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THE REACTION OF HEXAMETHYLDISILANE WITH DIHALONITROBENZENES IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0). SYNTHESIS OF BIS(TRIMETHYLSILYL)NITROBENZENES AND (TRIMETHYLSILYL)CHLORONITROBENZENES

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Summary

Bis(trimethylsilyl)nitrobenzenes and (trimethylsilyl)chloronitrobenzenes were prepared in moderate yield by the reaction of hexamethyldisilane with dihalonitrobenzenes in the presence of tetrakis(triphenylphosphine)palladium(0).

Introduction

The palladium-catalyzed reaction of disilanes with organic halides (eqn. 1) has offered a useful method for the formation of new types of the silicon—carbon bonds, and several functional silicon compounds such as arylsilanes, allylsilanes, vinylsilanes and acylsilanes have been prepared by such reactions [1—9].

$$\equiv\text{Si—Si}\equiv + \equiv\text{C—X} \xrightarrow{[\text{Pd}]} \equiv\text{Si—C}\equiv + \equiv\text{Si—X} \qquad (1)$$

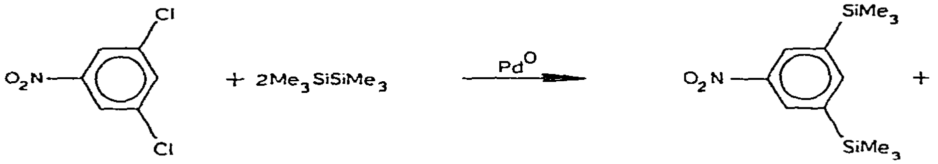
$$(\text{X} = \text{Br or Cl})$$

Previous studies have demonstrated that the tetrakis(triphenylphosphine)palladium(0)-catalyzed reaction of hexamethyldisilane with monohalonitrobenzenes (e.g., *o*-, *m*- and *p*-chloronitrobenzenes, and 3,5-dinitrochlorobenzene) provides a convenient synthesis of (trimethylsilyl)nitrobenzenes which are not always accessible by other methods [2—4]. In this work, we extended the palladium(0)-catalyzed disilane reaction to the synthesis of bis(trimethylsilyl)nitrobenzenes and (trimethylsilyl)chloronitrobenzenes, for most of which no synthetic routes have been described to date [10].

Results and discussion

Examples of the synthesis of bis(trimethylsilyl)nitrobenzenes and (trimethylsilyl)chloronitrobenzenes from dihalonitrobenzenes are shown in Table 1. The physical properties of the compounds prepared are summarized in Table 2.

Typically 3,5-dichloronitrobenzene, excess (10 equiv.) hexamethyldisilane and mesitylene as a solvent were placed in a stainless steel reaction vessel with tetrakis(triphenylphosphine)palladium(0) (6 mol%), and the mixture was heated at 160° C. Figure 1 shows time-conversion curves for this reaction, indicating the initial formation of 3-(trimethylsilyl)-5-chloronitrobenzene and then its gradual conversion to 2,5-bis(trimethylsilyl)nitrobenzene. Continuation of the reaction until virtual disappearance of the monosilylnitrobenzene resulted in the formation of the desired bis(silyl)nitrobenzene. Thus, a 30 mmol scale reaction of the dichloronitrobenzene gave a 30% isolated yield of the bis(silyl) product in 98% purity.



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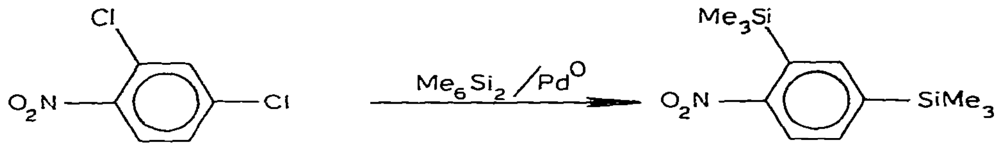
Similarly, 2,4-bis(trimethylsilyl)nitrobenzene was obtained in 32% isolated yield from the corresponding dichloronitrobenzene.



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The reaction of 2,5-dichloronitrobenzene with hexamethyldisilane was rather slow even at 170° C and yielded a mixture of the disilyl and monosilyl derivatives which were difficult to separate by distillation. Thus, heating a

TABLE 1

REACTIONS OF HEXAMETHYLDISILANE WITH DIHALONITROBENZENES IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0)

Dihalonitrobenzene	Conditions	(Trimethylsilyl)-nitrobenzene obtained	Yield (%) [a]
3,5-$Cl_2C_6H_3NO_2$	160° C, 40 h, in mesitylene [b]	3,5-$(Me_3Si)_2C_6H_3NO_2$	30
2,4-$Cl_2C_6H_3NO_2$	160° C, 22 h, in mesitylene [b]	2,4-$(Me_3Si)_2C_6H_3NO_2$	32
2,5-$Br_2C_6H_3NO_2$	reflux, 22 h, in mesitylene [c]	2,5-$(Me_3Si)_2C_6H_3NO_2$	30
2,5-$Cl_2C_6H_3NO_2$	reflux, 3 h, in HMPA [d]	2-(Me_3Si)-5-$ClC_6H_3NO_2$	62
3,5-$Cl_2C_6H_3NO_2$	reflux, 40 h, in HMPA [d]	3-(Me_3Si)-5-$ClC_6H_3NO_2$	43
2,4-$Cl_2C_6H_3NO_2$	reflux, 6 h, in HMPA [d]	2-(Me_3Si)-4-$ClC_6H_3NO_2$ (60) 2-Cl-4-$(Me_3Si)C_6H_3NO_2$ (40)	41 [e]

[a] Isolated yields (based on the dihalonitrobenzene charged) unless otherwise stated. [b] [Halobenzene]/[disilane]/[catalyst] = 1/10/0.06. [c] [Halobenzene]/disilane]/[catalyst] = 1/10/0.02. [d] [Halobenzene]/[disilane]/[catalyst] = 1/2/0.01. [e] Determined by GLC.

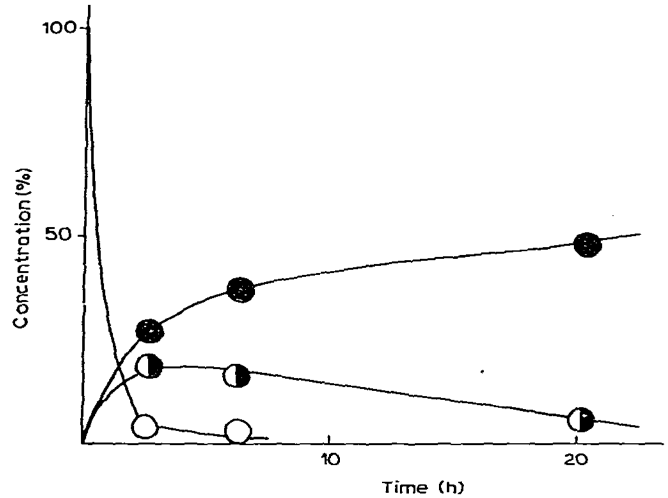
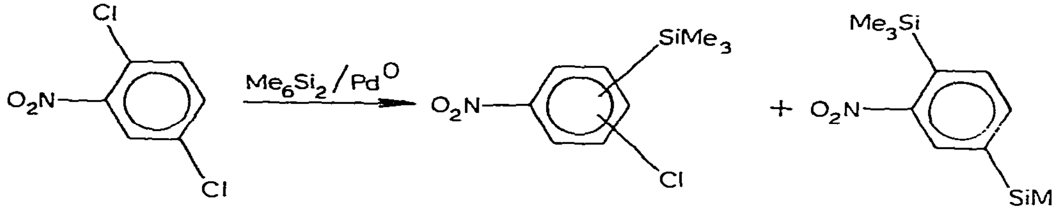


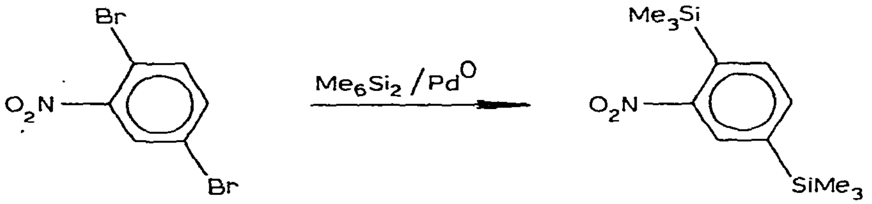
Fig. 1. Time-conversion curves for the reaction of 3,5-dichloronitrobenzene with hexamethyldisilane in the presence of $Pd(PPh_3)_4$ at 160°C: (○) 3,5-dichloronitrobenzene disappearance curve; (◑) 3-(trimethylsilyl)-5-chloronitrobenzene formation curve; (●) 3,5-bis(trimethylsilyl)benzene formation curve.

1 : 10 mixture of the dichloronitrobenzene and the disilane at 170°C for 45 h in the presence of 6 mol% of the palladium(0) complex gave a 20 : 80 mixture of the monosilylated and disilylated products.



(4)

However, we found that the preparation of pure 2,5-bis(trimethylsilyl)nitrobenzene could be achieved by using the corresponding dibromonitrobenzene. The reaction proceeded at reflux and reached completion within 22 h to give the expected bis(silyl)benzene in 30% yield.



(5)

Thus the Si—Si cleavage reaction opens a novel route to the preparation of bis(trimethylsilyl)nitrobenzenes. This method has advantages of simplicity of the reaction procedure and ready availability of the starting materials and catalyst.

An attempt was next made to prepare (trimethylsilyl)chloronitrobenzenes.

TABLE 2

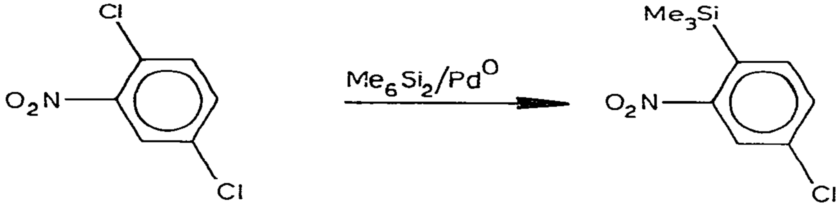
CHARACTERIZATION OF (TRIMETHYLSILYL)NITROBENZENES OBTAINED

Compound	Bp (°C/mmHg) [mp (°C)]	IR, principal absorptions (cm^{-1})	NMR (δ, ppm) [a]	Anal. found (calcd) (%)			
				C	H	N	Cl
3,5-$(Me_3Si)_2C_6H_3NO_2$ $(C_{12}H_{21}NO_2Si_2)$	[87–88]	1593m, 1511s, 1335s, 1251s, 1136m, 830s	0.37 (s, 18 H), 7.89 (m, 1 H), 8.25 (s, 2 H)	53.20 (53.87)	8.15 (7.93)	5.12 (5.24)	
2,5-$(Me_3Si)_2C_6H_3NO_2$ $(C_{12}H_{21}NO_2Si_2)$	76–77/1	1599m, 1530s, 1352s, 1252s, 1130s, 835s	0.33 (s, 18H), 7.64 (s, 2 H), 8.17 (s, 1 H)	53.87 (53.87)	7.95 (7.93)	5.21 (5.24)	
2,4-$(Me_3Si)_2C_6H_3NO_2$ $(C_{12}H_{21}NO_2Si_2)$	102/4	1591m, 1513s, 1342s, 1251s, 1120s, 830s	0.32 (s, 9 H), 7.60 (dd, 1 H, J = 2 and 8 Hz), 7.82 (d, 1 H, J = 2 Hz), 8.02 (d, 1 H, J = 8 Hz)	53.87 (53.87)	7.89 (7.93)	5.16 (5.24)	
2-(Me_3Si)-5-$ClC_6H_3NO_2$ $(C_9H_{12}NO_2SiCl)$	70/1.5	1525s, 1348s, 1252s, 1108s, 840s	0.33 (s, 9 H), 7.53 (m, 2 H), 8.07 (m, 1 H)	47.45 (47.04)	5.19 (5.28)	6.34 (6.10)	15.60 (15.45)
3-(Me_3Si)-5-$ClC_6H_3NO_2$ $(C_9H_{12}NO_2SiCl)$	117/8	1595m, 1528s, 1345s, 1252s, 1155s, 835s	0.37 (s, 9 H), 7.70 (m, 1 H), 8.13 (m, 2 H)	47.64 (47.04)	5.88 (5.28)	6.21 (6.10)	15.72 (15.45)
2-(Me_3Si)-4-$ClC_6H_3NO_2$ $(C_9H_{12}NO_2SiCl)$	[49–50] [b]	1592m, 1525s, 1343s, 1255s, 1120s, 840s	0.38 (s, 9 H), 7.44 (dd, 1 H, J = 2 and 8 Hz), 7.60 (d, 1 H, J = 2 Hz), 8.07 (d, 1 H, J = 8 Hz)	47.40 (47.04)	5.13 (5.28)	5.85 (6.10)	15.36 [d] (15.45)
2-Cl-4-$(Me_3Si)C_6H_3NO_2$ $(C_9H_{12}NO_2SiCl)$	— [c]	1595m, 1525s, 1345s, 1250s, 1120s, 845s	0.37 (s, 9 H), 7.40 (d, 1 H, J = 8 Hz), 7.52 (s, 1 H), 7.71 (d, 1 H, J = 8 Hz)				

[a] CCl_4 solution with Me_4Si. [b] Lit. [11] mp. 50–51°C. [c] liquid; bp. not measured. [d] As a 60 : 40 mixture of 2-(Me_3Si)-4-$ClC_6H_3NO_2$ and 2-Cl-4-$(Me_3Si)C_6H_3NO_2$.

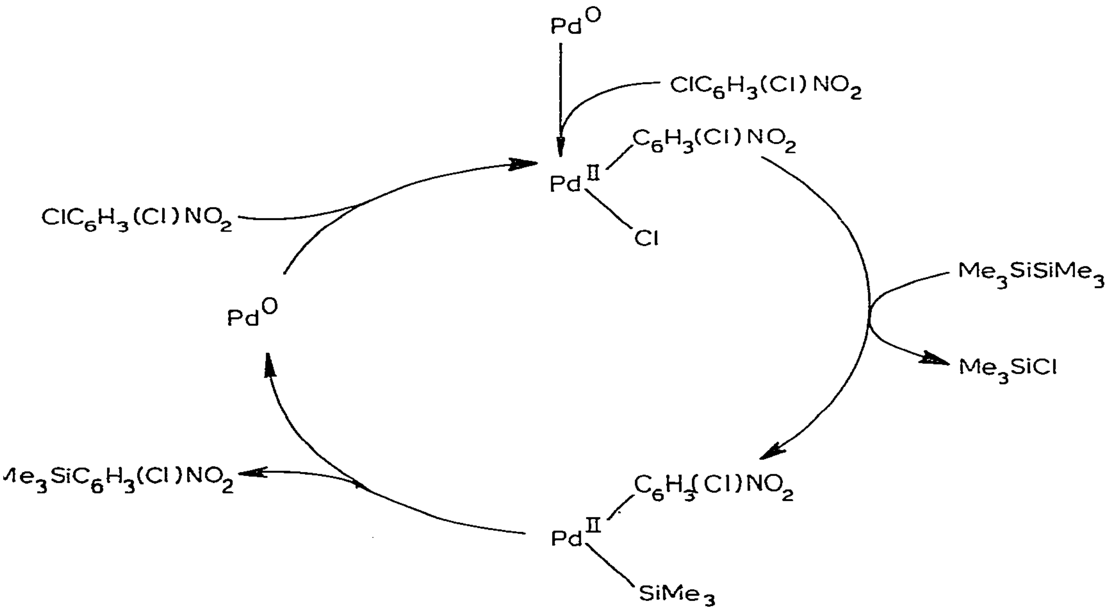
To date, for the synthesis of monosilylchloronitrobenzenes, only one report was published by Hashimoto who found that the reaction of 3-(trimethylsilyl)-chlorobenzene with acetyl nitrate afforded 2-(trimethylsilyl)-4-chloronitrobenzene in good yield [11]. However, the nitration of 4-(trimethylsilyl)chlorobenzene with acetyl nitrate is unsatisfactory, since the reaction was reported to produce a desilylated product, 4-chloronitrobenzene, rather than (trimethylsilyl)chloronitrobenzenes [11].

We found that 2-(trimethylsilyl)-5-chloronitrobenzene was simply prepared by the reaction of 2,5-dichloronitrobenzene with hexamethyldisilane in the presence of the palladium(0) complex. The silylchloronitrobenzene could be prepared selectively when the reaction was conducted using hexamethylphosphoramide (HMPA) as a solvent. Thus, the dichloronitrobenzene was refluxed in HMPA with 2 equiv. of the disilane for 3 h in the presence of 1 mol% of the catalyst. The reaction gave exclusively 2-(trimethylsilyl)-5-chloronitrobenzene, and work-up afforded this compound in 62% yield.



(6)

The formation of the other possible isomer, 2-chloro-5-(trimethylsilyl)nitrobenzene, was negligible. A structure proof of 2-(trimethylsilyl)-5-chloronitrobenzene was accomplished by reduction of the compound to the aniline which was readily subjected to protodesilylation [11,12]. 3-Chloroaniline was obtained in

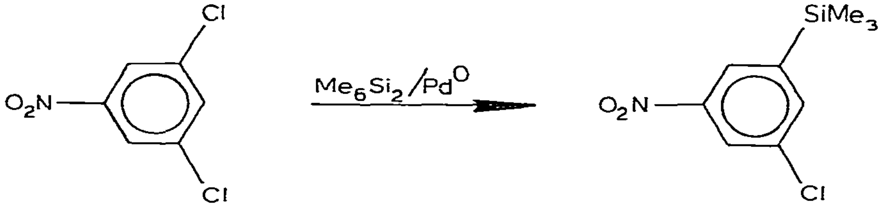


SCHEME 1

83% yield after treating the monosilyl derivative with a mixture of zinc and hydrochloric acid.

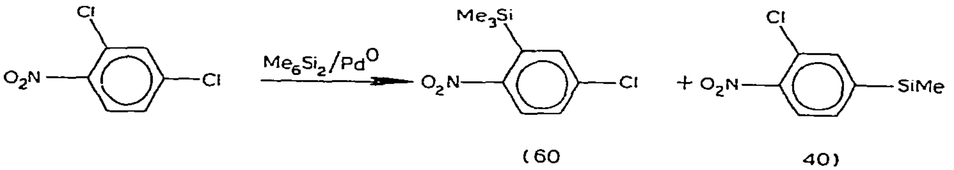
Apparently, substitution of the 2-chlorine atom in the dichloronitrobenzene by silicon predominates much over that of 5-chlorine atom. The *ortho-para* activating effect of the nitro group was also experienced in the previously reported disilane reaction in which 2 - and 4-chloronitrobenzenes reacted much more smoothly than 3-chloronitrobenzene [4]. Although any detailed mechanistic study is still lacking, the initial step must involve the oxidative addition of a dichloronitrobenzene to the palladium(0) complex (Scheme 1). The observed result may be attributable to the difference in reactivity between 2- and 5-chlorine atoms towards the oxidative addition. In this connection, it should be recalled that Fitton and Rick reported that 2-chloronitrobenzene underwent oxidative-addition to the palladium(0) complex more readily than 3-chloronitrobenzene [13].

Encouraged by this successful result, we also attempted to prepare other (trimethylsilyl)chloronitrobenzenes by the present reaction. Thus, 3,5-dichloronitrobenzene was allowed to react with 2 equiv. of the disilane in HMPA for 40 h at reflux. Work-up gave 3-(trimethylsilyl)-5-chloronitrobenzene in 43% isolated yield. The structural assignment for this compound was made based on its elemental analysis, and IR and NMR spectra (Table 2).



(7)

Despite the aforementioned selective preparation of silylchloronitrobenzenes, the reaction of 2,4-dichloronitrobenzene with $Me_3SiSiMe_3$ in HMPA gave a mixture of 2-(trimethylsilyl)-4-chloronitrobenzene and 2-chloro-4-(trimethylsilyl)nitrobenzene (41% combined yield). GLC analysis of the reaction mixture disclosed the presence of two products (60 : 40) which were found by elemental and NMR analyses to be isomeric (trimethylsilyl)chloronitrobenzenes. Each component was isolated in pure form by GLC separation. The melting point of the first eluted product (GLC) was identical with that of 2-(trimethylsilyl)-4-chloronitrobenzene [11]. Hence, the compound which eluted second was 2-chloro-4-(trimethylsilyl)nitrobenzene.



(8)

Experimental

Boiling and melting points are uncorrected. IR spectra were taken on a Hitachi EPI-3G spectrophotometer. NMR spectra were taken on a Varian EM-

360 instrument. GLC analyses were carried out with an Ohkura 802T instrument, using Teflon columns (100—200 × 0.4 cm) packed with Silicone KF-96, SF-96 and DCQF-1, and polydiethylene glycol adipate on Celite 545 (60/80). Corrections were made for thermal conductivity of various components.

2,4-, 2,5- and 3,5-Dichloronitrobenzenes, and 2,5-dibromonitrobenzene were commercially available as special grade and used without further purification. Hexamethyldisilane [14] and tetrakis(triphenylphosphine)palladium(0) [15] were prepared according to literature directions. Other organic and inorganic reagents were commercially available and used without further purification.

Procedure for the synthesis of (trimethylsilyl)nitrobenzenes

The reactions of hexamethyldisilane with dihalonitrobenzenes were carried out under nitrogen at temperatures of 120—170°C either in a refluxing system or in a sealed stainless steel reaction vessel. Typical examples are described below.

(a) 3,5-Bis(trimethylsilyl)nitrobenzene. 3,5-Dichloronitrobenzene (5.8 g, 30 mmol), hexamethyldisilane (45 g, 300 mmol), tetrakis(triphenylphosphine)-palladium(0) (2.0 g, 1.7 mmol) and mesitylene (50 ml) were introduced into a stainless steel reaction vessel. The vessel was well flushed with nitrogen, sealed and heated at 160°C for 40 h. GLC analysis of the resulting mixture disclosed the production of a 51% yield of 3,5-bis(trimethylsilyl)nitrobenzene with 99% conversion. The mixture was then diluted with petroleum ether and the precipitated catalyst was filtered. Concentration of the filtrate resulted in the separation of crude solid which was recrystallized from n-hexane to give 2.4 g (30% yield) of the bis(silyl)nitrobenzene as yellow crystals.

(b) 2-(Trimethylsilyl)-5-chloronitrobenzene. A solution of 2,5-dichloronitrobenzene (10.0 g, 52 mmol), hexamethyldisilane (15.0 g, 102 mmol), the palladium(0) complex (0.58 g, 0.51 mmol) and HMPA (20 ml) was refluxed for 3 h with stirring. GLC analysis of the resulting mixture disclosed that the starting chloronitrobenzene had been almost completely consumed and that 2-(trimethylsilyl)-5-chloronitrobenzene had been produced in 68% yield, together with only traces of 2,5-bis(trimethylsilyl)nitrobenzene. The mixture was then diluted with petroleum ether and the precipitated catalyst was removed by filtration. The filtrate was washed with water to remove HMPA and dried over calcium chloride. Evaporation of low boiling materials and subsequent distillation gave 7.4 g (62% yield) of the silylchloronitrobenzene as a yellow liquid.

Structure proof of 2-(trimethylsilyl)-5-chloronitrobenzene

A mixture of the silylchloronitrobenzene (5.3 g, 20 mmol) and granulated tin (4.5 g, 38 mmol) was stirred vigorously, and concentrated hydrochloric acid (10 ml) was added dropwise with careful control of the evolution of gas. After all of the acid had been added, the reaction mixture was diluted with water and refluxed for 15 h. The resulting mixture was then cooled, made strongly basic with sodium hydroxide solution and extracted with ether. The ether extract was dried over anhydrous sodium hydroxide. Evaporation of the solvent and subsequent distillation under nitrogen atmosphere afforded 2.35 g (83% yield) of 3-chloroaniline, bp. 85—87°C (5 mmHg).

Time-conversion curves for the reaction of 3,5-dichloronitrobenzene with hexamethyldisilane in the presence of the palladium(0) complex

A mixture of the dichloronitrobenzene (0.58 g, 3 mmol), the disilane (4.50 g, 30 mmol), the palladium(0) complex (0.20 g, 0.18 mmol) and mesitylene (5 ml) was heated in a sealed stainless steel reaction vessel. The course of the reaction was monitored by GLC. The results are shown in Fig. 1.

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