Chem. Soc.*, **94**, 4374 (1972); (b) K. Tamao, Y. Kiso, K. Sumitani, and M. Kumada, *Ibid.*, **94**, 9269 (1972).

(4) The structure of allylMgX in solution is best described as "dynamic η^1-allyl" coordination. See, for example, G. Wilke, B. Bogdanovcc, P. Hardt, P. Heimbach, W. Keim, M. Krondr, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter, and H. Zimmermann, *Angew. Chem.*, **78**, 157 (1966).

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Susumu Akutagawa
Central Research Laboratory, Takasago Perfumery Co. Ltd.
31-36 5-Chome, Kamata, Ohta-ku, Tokyo, 114

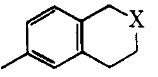
Sei Otsuka*
Department of Chemistry, Faculty of Engineering Science
Osaka University
Toyonaka, Osaka, Japan 560

Received June 30, 1975

Polar Field Effects on ^{19}F Chemical Shifts. An Important Effect

Sir:

Although our recent ^{19}F NMR studies[1] of model systems **1**, **2**, and **3** appeared to resolve the debate regarding the importance of polar field effects on ^{19}F chemical shifts,[2] Fukunaga and Taft[3a,b] have concluded on the basis of more recent work that the field phenomenon is relatively unimportant, a viewpoint diametrically opposed to ours. Thus, we are prompted to report in a preliminary form new data from systems **1** and **2** (X = CF_2) and **3** (X = NH, $^+NH_2$, O, CO and CF_2) which, together with the previously published results, not only strongly support our previous conclusions but, in addition, bring unambiguously to light an often neglected feature of the electric field model.



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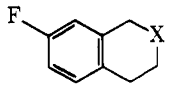

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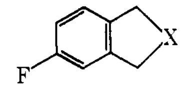

3

The relative ^{19}F chemical shifts in DMF and benzene are listed in Table I together with the previously published data.[4] An important conclusion follows from these results. Apart from the obvious fact that charged and strongly dipolar substituents (X = O, CO, CF_2, and SO_2) exert significant deshielding effects on ^{19}F chemical shifts in these

Table I. Relative ^{19}F Chemical Shifts (ppm) in Dimethylformamide and Benzene[a]

	Compound		
Substituent, X	**1**[b]	**2**[b]	**3**[c]
CO	−1.49 (−1.64)	−1.40 (−1.68)	−2.86 (−2.99)
O	−1.50 (−1.50)	−1.50 (−1.59)	−1.70 (−1.61)
NCH_3	−0.98 (−0.85)	−0.46 (−0.46)	
NH			−0.74 (−0.63)
$^{+}N(CH_3)_2$	−4.49	−3.04	
$^{+}NH_2$			−6.70[d]
S	−1.83 (−1.83)	−1.19 (−1.35)	−0.64 (−0.55)
SO_2	−3.78 (−4.18)	−2.06 (−2.69)	−5.20 (−5.53)
$^{+}SCH_3$	−6.17	−3.56	
CF_2	−1.56 (−1.61)	−1.05 (−1.20)	−2.98 (−3.04)

[a] In parentheses. [b] Chemical shifts relative to 6-fluorotetralin. [c] Chemical shifts relative to 5-fluoroindan. [d] Solvent, CF_3CO_2H.

model systems (−6.7 ppm when X = $^{+}NH_2$ in **3**!), *note* that for all the strong dipolar substituents (X = CO, CF_2, and SO_2), except for X = O, there is a marked enhancement in the electron-withdrawing power (twofold) of these groups when located in model system **3** as compared to **1** and **2**. Stereochemical factors (ring strain effects)[2] as the possible origin of this effect can be readily dismissed on a number of grounds.[5] Therefore, since the inherent structural features[6] in our model systems are such that localized π-polarization effects (π-inductive and mesomeric effects) are substantially minimized, if not entirely eliminated in system **3**, the observed phenomenon demands an explanation in terms of a predominant polar field effect.[7] Surprisingly, based on a simple electric field model for ^{19}F chemical shifts,[2,8] the through-space component (angular and distance factors) of the polar field effect is computed to be approximately the *same* for all systems (**1**, **2**, and **3**). How then can this apparent anomaly be accounted for?

The solution lies in the distinct differences in molecular geometry between systems **1** (or **2**) and **3**. An examination of Dreiding models indicates that whereas the dipole or group moment for all the substituents in system **3** are essentially in the molecular plane, the dipole or group moments for X = CO, CF_2, and SO_2 in **1** or **2** lie in a plane which makes an angle of approximately 45-50° with the plane containing the aromatic ring.[9] Only where X = O in **1** or **2** does the plane containing the dipole almost coincide with the molecular plane (*note* that where X = O, no marked enhancement of the electron-withdrawing power of the group is observed in **3** relative to **1** (or **2**)). Now since there is good experimental[1,10] and theoretical[11] evidence for the belief that substituent-induced perturbations of ^{19}F chemical shifts are determined by the degree of polarization of the potential π-component of the CF bond, the electrostatic effect of the charged or dipolar substituents must by necessity operate on the whole π-system. Obviously, the lines of force emanating from the various groups will be most effective when constrained to operate in the plane of the aromatic ring (system **3**). This explanation can be put in another way. The field effect model[12] for substituent effects consists of two parts, a direct effect (through-space component) and a polarization effect. Whereas the direct effect is a function of angle and distance factors (computed to be virtually indistinguishable for **1**, **2**, and **3**), the latter effect depends on the nature of the intervening dielectric material. Consequently, in system **3**, where the major lines of force traverse the very polarizable π-system, the polarization term should be much greater than in **1** or **2**.[13] It is important to note that this *nonlocalized* π-polarization effect has been considered to be important in connection with substituent effect studies on proton[14] and carbon-13 chemical shifts.[15]

An important comparison that exemplifies the significance of polar field effects on ^{19}F chemical shifts is the fact that in system **3**, where X = CF_2, the relative shift is −3.00 ppm (Table I), yet when CF_3 is para disposed and directly attached to the phenyl ring the ^{19}F SCS is only −5.15 ppm (benzene as solvent).[16] Interestingly, the DSP analysis[17] of the ^{19}F chemical shifts of para-substituted fluorobenzenes indicates that the polar effect of the CF_3 group contributes predominantly (−3.51 ppm) to this total effect.

Our results and interpretation here clearly invalidate the recent conclusion of Fukunaga and Taft.[3a] Thus, their results from two questionable model systems[18] do not impinge in any way on the validity of Dewar's FMMF method.[8]

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(3) (a) J. Fukunaga and R. W. Taft, *J. Am. Chem. Soc.*, **97**, 1612 (1975). (b) Although Fukunaga and Taft[3a] have not explicitly stated the electronic mechanism responsible for the observed transmission of polar substituent effects upon ^{19}F NMR shifts via the π-electron system, they have specifically rejected field phenomena. Previous papers by Taft and coworkers clearly lead one to believe that they strongly favor the π-inductive mechanism: S. K. Dayal, S. Ehrenson, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 9113 (1972); S. K. Dayal and R. W. Taft, *ibid.*, **95**, 5595 (1973).

(4) The fluorine NMR spectra were measured with a modified Varian DP60 operating at 56.4 MHz using solutions containing 10% (w/w) of the fluoro compound, together with 5% (w/w) of 1,1,2,2,-tetrachloro-3,3,4,4-tetrafluorocyclobutane (TCTFB). All new compounds gave satisfactory analyses and their proton NMR spectra were in accordance with the assigned structures; details will be given in a main paper.

(5) Firstly, replacing methylene (X = CH_2) by the relatively large sulfur atom (X = S) in system **3** leads only to a relatively small downfield shift. Further, no dramatic structural changes should occur in proceeding from the divalent sulfide to the sulfone. This latter point also applies to the change, NH to $^{+}NH_2$. Secondly, it is inconceivable that the geminal difluoro group (X = CF_2) would effect profound structural changes in the aromatic ring of 5-fluoroindan.

(6) See ref 1 for a detailed discussion of the structural features incorporated into **1**, **2**, and **3** which allow a separation of polar and π-electron effects.

(7) Even if the π-inductive effect is not entirely eliminated by the interposition of a methylene group, this mechanism cannot account for the observations since it would be the same in all three systems. Further, hyperconjugative electron-withdrawing effects (ref 1) are completely eliminated in **3**.

(8) M. J. S. Dewar, R. Golden, and J. M. Harris, *J. Am. Chem. Soc.*, **93**, 4187 (1971), and references therein.

(9) (a) It is important to note that previous deductions from Dreiding models (see ref 9b and 9c) regarding the conformations of **1** or **2** (where X = $Si(CH_3)_2$) have subsequently been vindicated by x-ray crystallographic studies: P. J. P. Vidal, J. Lapasset, and J. Falgueirettes, *Acta Crystallogr., Sect. B*, **28**, 3137 (1972); P. J. P. Vidal and J. Falgueirettes, *ibid.*, **29** 2833 (1973); (b) W. Adcock, S. Q. A. Rizvi, and W. Kitching, *J. Am. Chem. Soc.*, **94**, 3657 (1972); (c) W. Kitching, A. J. Smith, W. Adcock, and S. Q. A. Rizvi, *J. Organomet. Chem.*, **42**, 373 (1972).

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(17) P. R. Wells, S. Ehrenson, and R. W. Taft, *Prog. Phys. Org. Chem.*, **6**, 147 (1968).

(18) Fukunaga and Taft's choice of model systems can be severely criticized on a number of points. First, since the substituents in their model systems 11 and 111 are directly attached to the aromatic ring, complications arising from concomitant localized π-polarization effects (π-inductive and mesomeric effects) have not been eliminated. Thus, rather artificial means (DSP analysis) have to be employed in order to separate

polar and π-electron effects. Secondly, although the angular and distance factors can be established with some confidence for their system 11, system 111 is a stereochemically ill-defined structure. Their crucial assumption that angular and distance factors are the same for 11 and 111 is an extremely gross one.

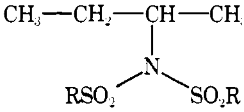
W. Adcock,* B. D. Gupta
School of Physical Sciences, Flinders University
Bedford Park, S.A., Australia
Received July 1, 1975

Orientation in Base-Promoted β Eliminations from 2-Butyl-*N*,*N*-disulfonimides

Sir:

Orientation in alkene formation by base-promoted β elimination has been a topic of research interest since the 1850's.[1] Early results[1,2] led to the formulation of the Hofmann and Saytzeff rules[3,4] for positional orientation.[5] Although these rules currently are recognized as only broad generalizations with numerous exceptions,[3] their existence underscores the pronounced effect of leaving group identity upon positional orientation.

Continuing investigations[6] of factors which control orientation in base-promoted β eliminations led us to examine the reaction of *N*-2-butyl-*N*,*N*-di(*p*-toluene)sulfonimide, **1a**, with *t*-BuOK–DMSO at 50°. To our surprise, the olefinic reaction product consisted *entirely* of 1-butene! It is estimated that 0.1% of *trans*-2-butene and/or *cis*-2-butene could have been detected. Subsequent experiments revealed that the observed regiospecificity was not due to some pecularity of the base-solvent system, since eliminations from **1a** promoted by MeONa–DMSO and MeONa–MeOH at 50° also yielded only 1-butene.



1a, R = $-C_6H_4$-*p*-CH_3
b, R = $-CH_3$
c, R = $-C_6H_4$-*m*-NO_2

The significance of these observations is revealed by comparison with literature data for orientation in reactions of *t*-BuOK–DMSO with a variety of 2-substituted butanes (Table I). Regiospecificity of base-induced eliminations from **1a** is greater than that found with any previously reported leaving group!

In order to probe the factors responsible for this remarkable orientation control, eliminations from other 2-butyldisulfonimides, **1b** and **1c**, were conducted. The elimination product which resulted from reaction of *N*-2-butyl-*N*,*N*-dimethylsulfonimide, **1b**, with *t*-BuOK–DMSO at 50° was solely 1-butene. The inessential nature of the aryl portion of disulfonimide leaving groups for the observed regiospecificity is therefore demonstrated. An alkene mixture comprised of 98.8% 1-butene and 1.2% 2-butenes resulted from reaction of *N*-2-butyl-*N*,*N*-di(*m*-nitrobenzene)sulfonimide, **1c**, with *t*-BuOK–DMSO at 50°. Formation of less terminal alkene with change to a more reactive[11] leaving group is consistent with previous observations for alkyl halides and tosylates.[3]

Table I. Positional Orientation in Eliminations from 2-Substituted Butanes Induced by *t*-BuOK–DMSO at 50°

Leaving group	% of 1-butene in total butenes	Ref
–I	21	7
–Br	30	8
–Cl	41	9
$-OSO_2C_6H_4$-*p*-CH_3	57	8
$-\overset{+}{N}(CH_3)_3{}^+$	97[a]	10

[a] The base was EtOK. However, only a small increase in % of 1-butene would be anticipated for a change from EtOK to *t*-BuOK in DMSO.[7]

According to Brown's steric theory of orientation,[12] very large leaving groups favor the formation of 1-alkene from a 2-substituted alkane. Destabilizing steric repulsions between the leaving group and α- and β-alkyl groups are smaller in the transition state for formation of terminal alkene than in those for production of internal olefins. It seems most reasonable to attribute the orientation control observed for eliminations from **1a–c** to a steric effect of the $-N(SO_2-)_2$ portion of the leaving group.

Qualitatively, the facility of the alkyl *N*,*N*-disulfonimide eliminations which were examined resembles that of corresponding alkyl chlorides. Reactivity of the disulfonimide leaving group is therefore anticipated to be considerably greater than that of the trimethylammonio leaving group.

Additional studies of mechanistic and synthetic aspects (e.g., conversion of 2-alkyl alcohols to pure 1-alkenes via the route 2-alkyl alcohol, tosylate, amine, disulfonimide, 1-alkene) of elimination reactions involving disulfonimide leaving groups are in progress.

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Richard A. Bartsch,* James R. Allaway
David D. Ingram, Jong-Gun Lee
Department of Chemistry, Texas Tech University
Lubbock, Texas 79409
Received August 4, 1975

Monomeric Methyl Metaphosphate. II. Electrophilic Aromatic Substitution

Sir:

In an earlier publication,[1] we described the evidence that monomeric methyl metaphosphate can be produced in the gas phase by the flash pyrolysis of methyl 2-butenylphostonate (A) and that the metaphosphate reacts at dry ice temperatures with *N*-methylaniline to produce a salt of methyl *N*-methyl-*N*-phenylphosphoramidate. We have now found that monomeric methyl metaphosphate will even attack the aromatic ring of *N*,*N*-diethylaniline at low temperature to