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REACTIONS OF GROUP IV ORGANOMETALLIC COMPOUNDS

XXIX*. INSERTION REACTIONS OF (TRIMETHYLSILYLMETHYLENE)-PHOSPHORANE WITH HETEROCUMULENES. INHIBITION OF WITTIG TYPE REACTIONS

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Summary

A reaction of (trimethylsilylmethylene)dimethylphenylphosphorane, $PhMe_2P=CHSiMe_3$ (I), with phenyl isocyanate affords a 2/1 insertion product, which results from insertion of phenyl isocyanate into both the C—Si and C—H bonds of I. By way of contrast, a reaction of isothiocyanate and carbon disulfide with I affords 1/1 products by insertion of these heterocumulenes into the C—Si bond of I. In these reactions, Wittig-type elimination of dimethylphenylphosphine oxide or sulfide did not occur because of irreversible migrations of the trimethylsilyl group to the anionic centers of the Zwitterionic intermediates.

Introduction

Selective preparations of olefins by Wittig reactions depend on the facile elimination of stable phosphine oxides from the Zwitterionic intermediate, $R_3P^+CCO^-$, which are formed by reactions of phosphonium ylides with carbonyl compounds [2]. Peterson has reported an isoelectronic olefin synthesis which employs α-organosilylcarbanions [3].

$$\geqslant P^+-CH_2^- + {>}C{=}O \xrightarrow{\text{Addn.}} \left[\geqslant P^+-CH_2-\underset{|}{\overset{|}{C}}-O^-\right] \xrightarrow{\text{Elimn.}} \geqslant P^+-O^- + H_2C{=}C{<}$$

$$\geqslant Si-CH_2^- + {>}C{=}O \xrightarrow{\text{Addn.}} \xrightarrow{\text{Elimn.}} \geqslant Si-O^- + H_2C{=}C{<}$$

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[*] For Part XXVIII, see ref. 1.

While Wittig and Peterson reactions do have common features, a recently published theoretical study (M.O. treatment) suggests that these reactions proceed by discretely different transition states [4].

Reaction of ketones with triorganosilylmethylenephosphorane, $R_3P^+\bar{C}HSiR'_3$ in which alkoxy-labile organophosphorus and organosilyl groups are linked to a common carbanion center, gave vinylphosphosphorus compounds as a result of exclusive organosilanolate elimination [5,6]. This variance of the Wittig process by the introduction of a triorganosilyl group was ascribed to its rapid migration to the oxygen atom of the intermediate and to the subsequent elimination of the Si—O bond [6]. We have reported similar findings in the reactions of trimethylsilyliminophosphorane with heterocumulenes [7].

We now report that Wittig-type eliminations of phosphine oxides or sulfides are also not of consequence in the reactions of (trimethylsilylmethylene)dimethylphenylphosphorane with various heterocumulene compounds.

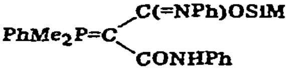
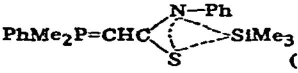
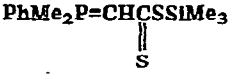
Results and discussion

Reactions of (trimethylsilylmethylene)dimethylphenylphosphorane, $PhMe_2P{=}CHSiMe_3$ (I), with phenyl isocyanate, isothiocyanates, and carbon disulfide were found to give these insertion products. The analytical results, yields, and m.p.'s of these adducts are summarized in Table 1, while the infrared and NMR spectroscopic results are shown in Table 2. The formation of dimethylphenylphosphine oxide or sulfide was not observed in any of these reactions.

Addition of phenyl isocyanate to I in ether gave a yellow crystalline product, and its analytical and NMR results suggested that the product was the in-

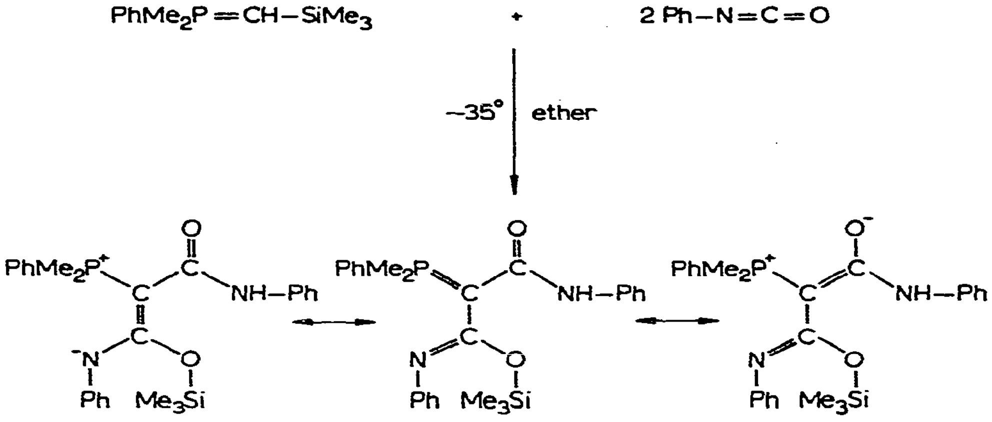
TABLE 1

INSERTION PRODUCTS BETWEEN $PhMe_2P{=}CHSiMe_3$ (I) AND VARIOUS HETEROCUMULENES

Compound		Yield (%)	B.p. [M.p.] (°C)	Analysis [found (calcd.) (%)]				
				C	H	N	P	S
$PhMe_2P{=}CHSiMe_3$	(I)	80.8	100/1.2 mm	64.07 (64.24)	9.35 (9.43)		13.71 (13.81)	
 $PhMe_2P{=}C(C({=}NPh)OSiMe_3)(CONHPh)$	(II)	84.5	[141—143]	67.30 (67.51)	6.65 (6.76)		6.66 (6.69)	
	(III)[a]	78.1	[127—129]	68.96 (69.42)	6.28 (6.10)	3.52 (3.26)		
 $PhMe_2P{=}CHC({=}S)NMeSiMe_3$	(IV)	87.5	[105—107]	56.35 (56.53)	7.84 (8.13)	4.79 (4.71)	10.67 (10.41)	
 $PhMe_2P{=}CHC({=}S)SSiMe_3$	(V)[a]	77.4	[94— 96]	52.28 (51.96)	6.82 (7.02)			21.89 (21.34)

[a] See text for a discussion of the correct structures of III and V.

sertion adduct composed of two moles of phenyl isocyanate and I. The appearance of a trimethylsilyl proton signal at relatively high field (δ −0.14) and that of a ν(Si—O) frequency at 1080 cm^{-1} indicates the presence of a Si—O bond in this 2/1 insertion product. This IR band is reasonably assigned to ν(Si—O) (1020—1090 cm^{-1} [8]) and is too high to assign to a ν(Si—N) (900—1000 cm^{-1} [9]) [10]. The other infrared absorptions supported the proposed structure II, since ν(C=O), ν(C=N), and ν(N—H) stretching frequencies were observed at 1610, 1571, and 3380 cm^{-1}, respectively. The low frequency shift of the ν(C=N) stretching frequency indicates the large contribution of the Zwitterionic resonance form IIa.



(IIa) (II) (IIb)

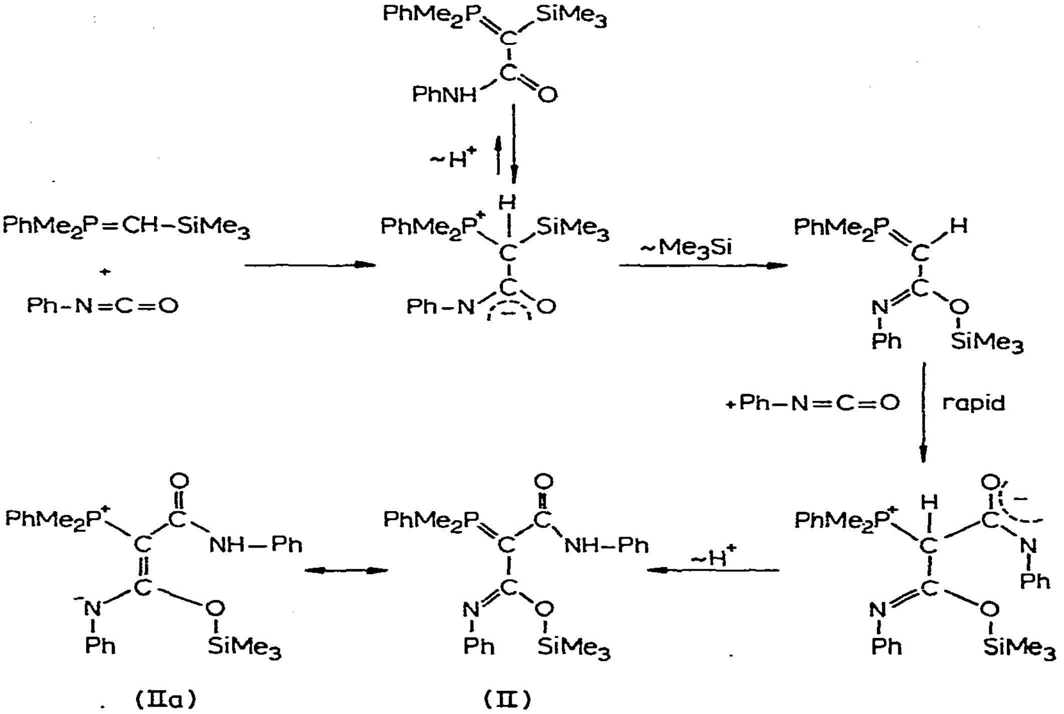
The major contribution of IIa is also in accord with an upfield shift of the trimethylsilyl proton signal based on the following consideration. A stereo model of IIa indicates that a methyl group of the trimethylsilyl group exists just above a phenyl ring which induces an anisotropic upfield shift. This effect may increase when an anionic charge conjugating with phenyl ring is present. The major contribution of the Zwitterionic resonance form IIa, therefore, causes an unusually high field shift of the trimethylsilyl proton signal (δ −0.14) in the case of the adduct II.

On the contrary, a similar consideration with a stereo model of another possible structure with a Si—N bond, $PhMe_2P{=}C(CONHPh)(CONPh \cdot SiMe_3)$, which was excluded by the presence of a ν(Si—O) frequency as discussed previously, suggested that all methyl groups of the trimethylsilyl group were located outside of the upfield anisotropic shift region of both phenyl rings.

When the above insertion reaction was performed with an equimolar ratio of components, the product became a mixture composed of II and the starting ylide I; therefore, the insertion of the second phenyl isocyanate to the intermediate 1/1 adduct was concluded to take place more readily than that of phenyl isocyanate to the remaining I. A plausible mechanism for the double insertion of phenyl isocyanate into I is represented by Scheme 1.

The migration of the trimethylsilyl group from carbon to oxygen was concluded to be irreversible, while that of a proton may be rapid but reversible.

Scheme 1

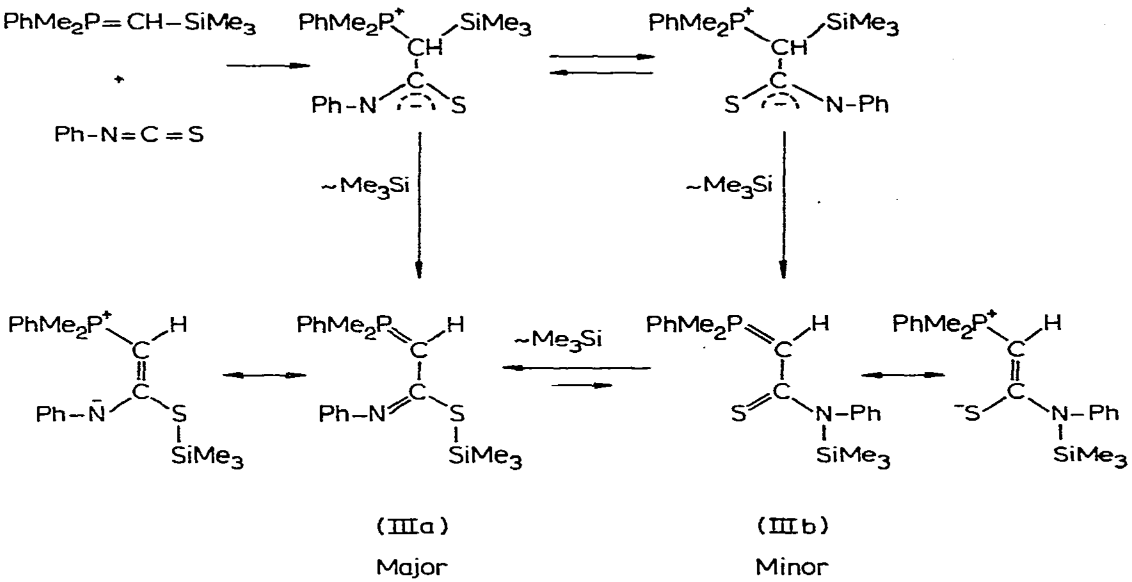


Thus the trimethylsilyl migration is favored thermodynamically compared to the proton migration.

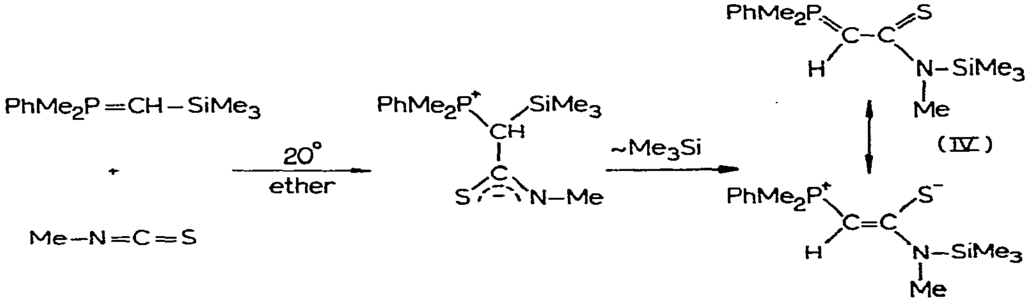
On the other hand, a reaction of phenyl isothiocyanate with I was concluded to give the 1/1 insertion product III based on analytical and the following spectroscopic evidence. A proton NMR spectrum of III showed the presence of two isomers, IIIa and IIIb. The major isomer, IIIa, showed the trimethylsilyl proton signal at δ 0.35 which is in accord with Me_3Si—S bonding [11]. The minor isomer, IIIb, was consistent with a structure with a Si—N bond because of the presence of the trimethylsilyl proton signals at δ 0.12. The relative ratio of IIIa/IIIb was estimated to be 3.5/1 at 25° in $CDCl_3$ from the intensities of the above two signals. The content of IIIb increased to an extent IIIa/IIIb = 1.5/1 on heating to 55°. The interconversion was reversible, so, IIIa and IIIb were in equilibrium. Furthermore, the appearance of two types of methine proton signals as doublets with large P—H coupling constants, δ 2.94 (J = 30 Hz) for IIIa and δ 4.05 (J = 27 Hz) for IIIb, strongly supported the view that the C—H bond of the starting ylide I remained intact and that the insertion reaction of phenyl isothiocyanate proceeded by the selective cleavage of the C—Si bond of I as shown in Scheme 2. The above NMR parameter of both IIIa and IIIb also indicates the significant contribution of the Zwitterionic resonance forms [12].

An infrared spectrum of III revealed both ν(C=N) and ν(C=S) stretching frequencies at 1590 and 1150 cm^{-1}. This is also consistent with the presence of the two isomers, IIIa and IIIb.

Scheme 2

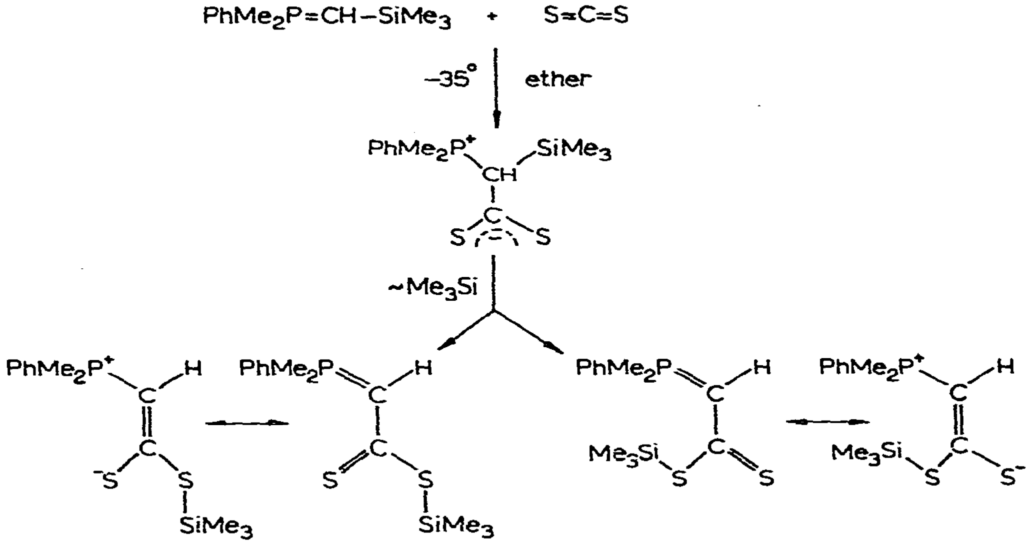


A reaction of methyl isothiocyanate with I similarly gave the 1/1 adduct IV in 87.5% yield. A NMR spectrum of IV showed the presence of only one isomer with a Si—N bond [$\delta(CH_3\text{—}Si)$ 0.14]. The infrared spectrum of IV also supports this conclusion, because no ν(C=N) absorption was detected.



The chemical shift (δ 3.29) and the P—H coupling constant (J = 27 Hz) in the methine proton signal of IV indicates a significant contribution of a Zwitterionic resonance form in a similar manner to IIIb. The presence of an electron donating methyl group relative to phenyl increases the nucleophilicity of the nitrogen atom in the Zwitterionic intermediate, indicating that the trimethylsilyl group preferentially bonds with the nitrogen atom in IV.

Carbon disulfide was also found to insert into the C—Si bond of I to give the 1/1 adduct V in 77.4% yield. In the NMR of V, the J(P—H) value of the ylidic methine proton (13.5 Hz) is lower than that of IIIb and IV (27 Hz), but larger than that of $Ph_3P=CH_2$ (7.0—7.5 Hz) [12]. This indicates that the contribution of the Zwitterionic resonance form is much smaller than that in IIIb and IV. However, the contribution of the Zwitterionic resonance form cannot be ignored, because this value is still sufficiently larger than non-conjugating ylides such as $Ph_3P{=}CH_2$, and the chemical shift of this proton (δ 4.59) is fairly olefinic in character. The presence of two kinds of trimethylsilyl proton signals at δ 0.18 (with a long range phosphorus—proton coupling; $J = 1.0$Hz) and at δ 0.08 (without any P—H coupling) in nearly equal intensities indicates that the 1/1 adduct V is composed of *cis* and *trans* isomers Va and Vb, respectively. This conclusion is consistent with the partial double bond character between the carbon—carbon bond.



(Va) (Vb)

In summary, it has been found that in reactions of (trimethylsilylmethylene)-dimethylphenylphosphorane (I) with heterocumulenes, Wittig-type eliminations of dimethylphenylphosphine oxide or sulfide are prohibited by an rapid and irreversible migration of the trimethylsilyl group to the anionic centers of the Zwitterionic intermediates.

Experimental

General comments

All procedures described herein were carried out under an atmosphere of argon. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Engelskirchen, West Germany. Measurements of NMR spectra were achieved by means of JEOL C-60HL spectrometer using tetramethylsilane as an internal standard. Infrared spectra were measured by JASCO DS-403G spectrometer.

Results of analyses, yields, and m.p.'s are summarized in Table 1 and those of the NMR and infrared spectra are in Table 2. Consequently, we describe here only the procedures for carrying out the reactions and subsequent product isolation.

(Trimethylsilylmethylene)dimethylphenylphosphorane (I)

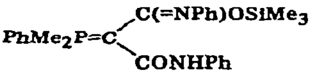
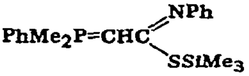
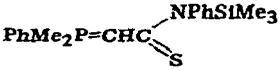
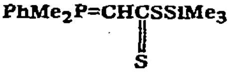
The preparation of I was by employing a modified method of Schmidbaur et al. [13] as follows. Trimethylsilylmethyldimethylphenylphosphonium chloride, $[PhMe_2PCH_2SiMe_3]Cl$ (16.6 g, 6.7 mmol), prepared by a quantitative reaction between chloromethyltrimethylsilane and dimethylphenylphosphine, was suspended in 40 ml of dry ether. A petroleum ether (b.p. 30—40°) solution of 1.35*M* n-butyllithium (49.8 ml) was added dropwise to the phosphonium salts at room temperature. After the addition was complete, the mixture was refluxed until the evolution of n-butane became quantitative (1590 ml). The color of solution gradually turned to light yellow with the precipitation of lithium chloride. Lithium chloride was removed by decantation and the solvent was removed by distillation. The residue was distilled under reduced pressure to give I in 80.8% yield (12.2 g) as a yellow liquid.

Reaction of I with phenyl isocyanate

A dry ether (10 ml) solution of I (0.610 g, 2.75 mmol) (cooled to —35°) was treated with an ether (5 ml) solution of phenyl isocyanate (0.650 g, 5.50 mmol) with stirring for over 5 min. The reaction took place instantaneously with the formation of yellow crystalline precipitates. The temperature of the reaction mixture was raised to 0°, then the yellow liquid layer was removed carefully by means of syringe (the syringe needle should be covered by absorbent cotton). The remaining yellow crystals were washed with dry ether and then dried under reduced pressure which gave the 2/1 adduct II in 84.5% yield (1.10 g).

TABLE 2

NMR AND INFRARED SPECTRA OF I AND INSERTION PRODUCTS

Compound		NMR δ J(P—H)[a]				IR (cm^{-1})[b]	
		CH_3—Si	CH_3—P	CH—P	CH_3—N	ν(C=N)	ν(C=X)
$PhMe_2P{=}CHSiMe_3$	(I)	0.37s[c]	1.37d[c]	—0.29d[c]			
			(12.0)	(8.7)			
 $PhMe_2P{=}C(C({=}NPh)OSiMe_3)(CONHPh)$	(II)	—0.14s	1.84d			1571	1610
 $PhMe_2P{=}CHC({=}NPh)SSiMe_3$	(IIIa)	0.35s	2.08d	2.94d		1590	
			(13.5)	(30.0)			
 $PhMe_2P{=}CHC(NPhSiMe_3){=}S$	(IIIb)	0.12s	2.19d	4.05d			1115
			(13.5)	(27.0)			
 $PhMe_2P{=}CHC({=}S)NMeSiMe_3$	(IV)	0.14s	2.11d	3.29d	2.90s		1111
			(13.5)	(27.0)			
 $PhMe_2P{=}CHC({=}S)SSiMe_3$	(V)	0.18d(1.0)	2.35d	4.59d			1112
		0.08s	(13.5)	(13.5)			

[a] Chemical shifts are in δ units (ppm) downfield from internal tetramethylsilane in $CDCl_3$ excepting I, and J(P—H) are in Herz units. [b] In chloroform solution. X = O for II and X = S for others. [c] In benzene solution.

Cooling of the yellow liquid part in a refrigerator overnight gave trace amounts (2.3%) of the desilylation product, $PhMe_2P{=}(CONHPh)_2$ (II'): m.p. 137—139°. (Anal. found. C 70.48; H 5.78; N 6.99; P 7.71. $C_{23}H_{23}N_2O_2P$ calcd: C 70.76; H 5.94; N 7.17; P 7.93%.)

Reaction of I with phenyl and methyl isothiocyanate

A dry ether solution (10 ml) of phenyl isothiocyanate (0.120 g, 0.89 mmol) was added dropwise to a 70 ml ether solution of I (0.200 g, 0.89 mmol) at room temperature with stirring. A reaction took place immediately. After 30 min, the solvent was removed under reduced pressure until a small amount of crystals appeared. The mixture was then heated slightly to redissolve the crystals, and the resulting solution was then kept in a refrigerator overnight. The resulting yellow needle crystals of the 1/1 adduct III were separated by removing the liquid phase with a syringe and were dried in vacuo after washing by dry ether. The yield of III was 78.1% (0.25 g).

A reaction of I with methyl isothiocyanate was performed in the described procedure as above with I (0.40 g, 1.78 mmol) and methyl isothiocyanate (0.13 g, 1.78 mmol) in dry ether (80 ml) to afford white needles of the 1/1 adduct IV in 87.5% yield (0.46 g).

Reaction of I with carbon disulfide

A dry ether (5 ml) solution of carbon disulfide (0.200 g, 2.69 mmol) was added dropwise to an ether (10 ml) solution of I (0.600 g. 2.69 mmol) at —35° with stirring. A pink crystalline product formed instantaneously during the addition. The solvent was removed by means of a syringe after the addition was complete. The remaining pink precipitate was washed with dry ether and then dried under reduced pressure, giving the 1/1 adduct V in 77.4% yield (0.75 g).

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