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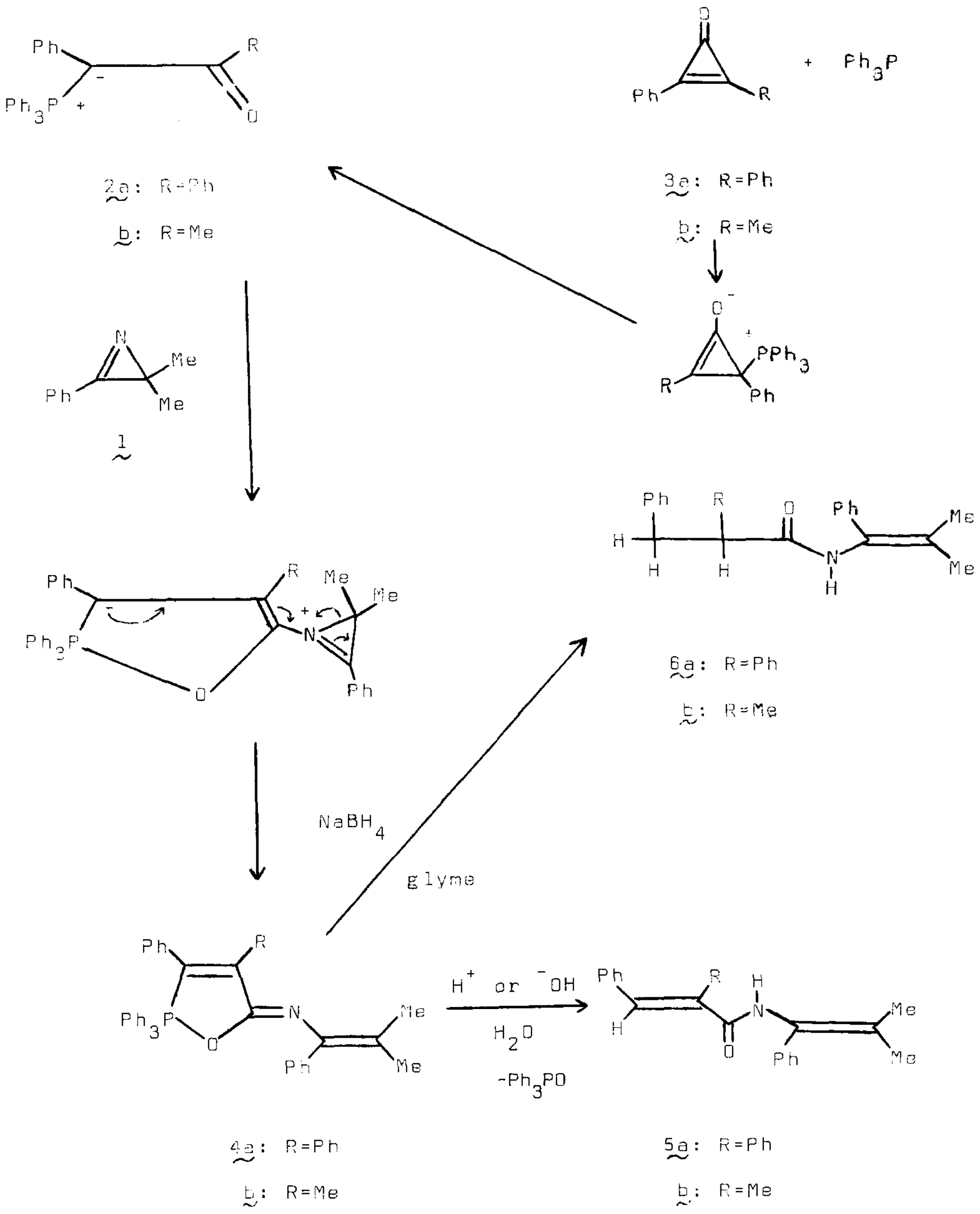
A ROUTE TO 2,2-DIHYDRO-5-IMINO-1,2-OXAPHOSPHOL-3-ENES

Albert Kascheres, Antonio Carlos Joussef, and Humberto C. Duarte
Instituto de Química, Universidade Estadual de Campinas,
Campinas, São Paulo, Brasil 13.100

Abstract: 3,3-Dimethyl-2-phenyl-1-azirine (1) reacted with 2a, generated from diphenylcyclopropenone (3a) and triphenylphosphine, to afford the oxaphospholene derivative (4a): Utilization of methylphenylcyclopropenone (3b) produced the 4-methyl isomer (4b).

1-Azirines (ie. 1) have been found to behave as nucleophiles[1] towards ketenes and as electrophiles[2] towards ylides. The recently reported[3] formation of α-triphenylphosphoranylidenebenzylphenylketene (2a) from the reaction of diphenylcyclopropenone (3a) with triphenylphosphine prompted us to investigate the behavior of a representative azirine, 3,3-dimethyl-2-phenyl-1-azirine (1), towards this system.

A dry benzene solution (15 ml) of 3a (3 mmol) and triphenylphosphine (3 mmol) developed a characteristic orange coloring during three hours under a nitrogen atmosphere, after which time 1 (3 mmol) was added. After 18 hours, removal of the benzene at room temperature followed by trituration of the resulting oil with dry hexane afforded 4a as an orange solid (see TABLE). The structure assignment was based on an observed facile hydrolysis (acid or base) to amide 5a[4] and triphenylphosphine oxide, in conjunction with the ^{13}C-nmr data for 4a which suggested the presence of only two sp^3 carbons pertaining to two different methyl groups[5], the ^{31}P chemical shift[6] for 4a of -38.6 ppm (upfield of the external trimethyl phosphate standard), and the ir spectrum of 4a which lacked characteristic carbonyl absorption. The mass-analyzed ion kinetic energy spectrum of the molecular ion of 4a showed a loss of triphenylphosphine oxide. Sodium borohydride reduction of 4a afforded 6a.[7] The oxaphospholene 4a may be postulated as arising from initial nucleophilic attack of the weakly basic azirine nitrogen at the electrophilic ketene carbon of 2a[8] with cyclization followed by opening of the azirine ring. This result represents the first example of a reaction of 2a wherein the phosphine moiety is incorporated into the final product.


2a: R=Ph
b: R=Me
3a: R=Ph
b: R=Me
1
6a: R=Ph
b: R=Me
NaBH4
glyme
H+ or -OH
H2O
-Ph3PO
4a: R=Ph
b: R=Me
5a: R=Ph
b: R=Me

TABLE

Cmpd	% Yield (mp ^{o}C)	Ir^{a}	Pmr^{b}	C^{13}-nmr^{b}
4a	85 (231-233)	1650(w) 1600	1.4(s,6H) 6.4-7.4(m,30H)	19.4^{c},20.4^{c},112.9,131.9 141.4,157.2(d,J_{P-C}=7Hz) 160.6(d,J_{P-C}=15Hz)
5a	85 (97.5-98.7)	3250 1640 1625 1520	1.75(s,6H) 6.6(br,1H) 7.0-7.5(m,15H) 7.9(s,1H)	-
6a	70 (153.5-155)	3270 1665 1525	1.55 (s, 3H) 1.75(s,3H) 2.85-3.8(m,3H) 6.5(br,1H) 6.85-7.35(m,15H)	-
4b	50 (172-174)	1645(w) 1590	1.45(s,6H) 2.2(d,3H,J_{P-C}=3Hz) 6.8-7.4(m,25H)	19.0^{c},19.2^{c},20.3^{c},112.9 123.4-141.5, 158.5(d,J_{P-C}=5Hz) 160.0(d,J_{P-C}=12Hz)
5b	70 (94-96)	3280 1655 1625 1520	1.75(s,6H) 2.0(s,3H) 7.1-7.5(m,12H)^{d}	-
6b	62 (121-123)	3250 1650 1525	1.2(d,3H,J=6Hz) 1.65(s,3H) 1.8(s,3H) 2.2-3.1(m,3H) 6.5(br,1H) 6.9-7.4(m,10H)	

(a) KBr-γ (cm^{-1}); (b) $CDCl_3$-TMS-δ (ppm); (c) Quartet in totally coupled spectrum;
(d) Falls to 11H on D_2O exchange.

In as much as the reactions of phosphines with cyclopropenones have been restricted to **3a**, it was considered to be of interest to examine the behavior of an unsymmetrical system (**3b**) for which ring opening at CO-CMe[9] and CO-CPh[10] have been reported. In this case, the oxaphospholene obtained (see TABLE) was designated as the 4-methyl isomer (**4b**) on the basis of hydrolysis to **5b** and sodium borohydride reduction to **6b**, the pmr spectrum of the latter containing a methyl doublet at δ1.2 (J = 6 Hz). This result is consistent with participation of **2b** as an intermediate. The effect of substituents in the azirine and phosphine on the above reaction is currently under investigation.

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(4) Amide **5a** was in turn hydrolyzed to α-phenyl-*trans*-cinnamic acid and isobutyrophenone under more vigorous conditions.

(5) Some C^{13}-nmr values for an imino ether prepared from **5a** and triethyloxonium fluoroborate are as follows:
PhCH=C(Ph)-C(OEt)=N-C(Ph)=C_BMe_2 (C_B 115; Me_2 19.8, 20.5).

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(7) Under the same conditions, **5a** suffered less than 7% conversion to **6a**, as determined by pmr analysis of the crude material.

(8) Control experiments showed that **1** did not react with **3a** or triphenylphosphine.

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