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SYNTHESIS OF KETENIMINE VIA (N-ALKYLIMINO)ACYLPALLADIUM COMPLEX INTERMEDIATE

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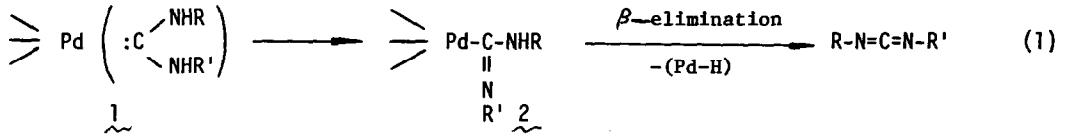
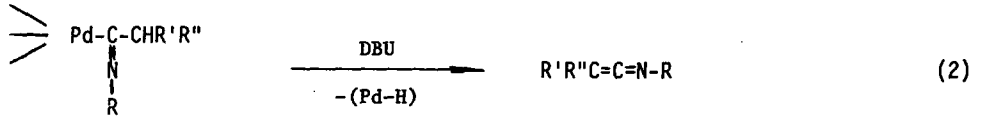
Recently we have reported[1] that diaminocarbene Pd(II) complex (1) is converted into carbodiimide in high yields when it is treated with base, such as butyllithium and potassium tert-butoxide, or with Ag_2O. The formation of carbodiimide was reasonably explained by a mechanism involving β-elimination of aminoiminomethylpalladium complex (2) in which Pd-H species is removed (eq 1). It is conceivable that base may assist the β-elimination of 2.



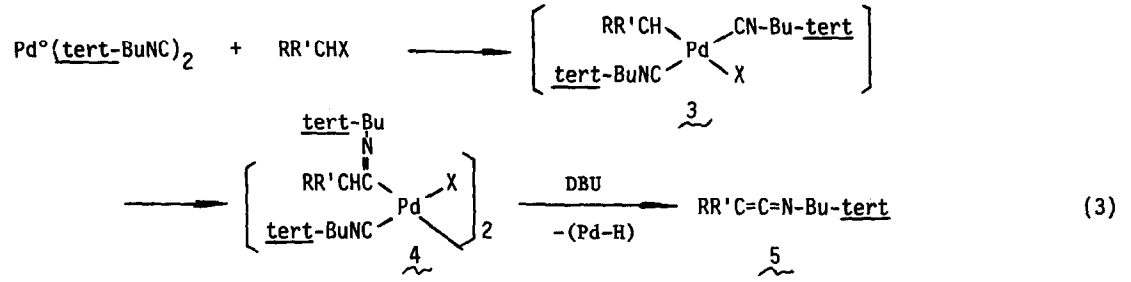
(1)

Here, we wish to report the base-assisted β-elimination of (N-tert-alkylimino)acylpalladium (II) complexes to give ketenimines (eq 2).



(2)

We found that (N-tert-butylimino)phenylacetylpalladium chloride (4a), which was prepared by oxidative addition of benzyl chloride onto Pd°(tert-$C_4H_9NC)_2$ followed by insertion of tert-butyl isocyanide,[2] was refluxed in benzene for 3 hr to produce N-tert-butyl-phenylketenimine (5a) in 84% yield. Ketenimine (5a) is derived from the β-elimination of 4a. Interesting is that the β-elimination of 4a is accelerated by 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU). When 4a was treated with 1 molar equiv of DBU in benzene at room temperature for 6 hr, 5a was produced in 82% yield (eq 3).

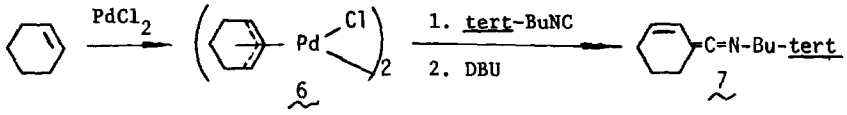


(3)

a : R=C_6H_5, R'=H, X=Cl b : R=n-Pr, R'=H, X=I c : R=R'=Me, X=I

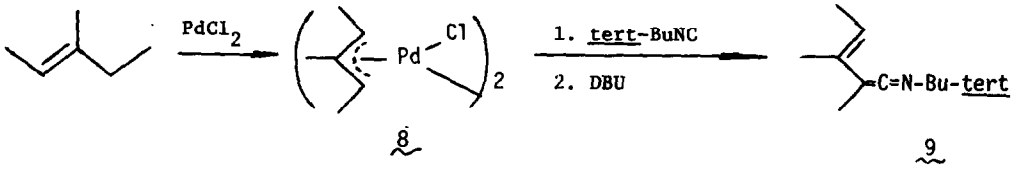
The acceleration effect of DBU on the β-elimination of 4 is remarkable with (N-tert-butylimino)-butyroylpalladium complex (4b) and (N-tert-butylimino)dimethylacetylpalladium complex (4c) which have less acidic β-hydrogens. When complexes 4b and 4c were heated in benzene at 60°, no β-elimination took place. But, complexes 4b and 4c were treated with DBU under the comparable reaction conditions to produce the corresponding ketenimine 5b and 5c in 61% isolated yield (reaction time: 13 hr) and 27% isolated yield (reaction time: 22 hr), respectively.

Usefulness of the present ketenimine synthesis is demonstrated by the conversions of some π-allyl palladium complexes and cycloalkenylpalladium complexes into ketenimine derivatives. For example, π-allyl palladium complex (6), which was prepared from cyclohexene and $PdCl_2$ according to the Trost's procedure,[3] was treated subsequently with 3 molar equiv of tert-butyl isocyanide for 1 hr at room temperature and then with 1 molar equiv of DBU for 7 hr producing the desired ketenimine (7) in 55% isolated yield (eq 4).



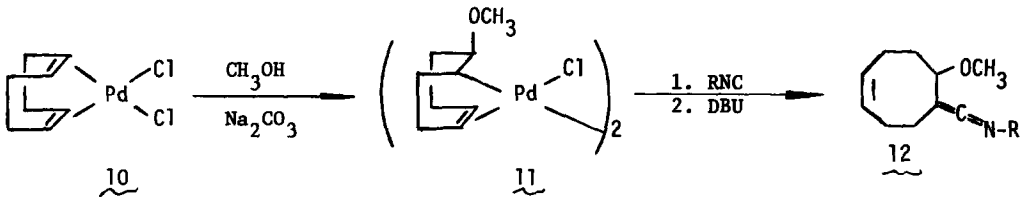
(4)

Similarly, 3-methyl-2-pentene was successfully converted into the corresponding ketenimine (9) in an isolated yield of 38% (eq 5).



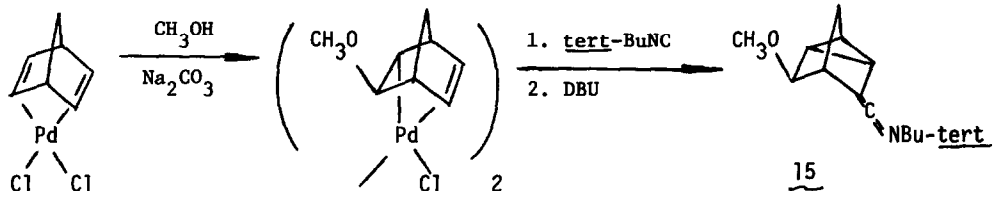
(5)

Some ketenimine syntheses starting with 1,5-cyclooctadiene-palladium dichloride complex (10)[4] and norbornadiene-palladium dichloride complex (13)[5] are summarized in the following scheme.



10 11 12

a : R=tert-Bu Yield=50% (11→12) b : R=2,2,4,4-tetramethylbutyl Yield=60% (11→12)



13 14 15

Yield=38% (14→15)

A drawback to the present ketenimine synthesis is that isocyanides employed are limited to sterically hindered alkyl isocyanides such as tert-butyl isocyanide and 2,2,4,4-tetramethylbutyl isocyanide. The use of cyclohexyl isocyanide in the above ketenimine synthesis did not afford any trace of the corresponding ketenimine. The failure in the ketenimine synthesis with cyclohexyl isocyanide may be due to another type of reaction, i.e., a successive insertion of cyclohexyl isocyanide into alkyl palladium complex.[6]

Finally, we found a catalytic process with Pd(II) catalyst to prepare N-tert-alkyl-aryl-ketenimine and N-tert-alkyl-vinylketenimine on the basis of the above findings. A typical procedure is illustrated by $Pd(II)(OAc)_2$ catalyzed synthesis of N-tert-butyl-phenylketenimine from benzyl chloride and tert-butyl isocyanide. To a stirring mixture of benzyl chloride (6 mM), tert-butyl isocyanide (5 mM) and a catalytic amount of $Pd(II)(OAc)_2$ (0.1 mM) in THF (2 ml), DBU (6 mM) was added dropwise. And the mixture was stirred for 24 hr at room temperature under nitrogen. As the reaction progressed, HCl salt of DBU precipitated. The reaction mixture was extracted with THF and the extract was distilled in vacuo to yield N-tert-butyl-phenylketenimine. Some results are summarized in Table 1. 1,5-Diazabicyclo[4.3.0]non-5-ene (DBN) and triethylamine can also be used in the ketenimine synthesis, but they are less effective than DBU.

N-tert-Butyl ketenimines thus obtained were treated with 20 mole% of p-toluenesulfonic acid in chloroform at 35° to produce nitrile derivatives and isobutylene in a quantitative yield according to eq 6.

$$RCH{=}C{=}N\text{-}Bu\text{-}tert \xrightarrow{\text{p-toluenesulfonic acid}} RCH_2CN + CH_2{=}C(CH_3)_2 \qquad (6)$$

Table 1. Syntheses of Ketenimines

Chloride	Isonitrile	Ketenimine (Isolated Yield %)	
$PhCH_2Cl$	tert-C_4H_9NC	$PhCH{=}C{=}N\text{-}C_4H_9$-tert	(65)
	tert-$C_8H_{17}NC$ [a]	$PhCH{=}C{=}N\text{-}C_8H_{17}$-tert	(57)
p-CH_3-C_6H_4-CH_2Cl	tert-$C_8H_{17}NC$ [a]	p-CH_3-C_6H_4-$CH{=}C{=}N\text{-}C_8H_{17}$-tert	(40)
$CH_2{=}CHCH_2Cl$	tert-C_4H_9NC	$CH_2{=}CHCH{=}C{=}N\text{-}C_4H_9$-tert	(20)
$PhCH{=}CHCH_2Cl$	tert-C_4H_9NC	$PhCH{=}CHCH{=}C{=}N\text{-}C_4H_9$-tert	(20)

a) tert-C_8H_{17} = 2,2,4,4-tetramethylbutyl

A full scope of the present ketenimine synthesis and synthetic utilities for N-tert-alkyl keten imines, especially N-tert-alkyl vinylketenimines are being investigated.

References

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4) J. Chatt, L. M. Vallarino and L. M. Venanzi, J. Chem. Soc., 3413 (1957)

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6) Y. Yamamoto and H. Yamazaki, Bull. Chem. Soc. Japan., 43, 2653 (1970).

7) Products of ketenimines 5, 7, 9, 12 and 15 were identified by ir and nmr spectra, and their hydrolysis to the corresponding N-alkyl carboxamide. 5a : ir (neat) 2016 cm^{-1}; nmr ($CDCl_3$) δ 1.35 (s, 9H), 4.78 (s, 1H), 6.9~7.4 (m, 5H). 5b : ir (neat) 2020 cm^{-1}; nmr ($CDCl_3$) δ 0.92 (m, 3H), 1.22 (s, 9H), 1.3~2.3 (m, 4H), 3.64 (t, 1H). 5c : ir (neat) 2019 cm^{-1}; nmr ($CDCl_3$) δ 1.21 (s, 9H), 1.61 (s, 6H). 7 : ir (neat) 2008 cm^{-1}; nmr ($CDCl_3$) δ 1.25 (s, 9H), 1.4~2.5 (m, 6H), 5.2~5.7 (m, 1H), 5.8~6.2 (m, 1H). 9 : ir (neat) 2006 cm^{-1}; nmr ($CDCl_3$) δ 1.30 (s, 9H), 1.6~1.9 (m, 9H), 4.9~5.3 (m, 1H). 12a : ir (neat) 2018 cm^{-1} ; nmr (CCl_4) δ 1.17 (s, 9H), 1.3~2.5 (m, 8H), 3.16 (s, 3H), 3.2~3.5 (m, 1H), 5.2~5.8 (m, 2H). 12b : ir (neat) 2013 cm^{-1} ; nmr ($CDCl_3$) δ 0.95 (s, 9H), 1.22 (s, 6H), 1.47 (s, 2H), 1.3~2.5 (m, 8H), 3.14 (s, 3H), 3.3~3.6 (m, 1H), 5.3~5.8 (m, 2H). 15 : ir (neat) 3050 2031, 827 cm^{-1} ; nmr ($CDCl_3$) δ 1.22 (s, 9H), 1.2~2.5 (m, 6H), 3.27 (s, 3H), 3.3~3.5 (m, 1H).