PERKIN 2

# Effect of a trimethylsilyl moiety on the nucleophilic character of the C=C bond: a comparative kinetic investigation of the epoxidation of substituted and unsubstituted cycloalkenes

**Govindagouda S. Patil and Gopalpur Nagendrappa ***

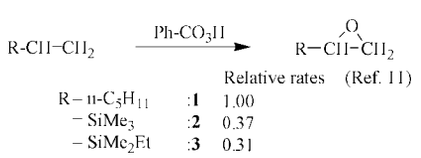
*Department of Chemistry, Bangalore University (Central College Campus), Bangalore-560 001, India*

***Received (in Cambridge, UK) 23rd February 2001, Accepted 14th May 2001***
***First published as an Advance Article on the web 12th June 2001***

The rates of epoxidation of twelve cycloalkenes (**6**–**17**) with MCPBA were determined at four temperatures (298, 303, 308 and 313 K). All of them were found to follow second-order kinetics. The silylated cycloalkenes (**10**–**13**) react faster than the corresponding unsubstituted cycloalkenes (**6**–**9**), but slower than the corresponding methyl cycloalkenes (**14**–**17**). Thus, for epoxidation, the silyl moiety is a deactivating group relative to an alkyl group, while it is activating in comparison with hydrogen. When the homologous series **6**–**9**, **10**–**13** and **14**–**17** are considered, the order of the rates of epoxidation in each series seems to follow the order of strain energy of its members, *i.e.*, the rate decreases in the sequence: 5-membered > 8-membered > 7-membered > 6-membered. The rate data obtained at four temperatures were employed to calculate $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$, based on which a common reaction mechanism is proposed.

## Introduction

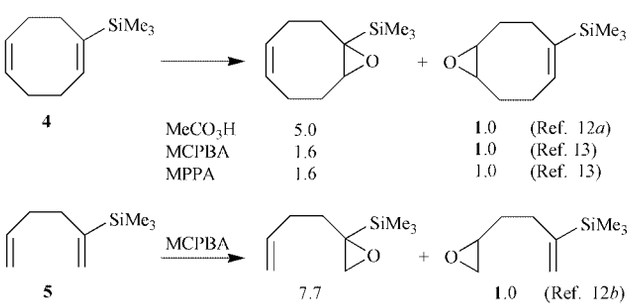
The ionization energies measured by photoelectron and mass spectroscopy,[1] and the EPR,[2] NMR,[3] vibrational[4] and electron transmission spectra[5] of various organosilicon compounds, and also the theoretical calculations of their molecular orbital energies[6] have shown that a vinylic silyl group decreases the nucleophilicity of the C=C bond due to $(p–d)_{\pi}$ back bonding or the interaction of the σ* orbital of the Si–C bond with vicinal π electrons. A decrease in the nucleophilicity of the C=C bond due to the presence of a vinylic silyl group, relative to an unsilylated olefin, has been observed in some reactions of vinylsilanes with electrophilic reagents such as free radicals,[7] carbenes,[8] iodomethylzinc iodide[9] and singlet oxygen.[10] Kinetic studies of the epoxidation of hept-1-ene (**1**) and vinylsilanes **2** and **3** with perbenzoic acid have shown that the vinylsilanes are less reactive than hept-1-ene (**1**)[11] (Scheme 1). However, reports




**Scheme 1**

on the relative rates of the epoxidation of vinylsilanes and simple olefins are rather confusing. While two examples show the epoxidation of the unsilylated double bond to be faster than that of the silylated double bond[11] (Scheme 1), a few other cases indicate the opposite.[12]

The epoxidation of 1-trimethylsilylcycloocta-1,5-diene (**4**) with peracetic acid,[12a] monoperphthalic acid (MPPA)[13] and *m*-chloroperbenzoic acid (MCPBA)[13] has been found to give, in each case, a mixture of monoepoxides, with the epoxide of the silylated double bond in excess of the unsilylated epoxide. The reaction of 2-trimethylsilylhexa-1,5-diene (**5**) with MCPBA has also shown that the silylated double bond is considerably more reactive towards epoxidation than the unsilylated one[12b] (Scheme 2). Peterson[12b] gave the following explanation for the




**Scheme 2**

observed behaviour of silylated and unsilylated C=C bonds in **5**: "Although the vinylsilane group is said to be mildly deactivating towards electrophilic attack owing to electron acceptor properties of *d* orbital or antibonding orbitals, examination of reported epoxidation rates shows that it is the replacement of carbon by silicon which results in deactivation. The silylated double bond in **5** differs from the unsilylated one in that hydrogen has been replaced by silicon to give a more substituted double bond, possibly activated towards epoxidation . . ." The same explanation may be extended to the epoxidation of **4**. However, no systematic investigation to correlate the characteristics of the silylated double bond with those of unsilylated or alkylated double bonds towards epoxidation has so far been reported. It is important, in the chemistry of vinylsilanes, that we have clear understanding of the role of the silyl moiety in such reactions and resolve the controversies noted earlier. We report here the results of a kinetic study of the epoxidation of several cycloalkenes aimed at appreciating the comparative role of the trimethylsilyl group.

## Experimental

### Materials

Cycloheptene (**8**), (*Z*)-cyclooctene (**9**), 1-methylcyclopentene (**14**) and 1-methylcyclohexene (**15**) were commercial analytical reagent grade samples and were distilled before use. MCPBA

DOI: 10.1039/b101752g

(Lancaster, UK) was estimated by an iodimetric method for its peracid content. Cyclopentene (**6**), cyclohexene (**7**), 1-methylcycloheptene (**16**) and 1-methylcyclooctene (**17**) were prepared by the dehydration of their respective alcohols.[14] 1-Trimethylsilylcycloalkenes (**10**–**13**) were prepared by the reported procedure.[15] All the solvents were distilled before use.

### Kinetic measurements

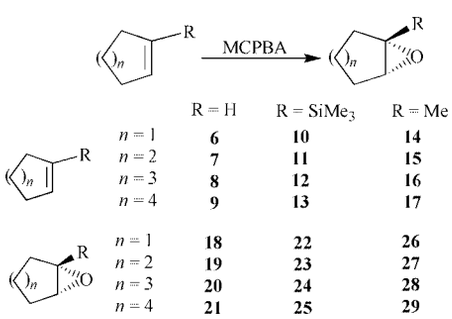
Equal volumes (12.5 mL each) of the solutions of an olefin (**6**–**17**, 0.01 mol $dm^{-3}$) and MCPBA (0.01 mol $dm^{-3}$) in benzene, taken separately in 50 mL round-bottomed flasks, were thermostatted at the desired temperature for 30 min. When the solutions had attained the bath temperature, they were mixed rapidly and stirred magnetically. The progress of reaction was monitored by withdrawing aliquots at regular time intervals and determining the amount of unreacted MCPBA iodimetrically. The course of reaction was studied up to 85–95% conversion. The calculated second-order rate constants were reproducible to within ±3%.

### Qualitative examination of competitive epoxidation by GC

A mixture of equimolar quantities of *n*-dodecane (used as an internal standard), cycloalkene (**6**–**9**), and the corresponding 1-trimethylsilylcycloalkene (**10**–**13**) in $CH_2Cl_2$ was treated with MCPBA (1.5 equivalents divided into four portions, each portion being added at 30 min intervals). A GC trace was recorded before adding the first portion of MCPBA. Subsequently, GC analysis was performed after adding each of the remaining portions of MCPBA and stirring the mixture for 30 min.

## Results and discussion

For the present study of the kinetics of epoxidation, cycloalkenes **6**–**9**, the corresponding 1-trimethylsilylcycloalkenes **10**–**13**, and 1-methylcycloalkenes **14**–**17** were selected (Scheme 3).




**Scheme 3**

MCPBA was the reagent of choice for epoxidation because of its efficiency, convenience of handling, reliability of analysis and ready availability.

The reaction of olefins with peracid has been established as a second-order reaction, first order with respect to olefin and first order with respect to peracid.[16] Our experimental results show similar trends. The epoxidation of 1-trimethylsilylcycloalkenes by MCPBA is found to follow second-order kinetics, as observed from the straight line graph obtained by plotting $[MCPBA]^{-1}$ *versus* time, measured from aliquots of the reaction mixture taken at regular intervals. A typical graph is given in Fig. 1.

The kinetic data for the epoxidation of **6**–**17** at four different temperatures (298, 303, 308 and 313 K) were measured and the values of the activation parameters for the overall reactions were calculated from the Arrhenius plots of ln *k* *vs.* 1/*T* (Tables 1 and 2). A representative Arrhenius plot is given in Fig. 2.

It is evident from the relative rate constants furnished in Table 3 that the reactivity of cycloalkenes towards epoxidation is considerably influenced by the substituent at the vinylic position and the reactivity is found to increase in the following order: unsubstituted cycloalkenes < 1-trimethylsilylcycloalkenes < 1-methylcycloalkenes.

A qualitative examination of the competitive epoxidation of an equimolar mixture of a cycloalkene (**6**–**9**) and the corresponding 1-trimethylsilylcycloalkene (**10**–**13**) by MCPBA using a GC procedure (with internal standard) also indicated a similar trend. That is, in each mixture of cycloalkene and 1-trimethylsilylcycloalkene a higher proportion of cyclic vinylsilane was found to be epoxidized than its unsilylated analogue.

**Table 1** Second-order rate constants ($10k/dm^3\ mol^{-1}\ s^{-1}$) for the epoxidation of the cycloalkenes **6**–**17** with MCPBA in benzene at various temperatures[a]

| Cycloalkene | *T*/K 298 | 303 | 308 | 313 |
|---|---|---|---|---|
| **6** | 1.04 | 1.58 | 2.38 | 3.54 |
| **7** | 0.67 | 1.08 | 1.83 | 2.92 |
| **8** | 0.79 | 1.29 | 2.00 | 3.17 |
| **9** | 0.96 | 1.50 | 2.04 | 3.54 |
| **10** | 3.33 | 4.67 | 6.75 | 9.00 |
| **11** | 1.83 | 2.92 | 4.33 | 6.75 |
| **12** | 2.08 | 3.00 | 4.50 | 6.92 |
| **13** | 2.17 | 3.17 | 4.53 | 7.17 |
| **14** | 12.56 | 16.11 | 19.50 | —[b] |
| **15** | 4.50 | 6.00 | 8.00 | 10.25 |
| **16** | 6.06 | 8.00 | 10.00 | 12.90 |
| **17** | 7.78 | 10.37 | 12.67 | 16.00 |

[a] [MCPBA] = 0.01 mol $dm^{-3}$, [cycloalkene] = 0.01 mol $dm^{-3}$. [b] The reaction was too fast to follow.

**Table 2** Thermodynamic parameters for the epoxidation of the cycloalkenes **6**–**17** with MCPBA calculated using the *k* values in Table 1

| Cycloalkene | $E_a$/ kJ $mol^{-1}$ | $\Delta H^{\ddagger}$/ kJ $mol^{-1}$ | $\Delta S^{\ddagger}$/ J $K^{-1}$ $mol^{-1}$ | $\Delta G^{\ddagger}$/ kJ $mol^{-1}$ |
|---|---|---|---|---|
| **6** | 62.07 | 59.53 | −64.01 | 79.09 |
| **7** | 73.16 | 70.62 | −30.37 | 79.69 |
| **8** | 72.33 | 69.79 | −31.97 | 79.56 |
| **9** | 66.51 | 63.97 | −50.09 | 79.27 |
| **10** | 45.45 | 42.91 | −109.67 | 76.41 |
| **11** | 59.86 | 57.32 | −66.02 | 77.48 |
| **12** | 58.19 | 55.65 | −71.22 | 77.40 |
| **13** | 57.36 | 54.82 | −73.63 | 77.32 |
| **14** | 34.29 | 31.77 | −136.50 | 73.13 |
| **15** | 42.95 | 40.41 | −115.54 | 75.87 |
| **16** | 39.49 | 36.95 | −125.25 | 75.21 |
| **17** | 37.41 | 34.87 | −130.06 | 74.60 |

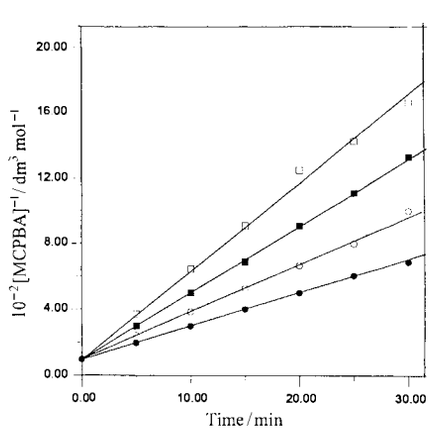



**Fig. 1** Epoxidation of 1-trimethylsilylcyclopentene (**10**) by MCPBA in benzene at 298 (●), 303 (○), 308 (■) and 313 K (□).

The observation that 1-methylcycloalkenes react faster than the corresponding 1-trimethylsilylcycloalkenes, which in turn react faster than the corresponding unsubstituted cycloalkenes, suggests that the discerning explanation given by Peterson[12b] referred to earlier (see Introduction section) about the influence of the trimethylsilyl group is correct. That is, the trimethylsilyl group deactivates the double bond relative to an alkyl group (as is seen while going from **14**–**17**, respectively, to **10**–**13**), but it is actually mildly activating if it is replacing a hydrogen (which is observed while going from **6**–**9**, respectively, to **10**–**13**). The diminished reactivity of silylated cycloalkenes as compared to 1-methylcycloalkenes can be explained as being due to the strong inductive and hyperconjugative effects of the methyl group, while the silyl group is mildly electron withdrawing by $(p–d)_\pi$ overlapping. The reason that the silylated double bond maintains still a certain higher degree of nucleophilic character, compared to its unsilylated counterpart, may lie in the fact that the electronegativity of silicon is less than that of hydrogen.

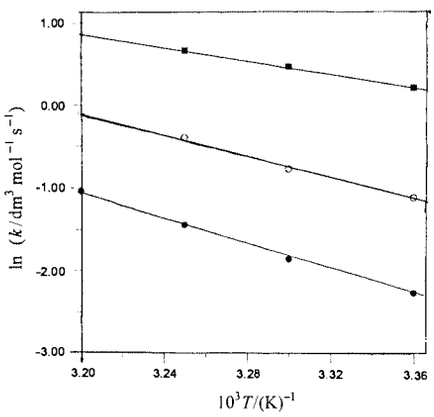



**Fig. 2** Arrhenius plots of **6** (●), **10** (○) and 14 (■).

**Table 3** Relative rate constants ($k_{substituted}/k_{unsubstituted}$) for rings of the same size

|  | *n* | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| H | 1.00 | 1.00 | 1.00 | 1.00 |
| $SiMe_3$ | 3.20 | 2.73 | 2.63 | 2.26 |
| $CH_3$ | 12.08 | 6.72 | 7.67 | 8.10 |

The deactivation by $(p–d)_\pi$ or (Si–C) σ*-π interaction is probably not sufficient to affect the slightly greater charge flow from Si to C in 1-trimethylsilylcycloalkenes than from H to C in simple cycloalkenes, at least in the case of epoxidation reactions. It is also likely that the inductive effect of the three $CH_3$ groups on Si plays some role in this charge distribution.

Another notable feature emerges when we analyze the kinetic data for the three sets of homologous series **6**–**9**, **10**–**13** and **14**–**17**. In each series it is observed that the five-membered cycloalkene (**6**, **10** and **14**) reacts faster than any other member of the series, while the six-membered cyclic analogue (**7**, **11** and **15**) reacts slower than the others (Table 4). The order of reactivity of cyclic olefins according to ring size is: 6-membered < 7-membered < 8-membered < 5-membered ring.

Similar trends have been noticed in the reactions of cycloalkenes with other electrophilic reagents, *e.g.*, iodine thiocyanate,[17] nitrosyl chloride,[17] iodomethylzinc iodide[18] and peracetic acid.[19]

The rate of electrophilic addition depends on several factors, such as the strain in the molecule, the electronic and steric effects of the substituents, *etc*. When an electrophile adds to a C=C bond the $sp^2$ hybridized carbons change their state to $sp^3$, resulting in the loss of a certain amount of strain due to the change of angle from 120 to 109.5° (or near to it). But in reactions involving three-centered cyclic activated complexes (as in the epoxidation of olefins) the change in the strain due to the transformation of the $sp^2$ hybrid state of the carbons of a C=C bond to a cyclic three-centered activated complex is very small.[20] Because of this the relative rates of electrophilic addition, which involves a cyclic three-centered activated complex, essentially reflect the strain energy differences (Table 5).

The energies of activation ($E_a$) and enthalpies of activation ($\Delta H^\ddagger$) for the epoxidation of the substrates **6**–**17** increase with the decrease in rates. This indicates that the epoxidation of all the substrates is enthalpy controlled. The negative values of entropy of activation ($\Delta S^\ddagger$) imply the formation of a rigid activated complex from the reactants. The free energies of activation ($\Delta G^\ddagger$) are nearly the same (73.13–79.69 kJ $mol^{-1}$) for all the substrates, which shows that the epoxidation of all the cyclic olefins, **6**–**17**, follows a similar mechanism. The mechanism of epoxidation of 1-trimethylsilylcycloalkenes, and of the other cycloalkenes studied here, may be visualized as involving the three-centered π complex that is proposed in the case of alkenes[16] (Scheme 4).

**Table 4** Relative rate constants for the epoxidation of homologous series of cycloalkenes

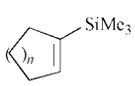
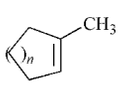
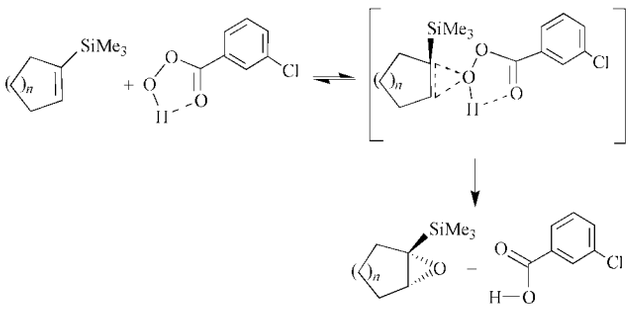
|  | | |  | | |  | | |
|---|---|---|---|---|---|---|---|---|
| | *n* | Relative rate | | *n* | Relative rate | | *n* | Relative rate |
| **6** | 1 | 1.55 | **10** | 1 | 1.82 | **14** | 1 | 2.74 |
| **7** | 2 | 1.00 | **11** | 2 | 1.00 | **15** | 2 | 1.00 |
| **8** | 3 | 1.18 | **12** | 3 | 1.14 | **16** | 3 | 1.34 |
| **9** | 4 | 1.43 | **13** | 4 | 1.19 | **17** | 4 | 1.73 |

**Table 5** Strain energies and relative rate constants for the reactions of cycloalkenes with various electrophilic reagents, taking $k_{cyclohexene} = 1.00$

| Cycloalkene | Strain energy/ kcal $mol^{-1}$ [a] | Relative rate constant ($k/k_{cyclohexene}$) | | | | |
|---|---|---|---|---|---|---|
| | | MCPBA [b] | ISCN [c] | NOCl [c] | $ICH_2ZnI$ [d] | $CH_3CO_3H$ [e] |
| **6** | 6.93 | 1.55 | 2.10 | 88.00 | 1.60 | 1.51 |
| **7** | 2.01 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| **8** | 7.35 | 1.18 | 1.90 | 29.00 | 1.18 | 1.36 |
| **9** | 8.21 | 1.43 | 1.10 | 27.00 | — | — |

[a] Ref. 21. [b] Present work. [c] Ref. 17. [d] Ref. 18. [e] Ref. 19.



**Scheme 4**

In conclusion, the trimethylsilyl group in cyclic vinylsilanes is found to enhance significantly the rate of epoxidation relative to that of unsilylated cycloalkenes, but it is less effective than a methyl group in the vinylic position. The results, we believe, are sufficiently convincing and should clear the prevailing confusion about the role of the trimethylsilyl moiety in influencing the rate of the epoxidation of vinylsilanes. The thermodynamic parameters give good insight into the nature and mechanism of the epoxidation of vinylsilanes.

## Acknowledgements

The authors thank the DST and the UGC (under the DRS programme), New Delhi for financial help. G. S. P. thanks the CSIR, New Delhi for a Senior Research Fellowship. Donation to G. N. of some equipment used in this work by the Alexander von Humboldt Foundation, Germany, is gratefully acknowledged.

## References

1 (*a*) P. Mollere, H. Bock, G. Becker and G. Fritz, *J. Organomet. Chem.*, 1972, **46**, 89; (*b*) H. Bock and H. Seidl, *J. Chem. Soc. B*, 1968, 1158; (*c*) W. Ensslin, H. Bock and G. Becker, *J. Am. Chem. Soc.*, 1974, **96**, 2757; (*d*) U. Weidner and A. Schweig, *J. Organomet. Chem.*, 1972, **39**, 261; (*e*) W. Kaim, H. Tesmann and H. Bock, *Chem. Ber.*, 1980, 3221.

2 (*a*) J. S. Sipe, Jr. and R. West, *J. Organomet. Chem.*, 1974, **70**, 353; (*b*) J. S. Sipe, Jr. and R. West, *J. Organomet. Chem.*, 1974, **70**, 357; (*c*) G. E. Evans, B. Jerome and N. H. Rees, *J. Chem. Soc.*, *Perkin Trans. 2*, 1973, **2**, 2091; (*d*) A. L. Alfred and W. Bush, *J. Am. Chem. Soc.*, 1968, **90**, 3352.

3 (*a*) C. S. Kraihanzel and M. L. Losee, *J. Organomet. Chem.*, 1967, **10**, 427; (*b*) M. P. Simonnin, *Bull. Soc. Chim. Fr.*, 1966, 1774; (*c*) W. F. Reynolds, G. K. Hamer and A. R. Bassindale, *J. Chem. Soc.*, *Perkin Trans. 2*, 1977, 971.

4 R. West and C. S. Kraihanzel, *Inorg. Chem.*, 1962, **1**, 967.

5 J. C. Giordan, *J. Am. Chem. Soc.*, 1983, **105**, 6544.

6 (*a*) Z. B. Maksic, K. Rupnik and N. Mileusnic, *J. Organomet. Chem.*, 1981, **219**, 21; (*b*) M. Horn and J. N. Morrell, *J. Organomet. Chem.*, 1974, **70**, 51; (*c*) F. Bennardi, M. Guerra and G. F. Pedulli, *Tetrahedron*, 1978, **34**, 2141; (*d*) A. C. Hopkinson and M. H. Lien, *J. Org. Chem.*, 1981, **46**, 998.

7 H. Sakurai, A. Hosomi and M. Kumada, *J. Org. Chem.*, 1969, **34**, 1764.

8 (*a*) I. A. Dyakonov, G. Y. Goldonikov and I. B. Repinskaya, *Zh. Obshch. Khim.*, 1965, **35**, 2181; *Chem. Abstr.*, 1966, **64**, 11238; (*b*) J. Culdin and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, 1962, **27**, 1658; (*c*) J. Culdin and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, 1963, **28**, 3088; (*d*) D. Seyferth and H. Dertoczos, *J. Organomet. Chem.*, 1968, **11**, 263.

9 D. Seyferth and H. M. Cohen, *Inorg. Chem.*, 1962, **1**, 913.

10 (*a*) W. E. Fristad, T. R. Bailey and L. A. Paquette, *J. Org. Chem.*, 1980, **45**, 3028; (*b*) W. E. Fristad, T. R. Bailey, L. A. Paquette, R. Gleiter and M. C. Bohm, *J. Am. Chem. Soc.*, 1979, **101**, 4420.

11 H. Sakurai, N. Hayashi and M. Kumada, *J. Organomet. Chem.*, 1969, **18**, 351.

12 (*a*) A. P. Davis, G. J. Hughes, P. R. Lowndes, C. M. Robbins, E. J. Thomas and G. H. Whitham, *J. Chem. Soc.*, *Perkin Trans. 1*, 1981, 1934; (*b*) P. E. Peterson, D. J. Nelson and R. Risener, *J. Org. Chem.*, 1986, **51**, 2381; (*c*) P. F. Hudrlik and A. M. Hudrlik, in *Advances in silicon chemistry*, ed. G. L. Larson, JAI Press, Greenwich CT, 1993, vol. 2, pp. 1–93.

13 B. S. Bandodakar, PhD Thesis, Bangalore University, Bangalore, 1992.

14 B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith and A. P. Tatchel, in *Text Book of Practical Organic Chemistry*, ed. A. I. Vogel, Longman, London, 1978, p. 332.

15 G. Nagendrappa, *Synthesis*, 1980, 704.

16 D. I. Metelitsa, *Russ. Chem. Rev. (Engl. Transl.)*, 1972, **41**, 807.

17 G. Collin, U. Jahnke, G. Just, G. Laurenz, W. Pritzkow, M. Rollig, L. Winguth, P. Dietrich, C. E. Doring, H. G. Hautal and A. Wiedenhoft, *J. Prakt. Chem.*, 1969, **311**, 238.

18 B. Rickborn and J. H.-H. Chan, *J. Org. Chem.*, 1967, **32**, 3578.

19 D. Swern, *J. Am. Chem. Soc.*, 1947, **69**, 1692.

20 F. Freeman, *Chem. Rev.*, 1975, **75**, 439.

21 N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, 1972, **94**, 5734.