ELSEVIER

Journal of Fluorine Chemistry 112 (2001) 283–286

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Cyanide initiated perfluoroorganylations with perfluoroorgano silicon compounds

Patricia Panne, Dieter Naumann, Berthold Hoge*

Institut für Anorganische Chemie, Universität zu Köln, Greinstr. 6, D-50939 Köln, Germany

Received 27 June 2001; accepted 31 August 2001

Dedicated to Professor Karl Otto Christe on the occasion of his 65th birthday

Abstract

Cyanophenylphosphanes, Ph_2PCN or $PhP(CN)_2$, do not react with Me_3SiCF_3 or $Me_3SiC_6F_5$ in the absence of cyanide ions. Catalytic amounts of ionic cyanides such as $[NEt_4]CN$, [18-crown-6-K]CN or NaCN initiate perfluoroorganylation reactions. The trifluoromethylphosphines, Ph_2PCF_3 and $PhP(CF_3)_2$, as well as the pentafluorophenylphosphines, $Ph_2PC_6F_5$ and $PhP(C_6F_5)_2$, are isolated in 60–75% yield. In dimethylformamide or acetone solutions, side reactions are observed while reactions in CH_2Cl_2 and acetonitrile proceed selectively. Me_3SiCF_3 addition to the carbonyl groups of dimethylformamide and acetone occurs on treatment of Me_3SiCF_3 solutions of these solvents with catalytic amounts of cyanide, cyanate or thiocyanate salts even at low temperature. The formation of the reactive silicate $[Me_3Si(CN)CF_3]^-$ in reactions with an excess of [18-crown-6-K]CN is proved by low temperature NMR investigations.

Keywords: Silicon; Phosphorus; Fluorine; Trifluoromethylation; Pentafluorophenylation

1. Introduction

Since our research interests lie in the synthesis of novel bis(perfluoroorgano)phosphane ligands [1], we are looking for a convenient access to perfluoroorgano phosphanes. While the direct synthesis of trifluoromethyl phosphanes—reacting white or red phosphorus with CF_3I—proceeds under high pressure giving product mixtures [2], Ruppert's procedure using $(P(NEt_2)_3/CF_3Br$ [3]) suffers from the difficult access of CF_3Br as a starting material.

The use of Ruppert's reagent (trifluoromethyltrimethylsilane, Me_3SiCF_3) as a convenient trifluoromethylating reagent especially in organic chemistry has become of considerable interest during the last decade [4,5]. The fluoride initiated trifluoromethylation capacity of Me_3SiCF_3 is not limited to organic compounds as has been demonstrated in the synthesis of several trifluoromethyl compounds, e.g. of silver [6,7], hypervalent bismuth [8], tellurium [9], iodine [9], phosphorus [10] and silicon [11,12]. The hypervalent silicon compounds, $[Me_3Si(F)CF_3]^-$ and $[Me_3Si(CF_3)_2]^-$, are of special interest because they have been proved to be the reactive intermediates in fluoride initiated trifluoromethylations [11]. Reactive intermediates of this type may also occur in the trifluoromethylation of hexafluorotricyclophosphazene [13] as well as in the trifluoromethylation of thiocyanates or selenocyanates with Me_3SiCF_3 in the presence of catalytic amounts of tetrabutylammonium fluoride [14]:

$$R{-}E{-}CN + Me_3SiCF_3 \overset{[NBu_4]F}{\rightarrow} R{-}E{-}CF_3 + Me_3SiCN, \quad (E = S, Se)$$

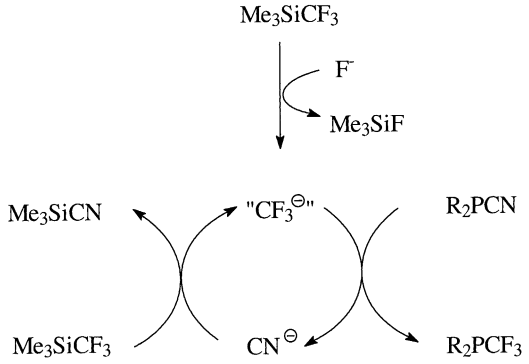
The authors of the last mentioned reaction additionally assume that in this nucleophilic substitution reaction, cyanide ions activate Me_3SiCF_3. To verify this assumption, we started to investigate the cyanide-induced nucleophilic perfluoroorganylation with perfluoroorgano silicon compounds.

2. Results and discussion

Cyanodiphenylphosphane (Ph_2PCN), slowly reacts with Me_3SiCF_3 at room temperature to Ph_2PCF_3 if catalytic amounts of CsF or tetramethylammonium fluoride (0.2 eq.) have been added. As pointed out by Langlois and co-workers [14], the use of catalytic amounts of fluoride ions indicates a cyanide ion generation during nucleophilic displacement reactions (Scheme 1). Following this assumption that

* Corresponding author. Fax: +49-221-470-5196.
E-mail address: b.hoge@uni-koeln.de (B. Hoge).

0022-1139/01/$ – see front matter
PII: S0022-1139(01)00513-9



Scheme 1. Fluoride initiated reaction of Me_3SiCF_3 with cyanophosphanes.

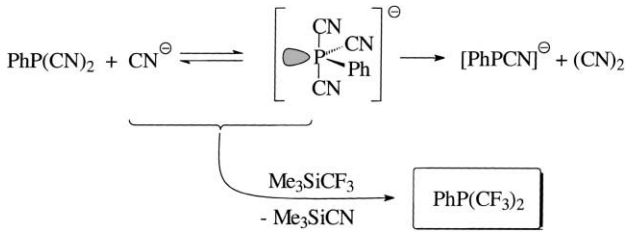
cyanide ions are involved in the activation of Me_3SiCF_3, we decided to replace the very hygroscopic and scarcely soluble fluoride salts with cyanide salts for initiation.

Indeed, cyanodiphenylphosphane reacts with Me_3SiCF_3 and catalytic amounts of NaCN at room temperature in CH_3CN solution slowly but selectively to Ph_2PCF_3:

$$Ph_2PCN + Me_3SiCF_3 \xrightarrow{NaCN} Ph_2PCF_3 + Me_3SiCN$$

Substituting the moderately soluble ionic cyanide by well soluble cyanide sources such as [18-crown-6-K]CN and tetraethylammonium cyanide the reaction is significantly accelerated. Thus, after mixing Ph_2PCN and Me_3SiCF_3 with 0.2 eq. of [18-crown-6-K]CN in CH_3CN at $-40\,^{\circ}C$ and gently warming to ambient temperature, complete conversion of Ph_2PCN to Ph_2PCF_3 occurs within 30 min. A very low cyanide concentration prolongs the reaction time, while an excess of cyanide leads to the formation of great amounts of HCF_3 in a side reaction. If an excess of Me_3SiCF_3 is used, a quantitative trifluoromethylation of the phosphane occurs in each case.

Dicyano(phenyl)phosphane ($PhP(CN)_2$) reacts even slower than Ph_2PCN with Me_3SiCF_3 and 0.2 eq. of [18-crown-6-K]CN or $[NEt_4]CN$. Again, the reaction time depends on the cyanide concentration. This behavior indicates that CN^- ions are involved in reactions with $PhP(CN)_2$. Deng and Dillon [15] reported that $PhP(CN)_2$ and cyanides form the phosphoranide, $[PhP(CN)_3]^-$. The ^{31}P NMR signal of $PhP(CN)_2$ is shifted about 14 ppm to higher field after adding 1 eq. of cyanide. Upon warming to ambient temperature, the phosphoranide, $[PPh(CN)_3]^-$, begins to decompose (Scheme 2). The phosphane–phosphoranide



Scheme 2. Cyanide initiated reaction of Me_3SiCF_3 with dicyanophenylphosphane.

equilibrium reduces the concentration of "free" cyanide ions and thus leads to the prolongation of the reaction time. Further addition of cyanide salts shortens, as expected, the reaction time but due to a shift of the equilibrium to the right side, decomposition of the $[PhP(CN)_3]^-$ anion into $[PhPCN]^-$ and $(CN)_2$ [15] occurs. As a consequence, the yield of $PhP(CF_3)_2$ is reduced. Cyanide initiated reactions of $P(CN)_3$ and Me_3SiCF_3 did not yield a uniform product so far.

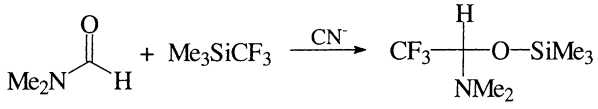
In a similar manner, perfluoroarylation is achieved by cyanide initiated reactions of $Me_3SiC_6F_5$ and Ph_2PCN and $PhP(CN)_2$, respectively

$$Ph_{3-n}P(CN)_n + nMe_3SiC_6F_5 \xrightarrow{CN^-} Ph_{3-n}P(C_6F_5)_n + nMe_3SiCN, \quad n = 1,2$$

The products $Ph_2PC_6F_5$ and $PhP(C_6F_5)_2$ are isolated after aqueous work-up in up to 70% yield.

To optimize the reaction conditions, several solvents, such as CH_2Cl_2, CH_3CN, acetone and DMF, were tested. Ethers such as THF or glyme, exhibit a very low solubility for $[NEt_4]CN$ and [18-crown-6-K]CN. While the reactions in CH_2Cl_2 and CH_3CN proceed selectively to the pure products, in acetone and DMF formal addition of Me_3SiCF_3 to the carbonyl groups occurs as a side reaction.

To characterize the by products, Me_3SiCF_3 has been treated in separate reactions in acetone and DMF solutions with catalytic amounts of cyanides. While the formal addition product of acetone, $Me_3SiOCMe_2CF_3$, has been isolated in 75% yield, the Me_3SiCF_3 addition to DMF is less selective and leads after an aqueous work-up to a 20% yield of $Me_3SiOC(H)(NMe_2)CF_3$:



In an attempt to characterize the reactive intermediate in the system Me_3SiCF_3/CN^-, solutions of Me_3SiCF_3 in CH_2Cl_2 and an acetonitrile/propionitrile mixture were treated with 1 eq. of [18-crown-6-K]CN at low temperature. While in CH_2Cl_2 solution even at $-90\,^{\circ}C$ only CF_3H was formed, NMR spectroscopic investigation of the acetonitrile/propionitrile reaction mixture at $-60\,^{\circ}C$ gave evidence for a new silicon compound. The large $^1J_{CF}$ coupling constant of 379 Hz, in comparison with 322 Hz for Me_3SiCF_3, appears to be characteristic for hypervalently bound trifluoromethyl groups in **3c–4e** units (Table 1). The ^{19}F NMR resonance

Table 1
^{19}F NMR data of trifluoromethyl silicon compounds [11]

	δ (^{19}F) (ppm)	$^1J_{CF}$ (Hz)	$^2J_{SiF}$ (Hz)
$[Me_3Si(CF_3)_2]$[a]	−62.6	378	6.0
$[Me_3Si(CF_3)F]$[a]	−63.9	375	4.5
$[Me_3Si(CF_3)CN]^-$	−63.7	379	–
Me_3SiCF_3[a]	−65.8	322	36.2

[a] See [9] and literature cited therein.

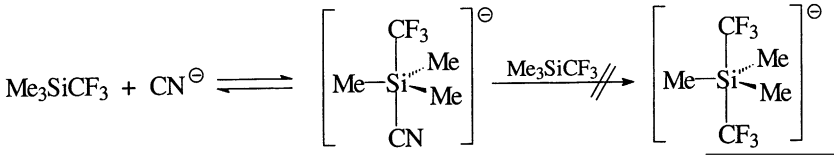
of −63.7 ppm indicates a downfield shift of about 2 ppm with respect to the neutral compound. A comparable low field shift of about 2 ppm is also observed for the $[Me_3Si(CF_3)F]^-$ ion. We interpret these observations in terms of a formation of a cyanosilicate, $[Me_3Si(CF_3)CN]^-$. Reaction mixtures with a 1:1 ratio of Me_3SiCF_3 and [18-crown-6-K]CN exhibit a turnover of only 20% at −60 °C. The turnover in a 1:3 mixture increases up to 80%, indicating an equilibrium reaction of Me_3SiCF_3 and cyanide ions.

The formation of the $[Me_3Si(CF_3)CN]^-$ anion in most organic solvents is accompanied by CF_3H evolution which increases with increasing $[Me_3Si(CF_3)CN]^-$ and CN^- concentration, respectively. Evolution of CF_3D in the reaction of Me_3SiCF_3 with cyanide ions in CD_3CN solution clearly indicates the reaction with the solvent.

Treatment of Me_3SiCF_3 in CH_3CN solution with 0.1 eq. of [18-crown-6-K]CN results in a conversion into Me_3SiCH_2-CN which was isolated after aqueous work-up. Comparable results were reported for the Me_3SiCF_3/F^- system [16]:

$$Me_3SiCF_3 + CH_3CN \overset{CN^-\,(0.1\,eq.)}{\rightarrow} Me_3SiCH_2CN + CF_3H$$

In contrast to $[Me_3Si(CF_3)F]^-$ generated from the Me_3SiCF_3/F^- system [11], $[Me_3Si(CF_3)CN]^-$ does not react with excess Me_3SiCF_3 to the bis(trifluoromethyl)silicate, $[Me_3Si(CF_3)_2]^-$:



This behavior reflects the lower reactivity of the Me_3SiCF_3/CN^- system compared with the Me_3SiCF_3/F^- system. But this "lower" reactivity could be useful for more selective and moderate reactions. For the reaction of Me_3SiCF_3 and DMF several ionic compounds were tested as initiators. The reaction is not only promoted by cyanide or fluoride ions but also by cyanate or thiocyanate ions. The possibility to use different nucleophiles for the activation step should be useful in the development of more selective trifluoromethylations.

3. Experimental section

3.1. Materials and apparatus

Chemicals were obtained from commercial sources and used without further purification. Literature methods were used for the synthesis of Ph_2PCN and $PhP(CN)_2$ [17]. Solvents were purified by standard methods [18]. Standard high-vacuum techniques were employed throughout all preparative procedures; nonvolatile compounds were handled in a dry N_2 atmosphere by using Schlenk techniques. Mass spectra (20 eV) were measured on a MAT CH5 instrument. The NMR spectra were recorded on a Bruker Model AC200 spectrometer (^{31}P, 81.01 MHz; ^{19}F, 188.31 MHz; ^{13}C, 50.32 MHz; ^{1}H, 200.13 MHz) with positive shifts being downfield from the external standards 85% orthophosphoric acid (^{31}P), CCl_3F (^{19}F) and TMS (^{13}C and ^{1}H).

3.2. Preparation of (trifluoromethyl)diphenylphosphane: general procedure

To a solution containing Ph_2PCN (0.7 g, 3.31 mmol) and Me_3SiCF_3 (0.5, 3.52 mmol) in CH_2Cl_2 (10 ml), [18-crown-6-K]CN (0.11 g, 0.33 mmol) was added at −78 °C. After warming to ambient temperature for 2 h, the brown reaction mixture was treated with Et_2O (200 ml) and filtered. The solvents are removed from the filtrate in vacuo. The residue was treated a second time with Et_2O (100 ml) filtered and the solvent removed in vacuo to give the Ph_2PCF_3 as a brown oil (0.6 g, 2.36 mmol, 70%). Spectroscopic data are comparable to literature [19]. ^{1}H NMR ($CDCl_3$) 6.8–7.2 ppm (m); ^{19}F NMR ($CDCl_3$) −55.3 ppm (d, $^{2}J_{PF} = 73$ Hz); ^{31}P $\{^{1}H\}$ NMR ($CDCl_3$) 2.7 ppm (q, $^{2}J_{PF} = 73$ Hz). MS *m/e* 254 (M^+, 70), 185 (Ph_2P^+, 100).

3.3. Preparation of bis(trifluoromethyl)phenylphosphane: general procedure

To a solution containing $PhP(CN)_2$ (0.77 g, 4.81 mmol) and Me_3SiCF_3 (1.36, 9.56 mmol) in CH_3CN (15 ml), $[NEt_4]CN$ (0.16 g, 0.1 mmol) dissolved in CH_3CN (5 ml) was added at −45 °C. After warming to ambient temperature for 2 h and stirring for 10 h, the brown reaction mixture was treated with CH_2Cl_2 (200 ml) and extracted three times with water. The organic phase was dried ($MgSO_4$) and the product separated from the solvent by fractional condensation (−64 °C, $CHCl_3$ slush bath), giving the pure compound as a colorless liquid (0.88 g, 3.57 mmol, 75%). NMR spectroscopic data are comparable to literature [20]. ^{1}H NMR ($CDCl_3$) 7.2–7.8 ppm (m); ^{19}F NMR ($CDCl_3$) −53.3 ppm (d, $^{2}J_{PF} = 80$ Hz); ^{31}P $\{^{1}H\}$ NMR ($CDCl_3$) 0.7 ppm (sep, $^{2}J_{PF} = 80$ Hz). MS *m/e* 246 (M^+, 85), 177 ($M^+ - CF_3$, 177), 127 ($PhCF_2^+$, 100).

Trimethylsilylacetonitrile was obtained as a colorless liquid in the reaction of Me_3SiCF_3 and excess CH_3CN following to the same procedure. NMR spectroscopic data are comparable to literature [21]. ^{1}H NMR ($CDCl_3$) 0.1 ppm (s, $Si(CH_3)_3$), 1.7 ppm (s, CH_2). ^{13}C $\{^{1}H\}$ NMR ($CDCl_3$) −2.0 ppm (s, $Si(CH_3)_3$), 4.6 ppm (CH_2), 119.1 ppm (CN). MS *m/e* 113 (M^+, 2), 98 ($M^+ - CH_3$, 40), 73 ($SiMe_3^+$, 40).

$Me_3SiOC(Me)_2CF_3$ was obtained as a colorless liquid in the reaction of Me_3SiCF_3 and excess acetone following to the same procedure: ^{1}H NMR ($CDCl_3$) 0.1 ppm (s, $Si(CH_3)_3$), 1.4 ppm (s, $C(CH_3)_2$). ^{13}C $\{^{1}H\}$ NMR ($CDCl_3$)

2.0 ppm (s, $Si(CH_3)_3$, $^1J_{SiC} = 60$ Hz), 24.1 ppm (s, $C(CH_3)_2$), 74.8 ppm (q, $^2J_{CF} = 29$ Hz, $CF_3C(CH_3)_2$), 127.1 ppm (q, $^1J_{CF} = 284$ Hz, CF_3). ^{19}F NMR ($CDCl_3$) −83.8 (s). MS *m/e* 185 ($M^+ - CH_3$, 5), 131 ($M^+ - CF_3$, 10), 89 ($OSiMe_3^+$, 100), 73 ($SiMe_3^+$, 60).

$Me_3SiOCH(NMe_2)CF_3$ was obtained as a colorless liquid in the reaction of Me_3SiCF_3 and excess DMF following to the same procedure: ^{1}H NMR ($CDCl_3$) −0.2 ppm (s, $Si(CH_3)_3$), 2.0 ppm (s, $N(CH_3)_2$) 4.4 ppm (q, $^3J_{HF} = 5.8$ Hz). ^{13}C {^{1}H} NMR ($CDCl_3$) 0.4 ppm (s, $Si(CH_3)_3$), 39.4 ppm (q, $^4J_{CF} = 1.7$ Hz, $N(CH_3)_2$), 84.3 (q, $^2J_{CF} = 32.3$ Hz, CF_3C) 123.6 ppm (q, $^1J_{CF} = 286$ Hz, CF_3). ^{19}F NMR ($CDCl_3$) −77.2 ppm (d, $^3J_{HF} = 5.8$ Hz), $\Delta(\delta(F^{12}C-F^{13}C)$ 0.12 ppm, $^1J_{CF} = 286$ Hz). MS *m/e* 215 (M^+, 1), 200 ($M^+ - CH_3$, 10), 146 ($M^+ - CH_3$, 100), 126 ($CF_3CH(NMe_2)$, 70), 73 ($SiMe_3^+$, 80).

3.4. Preparation of bis(pentafluorophenyl)phenylphosphane: general procedure

To a solution containing $PhP(CN)_2$ (0.31 g, 1.94 mmol) and $Me_3SiC_6F_5$ (1.16, 4.83 mmol) in CH_3CN (15 ml), [18-crown-6-K]CN (0.16 g, 0.48 mmol) dissolved in CH_3CN (5 ml) was added at −45 °C. After warming to ambient temperature for 2 h and stirring for 1 h, the brown reaction mixture was treated with CH_2Cl_2 (200 ml) and extracted with water four times. The organic phase was dried ($MgSO_4$) and the solvent removed in vacuo yielding $PhP(C_6F_5)_2$ (0.56 g, 68%) as a slight brown oil. Spectroscopic data are comparable to literature [22]. ^{1}H NMR ($CDCl_3$) 7.1–7.6 ppm (m); ^{19}F NMR ($CDCl_3$) −160.5 ppm (m, 2F), −150.1 ppm (m, 1F), −129.5 to 128.5 ppm (m, 2F); ^{31}P NMR ($CDCl_3$) −45.9 ppm (quin, $^3J_{PF} = 30$ Hz).

(Pentafluorophenyl)diphenylphosphane was obtained according to the same procedure as a slight brown solid (0.66 g, 56%). Spectroscopic data are comparable to literature [22]. ^{1}H NMR ($CDCl_3$) 6.9–7.3 ppm (m); ^{19}F NMR ($CDCl_3$) −160.5 ppm (m, 2F), −150.2 ppm (m, 1F), −126.8 to 127.8 ppm (m, 2F); ^{31}P NMR ($CDCl_3$) −24.6 ppm (t, $^3J_{PF} = 38$ Hz). Anal. Calcd. for $C_{18}H_{10}F_5P$ (352.2): C, 61.38%; H, 2.86%. Found: C, 61.40%; H, 3.23%. MS *m/e* 352 (M^+, 100), 275 ($PhPC_6F_5^+$, 3), 154 (Ph_2^+, 40).

Acknowledgements

We are grateful to the Fonds der Chemischen Industrie for financial support. Thanks to Dr. W. Tyrra for discussion and providing $Me_3SiC_6F_5$.

References

[1] B. Hoge, P. Panne, in preparation.
[2] F.W. Bennett, H.J. Emeléus, R.N. Haszeldine, J. Chem. Soc. (1953) 1565.
[3] W. Volbach, I. Ruppert, Tetrahedron Lett. 24 (1983) 5509.
[4] G.K.S. Prakash, A.K. Yudin, Chem. Rev. 97 (1997) 757.
[5] R.P. Singh, J.M. Shreeve, Tetrahedron 56 (2000) 7613.
[6] W. Tyrra, in: Proceedings of the 15th Winter Fluorine Conference, St. Petersburg, Florida, 2001.
[7] W. Tyrra, J. Fluorine Chem. 112 (2001) 149.
[8] W. Tyrra, D. Naumann, N.V. Kirij, A.A. Kolomeitsev, Y.L. Yagupolskii, J. Chem. Soc., Dalton Trans. (1999) 657.
[9] N.V. Kirij, Y.L. Yagupolskii, N. Maggiarosa, W. Tyrra, D. Naumann, J. Fluorine Chem., accepted.
[10] A. Kolomeitsev, M. Görg, U. Dieckbreder, E. Lork, G.-V. Röschenthaler, Phosphorus, Sulfur, Silicon Relat. Elem. 109/110 (1996) 597.
[11] N. Maggiarosa, W. Tyrra, D. Naumann, N.V. Kirij, Y.L. Yagupolskii, Angew. Chem. 111 (1999) 2392.
[12] A. Kolomeitsev, G. Bissky, E. Lork, V. Movchun, E. Rusanov, P. Kirsch, G.-V. Röschenthaler, Chem. Commun. (1999) 1107.
[13] R.P. Singh, A. Vij, R.L. Kirchmeier, J.M. Shreeve, Inorg. Chem. 39 (2000) 375.
[14] T. Billard, S. Large, B.R. Langlois, Tetrahedron Lett. 38 (1997) 65.
[15] R.M.K. Deng, K.B. Dillon, Chem. Commun. (1981) 1170.
[16] D.J. Adams, J.H. Clark, L.B. Hansen, V.C. Sanders, S.J. Tavener, J. Fluorine Chem. 92 (1998) 123.
[17] C.E. Jones, K.J. Coskran, Inorg. Chem. 10 (1971) 1536.
[18] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, England, 1980.
[19] H. Lesiecki, E. Lindner, G. Vordermaier, Chem. Ber. 112 (1979) 793.
[20] K. Gosling, D.J. Holman, J.D. Smith, B.N. Ghose, J. Chem. Soc. (A) (1968) 1909.
[21] W. Zarges, M. Marsch, K. Harms, G. Boche, Chem. Ber. 122 (1989) 1307.
[22] D.I. Nichols, J. Chem. Soc. (A) (1969) 1471.