JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 6, 685–689 (1993)

ACIDITIES OF 4-SUBSTITUTED BENZOIC, BICYCLO[2.2.2]OCT-1-YL AND BICYCLO[2.2.2]OCT-2-ENYL CARBOXYLIC ACIDS

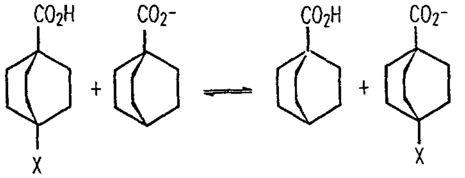
I. A. KOPPEL
Department of Chemistry, Tartu University, EE2400 Tartu, Estonia
M. MISHIMA
Institute for Molecular Sciences, Myodaiji, Okazaki, 444, Japan
L. M. STOCK
Department of Chemistry, University of Chicago, Chicago, Illinois 60634, U.S.A.
R. W. TAFT
Department of Chemistry, University of California, Irvine, California 92717, U.S.A.
AND
R. D. TOPSOM
Department of Chemistry, La Trobe University, Bundoora, 3083, Australia

Experimental gas-phase acidities are reported for a series of 4-substituted bicyclo[2.2.2]oct-1-yl carboxylic acids and for a limited number of the corresponding bicyclo[2.2.2]oct-2-enyl carboxylic acids. Similar acidities are also reported for additional 4-substituted benzoic acids, allowing a comparison of field and resonance effects between the three series. *Ab initio* molecular orbital calculations for these series of acids confirm the conclusion that the aromatic acids display direct field and resonance effects, whereas the acidities in the aliphatic series acids are largely determined by direct field effects.

INTRODUCTION

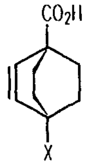
In recent years, we have reported gas-phase results for proton transfer equilibria of various series of molecules to establish the inherent substituent effects in the absence of a solvent. We have coupled these results with the use of *ab initio* molecular orbital calculations, both to establish the utility of such calculations and to use them to increase our understanding as to how substituent effects are transmitted. To date, we have reported such data for substituted methylamines,[1] acetic acids,[2] cyanides,[3] phenols,[4,5] pyridines,[6,7] anilines,[6] quinuclidines[8] and bicyclo[2.2.2]oct-1-yl amines.[8]

We now report both gas-phase proton transfer energies (relative acidities) and *ab initio* molecular orbital calculations (STO-3G basis level) for the important series of 4-substituted bicyclo[2.2.2]oct-1-yl carboxylic acids [equation (1)].



(1)

This equilibrium has been much used[9,10] as the basis for scales of field effects (σ_F or the earlier σ_I designation). We also report gas-phase acidities for some 4-substituted bicyclo[2.2.2]oct-2-enyl carboxylic acids (**I**)

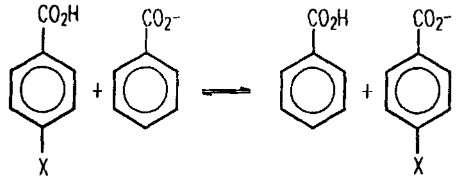


(I)

0894–3230/93/120685–05$07.50

Received 14 May 1993
Revised 23 July 1993

and additional gas-phase experimental figures and molecular orbital calculations to extend the results available[11] for the energies of the proton transfer equilibrium for 4-substituted benzoic acids [equation (2)].



(2)

In solution, the acidities of process (2) are affected[10] by both field and resonance effects and it was earlier suggested[12] that the differences in acidities for corresponding substituents between series (1) and (2) is a measure of the resonance effect of substituents (σ_R). *Ab initio* molecular orbital calculations have also been previously reported[13] for the acidities of some 4-substituted benzoic acids, but for our purposes we wished to have values for the complete series listed, using standard geometries.

EXPERIMENTAL

Samples were available from previous work on bicyclo[2.2.2]oct-2-enyl carboxylic acids[14] and for most of the compounds from work on bicyclo[2.2.2]oct-1-yl carboxylic acids.[15] The 4-fluoro- and 4-chlorobicyclooctyl acids were kindly supplied by Dr W. Adcock and the 4-methyl derivative[15] was synthesized by Dr N. Pirzada. Commercial samples of the benzoic acids in Table 3 were used.

The ion cyclotron resonance (ICR) technique, described earlier,[4] was used at the University of California for the determination of the gas-phase acidities [$\delta\Delta G^\circ$ in kcal mol^{-1} (1 kcal = 4·184 kJ), at 100 °C] of the above-mentioned acids. Preliminary data have been reported previously.[10,16,17]

The gas-phase acidities of the bicyclo[2.2.2]oct-1-yl carboxylic acids are given in Table 1, of the bicyclooctenyl acids in Table 2 and of the additional 4-substituted benzoic acids measured in Table 3. They were obtained by the ICR spectroscopic methods given in Ref. 18, or cited therein. The values of $\delta\Delta G^\circ$ refer

Table 1. Gas-phase acidities of 4-substituted bicyclo[2.2.2]oct-1-yl carboxylic acids (X = 4-substituent, ΔG° values in kcal mol^{-1}, + sign indicates acid weaker than standard)

X	Reference acid	$\delta\Delta G^\circ$	$\Delta G^\circ_{\mathrm{Std}}$	$\Delta G^\circ_{\mathrm{H^+}}$	$\Delta G^\circ_{\mathrm{H^+(bv)}}$	$\delta_X\Delta G^\circ$
H	*m*-$\mathrm{FC_6H_4OH}$	+0·4	336·8	337·2		
	o-$\mathrm{FC_6H_4OH}$	−1·8	339·0	337·2	337·2	0·0
$\mathrm{CH_3}$	*m*-$\mathrm{FC_6H_4OH}$	−0·6	336·8	336·2		
	m-$\mathrm{ClC_6H_4CH_2CN}$	−1·3	337·5	336·2	336·2	1·0
$\mathrm{OCH_3}$	*m*-$\mathrm{ClC_6H_4OH}$	−0·4	335·0	334·6		
	m-$\mathrm{CH_3COC_6H_4OH}$	−1·0	335·6	334·6	334·6	2·6
F	$\mathrm{FCH_2CO_2H}$	+0·3	331·3	331·6		
	p-$\mathrm{CF_3C_6H_4OH}$	+1·4	330·1	331·5	331·6	5·6
Cl	*p*-$\mathrm{CF_3C_6H_4OH}$	−0·9	330·1	331·0		
	m-$\mathrm{CF_3C_6H_4OH}$	−1·3	332·4	331·1	331·0	6·2
Br	*m*-$\mathrm{CF_3C_6H_4OH}$	−2·0	332·4	330·4		
	p-$\mathrm{CF_3C_6H_4OH}$	+0·2	330·1	330·3	330·3	6·9
$\mathrm{CF_3}$	*m*-$\mathrm{CF_3C_6H_4OH}$	−1·6	332·4	330·8		
	p-$\mathrm{CF_3C_6H_4OH}$	+0·6	330·1	330·7	330·7	6·5
CN	*p*-$\mathrm{SCF_3C_6H_4OH}$	+0·3	328·4	328·7		
	p-$\mathrm{CNC_6H_4CH_2CN}$	+0·6	327·9	328·5	328·6	8·6
$\mathrm{NO_2}$	*p*-$\mathrm{CF_3C_6H_4OH}$	−1·5	330·1	328·6		
	$\mathrm{CF_3CH_2CO_2H}$	+0·7	327·7	328·4	328·4	8·8

Table 2. Gas-phase acidities of 4-substituted bicyclo[2.2.2]oct-2-enyl carboxylic acids (X = 4-substituent, ΔG° values in kcal mol^{-1}, + sign indicates acid weaker than standard)

X	Reference acid	$\delta\Delta G^\circ$	$\Delta G^\circ_{\mathrm{Std}}$	$\Delta G^\circ_{\mathrm{H^+}}$	$\Delta G^\circ_{\mathrm{H^+(bv)}}$	$\delta_X\Delta G^\circ$
H	*m*-$\mathrm{FC_6H_4OH}$	−1·6	336·7	335·1		
	m-$\mathrm{ClC_6H_4OH}$	+0·3	335·0	335·3	335·2	(0·0)
$\mathrm{CO_2Et}$	*m*-$\mathrm{CF_3C_6H_4OH}$	−0·5	332·4	331·9	331·9	3·3
Cl	*p*-$\mathrm{CF_3C_6H_4OH}$	−1·2	330·1	328·9	328·9	6·3
$\mathrm{CF_3}$	*m*-$\mathrm{CNC_6H_4OH}$	0·0	328·9	328·9	328·9	6·3
CN	*o*-$\mathrm{CNC_6H_4OH}$	−0·5	327·1	326·6	326·6	8·6

Table 3. Gas-phase acidities of 4-substituted benzoic acids (X = 4-substituent, ΔG° values in kcal mol^{-1}, + sign indicates acid weaker than standard)

X	Reference acid	$\delta \Delta G^\circ$	$\Delta G^\circ_{\mathrm{Std}}$	$\Delta G^\circ_{\mathrm{H^+}}$	$\Delta G^\circ_{\mathrm{H^+(bv)}}$	$\delta_X \Delta G^\circ$
H	–	–	–	–	333·0	(0·0)
CH_3CO	$CF_3CH_2CO_2H$	−0·4	327·7	327·3	327·3	5·7
CHO	p-CNC_6H_4OH	+0·5	325·3	325·3	325·8	7·2
CF_3	p-CNC_6H_4OH	0·0	325·3	325·3	325·3	7·7
CO_2Et	p-$CHOC_6H_4OH$	+0·2	325·8	326·0		
	3,5-diClC_6H_3OH	−0·9	327·5	326·6	326·3	6·7

Table 4. Calculated (STO-3G) total electronic energies. (−E) for 4-substituted benzoic and 4-substituted bicyclo[2.2.2]oct-1-yl carboxylic acids

	−E (hartree)			
X	$XC_6H_4CO_2H$	$XC_6H_4CO_2^-$	$XC_8H_{12}CO_2H$	$XC_8H_{12}CO_2^-$
H	412·9734	412·2155	492·5599	491·7853
$NH_{2(pl)}$	467·2865	466·5228	546·8542	546·0795
$NH_{2(tetr)}$	467·2946	466·5343	546·8704	546·0960
OMe	525·3811	524·6209	604·9555	604·1834
OH	486·8722	486·0544	566·3801	565·6087
Me	451·5579	450·7983	531·1328	530·3581
F	510·4337	509·6789	590·0133	589·2438
CF_3	743·9375	743·1882	823·5241	822·7538
NO_2	613·6647	612·9268	693·2515	692·4911
CN	503·5252	502·7830	583·1055	582·3427
CHO	524·1981	523·4476	603·7764	603·0062
COMe	562·7777	562·0267	642·3542	641·5818
CO_2Me	636·6365	635·8863	716·2108	715·4392

to the results obtained for the proton transfer equilibria with each of the indicated standard acids that have the $\Delta G^\circ_{\mathrm{H^+}}$ value given as $\Delta G^\circ_{\mathrm{Std}}$. The two $\Delta G^\circ_{\mathrm{H^+}}$ columns in Tables 1–3 are the individual $\Delta G^\circ_{\mathrm{H^+}}$ values and the best value, $\Delta G^\circ_{\mathrm{H^+(bv)}}$, obtained from them. All values of $\Delta G^\circ_{\mathrm{Std}}$ were taken from Ref. 19. The final column gives the substituent effect values, $\delta_X \Delta G^\circ = \Delta G^\circ_{\mathrm{H}} - \Delta G^\circ_{\mathrm{X}}$ for gas-phase acidities relative to the parent unsubstituted acid. The uncertainties of the measured quantities are within ± 0·1–0·2 kcal mol^{-1}.

CALCULATIONS

The theoretical calculations were made at the *ab initio* STO-3G basis level, using the Gaussian-82[20] and Gaussian-86[21] programs. The geometries were standard values.[22] Table 5 lists the calculated energies for processes (1) and (2).

Table 5. Gas-phase relative acidities of 4-substituted benzoic and 4-substituted bicyclo[2.2.2]oct-1-yl carboxylic acids (−ΔG°, −ΔE in kcal mol^{-1})

	4-$XC_6H_4CO_2H$		4-$XC_8H_{12}CO_2H$	
X	−$\delta \Delta E$	−$\delta \Delta G^\circ_{(g)}$	−$\delta \Delta E$	−$\delta \Delta G^\circ_{(g)}$
H	0·0	0·0	0·00	0·0
$NH_{2(pl)}$	−3·63	−2·3	0·06	
$NH_{2(tetr)}$	−1·47		0·13	
OMe	−1·40	−0·7	1·56	2·6
OH	0·06		2·02	
Me	−1·06	−1·1	−0·04	1·0
F	1·94	2·9	3·23	5·6
CF_3	5·39	7·7	2·76	6·5
NO_2	12·58	11·7	8·95	8·8
CN	9·83	10·9	7·45	8·6
CHO	4·69	7·2	2·79	
COMe	4·41	5·7	1·41	
CO_2Me	4·85	6·7[a]	1·89	

CO_2Et.

DISCUSSION

Experimental results

Table 1 lists the experimental gas-phase acidities [as $-\Delta G^\circ(\mathrm{g})$] for a series of eight 4-substituted bicyclo[2.2.2]oct-1-yl carboxylic acids having a representative range of substituent types. An analysis[10] can be done against field, resonance and polarizability parameters (electronegativity proves to be of no consequence in any of the analyses below if this term is included) using the equation

$$-\delta\,\Delta G^\circ = \rho_F\sigma_F + \rho_R\sigma_R + \rho_\alpha\sigma_\alpha + C \qquad (3)$$

The result for the acidities of the bicyclo[2.2.2]oct-1-yl carboxylic acids is

$$-\delta\,\Delta G^\circ = 1{\cdot}8(\pm 0{\cdot}7)\sigma_\alpha + 12{\cdot}8(\pm 0{\cdot}7)\sigma_F - 0{\cdot}03(\pm 0{\cdot}3) \qquad (4)$$

with a correlation coefficient of 0·992 and a standard deviation of 0·5; there is no significant dependence on the resonance term, σ_R. If the polarizability term is dropped from the analysis, the equation becomes

$$-\delta\,\Delta G^\circ = 13{\cdot}4(\pm 0{\cdot}9)\sigma_F + 0{\cdot}26(\pm 0{\cdot}4) \qquad (5)$$

with a correlation coefficient of 0·984, a standard deviation of 0·6 and a standard deviation in fit of ±0·47. Thus, an excellent fit is obtained with a small substituent polarizability term that is likely to be real for these gas-phase results.

A similar analysis can be done for the 4-substituted bicyclo[2.2.2]oct-2-enyl carboxylic acids with results available for five compounds. Here we obtain the equation

$$-\delta\,\Delta G^\circ = 14{\cdot}3(\pm 0{\cdot}2)\sigma_F - 0{\cdot}06(\pm 0{\cdot}8) \qquad (6)$$

with a correlation coefficient of 0·999 and a standard deviation of 0·9. Thus, both series of bicyclo[2.2.2]oct-1-yl carboxylic acids show a strong dependence on the field effect of the substituents. It was shown earlier[8] that a dependence on electronegativity or electronegativity plus resonance parameters gives a much worse fit and previously[23] that electronegativity and field (inductive) parameters were not linearly related. The absence of a statistically significant σ_α term in equation (6) is probably due to the small variation in this parameter for this limited data set. This conclusion is strongly supported by the fact that the three substituents (Cl, CF_3 and CN) that are common to both this and the octane set [from which equation (4) is obtained] have the same substituent effects, to within experimental error. This results in the ρ_F values of equations (4) and (6) being equal within the combined uncertainties.

In spite of the conclusions imposed by equations (4)–(6), there have been various suggestions, notably by Gasteiger and his workers,[24] that such substituent effects are due to electronegativity effects. Gasteiger and co-workers derived an electronegativity parameter by a method involving partial equalization of orbital electronegativity. They claimed that this could be moderately well correlated with the gas-phase proton affinities of a number of series of compounds. However, considering the number of intervening bonds, the method predicts no substituent effect at all from the 4-position of a 4-substituted bicyclooctane! Sacher[25] suggested that σ_F values are linear with electronegativity values such as the X_G values[26] of Mullay or the *i* values of Inamato and Masuda,[27] but the correlation coefficients are very low, 0·72–0·73. More recently, Masuda *et al.*[28] suggested that the parameters σ_F and *i* can be interrelated if a dipole distance term is included. This conclusion fits in with the basic concept of electronegativity differences producing the substituent dipole fields that are carried by framework and field to the reaction site.[10]

Several aspects of the solvent effects of water, aqueous alcohols, dimethyl sulphoxide and others on the relative acidities of 2-, 3- or 4-substituted bicyclo[2.2.2]octane carboxylic acids, 4-substituted bicyclo[2.2.2]octene carboxylic acids, 4-substituted cubane carboxylic acids and 2-, 3- or 4-substituted adamantane-1-carboxylic acids have been considered elsewhere.[29,30] The conclusion was reached that electrostatic field effects are dominant, as concluded also by Holtz and Stock[15] and recently by Masuda *et al.*[28]

With the additional results reported in Table 3 for the 4-substituted benzoic acids, we have results (Table 5) for eleven compounds. Analysis according to equation (3) leads to the equation

$$-\delta\,\Delta G^\circ = 15{\cdot}9(\pm 1{\cdot}0)\sigma_F + 14{\cdot}6(\pm 1{\cdot}3)\sigma_{R^+} - 0{\cdot}5(\pm 0{\cdot}4) \qquad (7)$$

with a correlation coefficient of 0·993 and a standard deviation of 0·7. According to Ref. 10, a small term in σ_α is statistically significant for the π-donor substituents but not for π-acceptor substituents.

Clearly in the benzoic acidities the resonance effect is an important controlling influence, as expected. The coefficient of transmission of σ_F also appears to increase slightly in equation (7) compared with that in equation (5) or (6). This is expected because of the polarization of the intervening π-systems by the charged probe site, the so-called π-inductive[29] or field-induced resonance effect.[30]

For condensed-phase equilibria, the difference between the relative acidities of the 4-substituted benzoic acids and the corresponding 4-substituted bicyclo[2.2.2]oct-1-yl carboxylic acids has been used as a measure of the substituent resonance effect.[12b] Such a treatment when applied to the gas-phase acidities introduces some relatively small errors due to omission of small contributions from substituent dipolar and polarizability effects.

Comparison of experimental ΔG° values with calculated ΔE values

Table 5 also lists the calculated $\delta\Delta E$ values for processes (1) and (2). The agreement between experiment and results calculated at the STO-3G basis level is generally good, as found in similar calculations for other proton transfer equilibria. This enables us to have confidence in using theoretical results, e.g. in equilibrium (1) for which gas-phase data are limited. Here we have $\delta\Delta E$ values for thirteen 4-substituted bicyclo[2.2.2]oct-1-yl carboxylic acids and analysis using equation (3) leads to the equation

$$-\delta\Delta E = 12\cdot 7(\pm 1\cdot 8)(\sigma_F - 1\cdot 2(\pm 0\cdot 8) \tag{8}$$

with a correlation coefficient of 0·93 and standard deviation of 0·6. Although the correlation coefficient is not high, the dependence on σ_F is almost identical with that for the experimental results; indeed, a correlation of experimental versus theoretical values gives a dependence of 1·02 and an intercept of −1·6 (correlation coefficient 0·92).

For the 4-substituted benzoic acids, analysis leads to the equation

$$-\delta\Delta E = 15\cdot 7(\pm 1\cdot 4)\sigma_F + 13\cdot 1(\pm 1\cdot 5)\sigma_{R^+} - 1\cdot 3(\pm 0\cdot 5) \tag{9}$$

with a correlation coefficient of 0·984 and a standard deviation of 0·9. Again, the major dependencies in equation (9) for the substituent effects are very similar to those found [equation (7)] for the experimental results.

REFERENCES

1. T. Silvestro, R. D. Topsom, C. W. Bock and R. W Taft, *J. Mol. Struct. Theochem* **184**, 33 (1989), and references cited therein.
2. C. Jinfeng, R. D. Topsom, A. D. Headley, I. Koppel, M. Mishima, R. W. Taft and S. Ueji, *J. Mol. Struct. Theochem* **168**, 141 (1988).
3. S. Marriott, R. D. Topsom, C. B. Lebrilla, I. Koppel, M. Mishima and R. W. Taft, *J. Mol. Struct. Theochem* **137**, 133 (1986).
4. M. Fujio, R. T. McIver, Jr, and R. W. Taft, *J. Am. Chem. Soc.* **103**, 4017 (1981).
5. T. Silvestro and R. D. Topsom, *J. Mol. Struct. Theochem.* **206**, 153 (1990).
6. M. Taagepera, K. D. Summerhays, W. J. Hehre, R. D. Topsom, A. Ross, L. Radom and R. W. Taft, *J. Org Chem.* **46**, 891 (1981).
7. G. Butt, R. D. Topsom and R. W. Taft, *J. Mol. Struct. Theochem* **153**, 141 (1987).
8. W. Adcock, F. Anvia, G. Butt, A. Cook, P. Duggan, C. A. Grob, S. Marriott, J. Rowe, M. Taagepera, R. W. Taft and R. D. Topsom, *J. Phys. Org. Chem.* **4**, 353 (1991).
9. R. D. Topsom, *Prog. Phys. Org. Chem.* **12**, 1 (1976), and references cited therein.
10. R. W. Taft and R. Topsom, *Prog. Phys. Org. Chem.* **16**, 1 (1987), and references cited therein.
11. J. B. Cumming and P. Kebarle, *Can. J. Chem.* **56**, 1 (1978), and references cited therein.
12. (a) J. D. Roberts and W. T. Moreland, *J. Am. Chem Soc.* **75**, 2167 (1953); (b) R. W. Taft, in *Steric Effects in Organic Chemistry*, edited by M. S. Newman, p. 595. Wiley, New York (1956).
13. N. Inamoto, S. Masuda and J. Niwa, *Bull. Chem. Soc. Jpn* **58**, 158 (1985); P. G. Mezey and W. F. Reynolds, *Can. J. Chem.* **55**, 1567 (1977); S. Bohm and J. Kuthan, *Int. J. Quantum Chem.* **26**, 21 (1984).
14. F. W. Baker and L. M. Stock, *J. Org. Chem.* **32**, 3344 (1967).
15. H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.* **86**, 5183 (1964).
16. I. A. Koppel, L. A. Moretskaya, V. I. Lantroyev, J. B. Koppel and V. O. Pihl, *Org. React. (Tartu)* **20**, 508 (1983).
17. I. A. Koppel, A. D. Korgesaar, J. B. Koppel and V. O. Pihl, *Org. React. (Tartu)* **25**, 272 (1988).
18. J. Catalan, R. M. Clarmunt, J. Elguero, J. Laynez, M. Menendez, F. Anvia, J. H. Quian, M. Taagepera and R. W. Taft, *J. Am. Chem. Soc.* **110**, 4105 (1988).
19. S. G. Lias, J. F. Bartmess, J. L. Liebman, R. D. Levin and G. W. Mallard, *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988).
20. J. S. Brinkley, M. Frisch, K. Raghavachari, D. DeFrees, H. B. Schlegel, R. Whiteside, F. Fluder, R. Seeger and J. A. Pople, *Gaussian 82, Release A*, Department of Chemistry, Carnegie–Mellon University, Pittsburgh, PA (1982).
21. M. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M., Fleuder and J. A. Pople, *Gaussian 86*. Carnegie–Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA (1984).
22. S. Marriott and R. D. Topsom, *J. Mol. Struct. Theochem* **110**, 337 (1984).
23. See, for example, N. Inamoto and S. Masuda, *Tetrahedron Lett.* 3287 (1977); W. F. Reynolds, *J. Chem. Soc., Perkin Trans. 2* 985 (1980); S. Marriott, W. F. Reynolds, R. W. Taft and R. D. Topsom, *J. Org. Chem.* **79**, 959 (1984).
24. See, for example, J. Gasteiger and M. Marsili, *Tetrahedron* **36**, 3219 (1980); M. G. Hutchings and J. Gasteiger, *Tetrahedron Lett.* 2541 (1983); M. G. Hutchins and J. Gasteiger, *J. Chem. Soc., Perkin Trans. 2* 455 (1986), and references cited therein.
25. E. Sacher, *Tetrahedron Lett.* 4683 (1986).
26. J. Mullay, *J. Am. Chem. Soc.* **107**, 7271 (1985), and references cited therein.
27. N. Inamoto and J. Masuda, *Chem. Lett.* 1007 (1982).
28. S. Masuda, N. Inamoto and J. Niwa, *Tetrahedron Lett.*, 6469 (1985).
29. (a) G. L. Anderson, R. C. Parish and L. M. Stock, *J. Am. Chem. Soc.* **93**, 6984 (1971); (b) W. F. Reynolds, I. R. Peat, M. H. Freeman and J. R. Lyerla, *Can. J. Chem.* **51**, 1857 (1973).
30. T. J. Broxton, G. Butt, R. Liu, L. H. Teo, R. D. Topsom and A. R. Katritzky, *J. Chem. Soc., Perkin Trans. 2* 463 (1974).