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VINYLIC SUBSTITUTION ON TROPONOID CATALYZED BY PALLADIUM COMPLEXES, AND FORMATION OF NEW C-Pd σ-COMPLEXES OF TROPONOID

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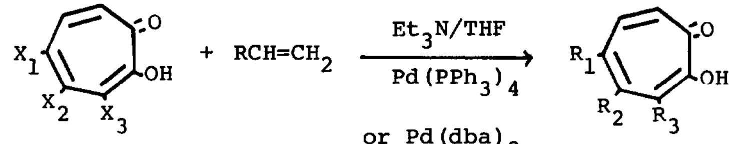
Summary: The reaction of 3-, 4- and 5-halotropolones with olefins catalyzed by palladium(0) complex gave 3-, 4- and 5-(substituted vinyl)tropolones respectively. Similarly, 2-chlorotropone gave 2-styryltropones. Some tropolonyl- and troponylpalladium-σ-complexes were synthesized.

Few carbon-carbon bond formation on tropolone or tropone nucleus has been reported.[1] Recent advancement of palladium-catalyzed vinylic substitution of organic halides[2] provides a new tool for the carbon-carbon bond formation. The advantage of its application to halotropolone or halotropone is to use zero-valent metal complex which can give a carbon-palladium σ-bonded complex without formation of tropylium cation. Little is known about the characterized transition metal σ-bonded complex of seven membered ring π-electron system,[3] although many examples of their π-bonded complexes have appeared.[1b, 1c, 4]

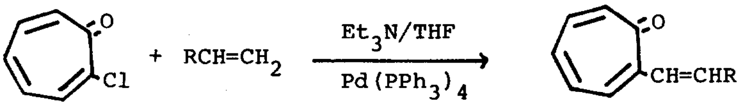
We wish to describe a palladium-catalyzed vinylic substitution of halotropolone and halotropone with olefins as well as the first example of tropolonyl- and troponylpalladium(II) σ-complexes.

A mixture of 5-bromotropolone (Ia) (2 mmol), styrene (0.7 ml), and triethylamine (0.7 ml) in THF (10 ml) was heated at 100° in the presence of $Pd(PPh_3)_4$ (0.1 mmol) in a sealed tube for 20 hr. Purification of the product by converting into sodium salt and subsequent acidification gave 5-styryltropolone (IIa) in 83% yield. The analogous reaction of Ia with p-methoxystyrene, 2-vinylpyridine, and methyl acrylate afforded the corresponding 5-(substituted vinyl)tropolones (IIb, IIc and IId). Similarly 4-bromotropolone (Ib) gave 4-styryltropolone (IIe). The reaction of 3-iodotropolone (Ic) with these olefins gave 3-(substituted vinyl)tropolones (IIf, IIg, IIh and IIi). Furthermore, 2-chlorotropone reacted with styrenes to afford 2-styryltropones (IVa, IVb and IVc) after purification by silica gel column chromatography. Bis(dibenzalacetone)palladium(0), $Pd(dba)_2$[5], though less active, can also be employed instead of $Pd(PPh_3)_4$. Addition of PPh_3 to the $Pd(dba)_2$ catalyst system improved the yield of IIa. The results of the vinylic substitution reactions are listed in Table 1.



Ia; X_1= Br, X_2=X_3= H
Ib; X_2= Br, X_1=X_3= H
Ic; X_3= I, X_1=X_2= H

IIa-IId; R_1= RCH=CH, R_2=R_3= H
IIe; R_2= RCH=CH, R_1=R_3= H
IIf-IIi; R_3= RCH=CH, R_1=R_2= H

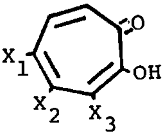


III

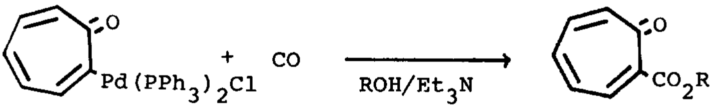
IVa; R= Ph
IVb; R= p-$MeOC_6H_4$
IVc; R= 2-C_5H_4N

The catalytic vinylation of aryl halide was explained by Heck to proceed *via* oxidative addition of organic halide to zero-valent palladium complexes.[2] On the other hand, halogeno(aryl)bis(triphenylphosphine)palladium(II) was synthesized by oxidative addition of aryl halide to $Pd(PPh_3)_4$.[6] Therefore, the catalytic vinylation of halotropolone or halotropone is assumed to proceed by way of tropolonyl- or troponylpalladium(II) σ-bonded complexes as the reaction intermedates. This prompted us to isolate and characterize the corresponding complexes by the reaction of 3-iodo-(Ic), or 5-iodotropolone (Id) with $Pd(PPh_3)_4$ in toluene at room temperature.

The complexes obtained are suggested to be iodo(5-tropolonyl)-, and iodo(3-tropolonyl)bis(triphenylphosphine)palladium(II), (Va)[7] and (Vb)[8], respectively, on the following basis: 1) IR and NMR spectra and elementary analyses, 2) posi-



	X_1	X_2	X_3	Yield (%)	dp
Va	$Pd(PPh_3)_2I$	H	H	89	214°
Vb	H	H	$Pd(PPh_3)_2I$	80	213°
Vc	$Pd(PPh_3)_2Br$	H	H	53	186°
Vd	H	$Pd(PPh_3)_2Br$	H	69	210°
Ve	H	H	$Pd(PPh_3)_2Br$	89	218°



VI

VIIa; R= Me
VIIb; R= Et

Table 1. Vinylic Substitution of Halotropolones (Ia, Ib and Ic) and Halotropone (III).

	Olefin ($RCH=CH_2$) R	Catalyst[a)]	Product	Yield[b)] (%)	mp (°C)
Ia	Ph	A	IIa (R_1= PhCH=CH, R_2=R_3= H)	83	133[c)]
Ia	p-$MeOC_6H_4$	A	IIb (R_1= p-$MeOC_6H_4CH$=CH, R_2=R_3= H)	65	195[c)]
Ia	2-C_5H_4N	A	IIc (R_1= 2-C_5H_4NCH=CH, R_2=R_3= H)	80	141.5
Ia	MeO_2C	A	IId (R_1= HO_2CCH=CH, R_2=R_3= H)	70	239(d)
Ia	Ph	B	IIa	39	
Ia	Ph	C	IIa	45	
Ia	Ph	D	IIa	77	
Ib	Ph	A	IIe (R_2= PhCH=CH, R_1=R_3= H)	33	87[d)]
Ic	Ph	A	IIf (R_3= PhCH=CH, R_1=R_2= H)	44	75[e)]
Ic	p-$MeOC_6H_4$	A	IIg (R_3= p-$MeOC_6H_4CH$=CH, R_1=R_2= H)	51	136
Ic	2-C_5H_4N	A	IIh (R_3= 2-C_5H_4NCH=CH, R_1=R_2= H)	43	97.5
Ic	MeO_2CCH=CH	A	IIi (R_3= HO_2CCH=CH, R_1=R_2= H)	49	224(d)[f)]
III	Ph	A	IVa (R= Ph)	25	92[g)]
III	p-$MeOC_6H_4$	A	IVb (R= p-$MeOC_6H_4$)	49	95[g)]
III	2-C_5H_4N	A	IVc (R= 2-C_5H_4N)	36	91.5[h)]

a) A; $Pd(PPh_3)_4$. B; $Pd(dba)_2$, dba= dibenzalacetone. C; $Pd(PPh_3)_4$ + PPh_3, Ratio of PPh_3 to $Pd(dba)_2$ is 4. D; Complex (Vc). b) Isolated yields based on halogene compounds. c) H. Higashi, K. Kurosawa, H. Matsumura, Bull. Chem. Soc. Japan, 43, 3236 (1970). d) T. Nozoe, Y. Kitahara, K. Doi, S. Masamune, M. Endo, M. Ishii, J. G. Sin, Sci. Repts. Tohoku Univ., I, 38, 257 (1955). e) Reported mp 112-112.5 by H. Matsumura [Nippon Kagaku Zasshi, 82, 774 (1961)] seems to be erroneous. f) Reported mp 233-234°(d) by E. Sebe, S. Matsumoto [Sci. Repts. Tohoku Univ., I, 38, 308 (1954)]. g) I. Kawamoto, Y. Sugimura, Y. Kishida, Tetrahedron lett., 1973, 877. h) Purified through picrate (dp. 206°).

tive ferric chloride test and the formation of cupric salts, 3) carbonylation with carbon monoxide in ethanol followed by hydrolysis to afford 3-carboxy- and 5-carboxytropolone in 68% and 78% yields, respectively. The bromide ligating complexes (Vc), (Vd) and (Ve) from 5-bromo-, 4-bromo-, and 3-bromotropolones were also obtained in the analogous way.

Extension of the reaction to 2-chlorotropone gave chloro(2-troponyl)bis(triphenylphosphine)palladium(II) (VI), mp 210°(dec.) in 85% yield.[9] Extraordinaly lower frequency of carbonyl stretching in its IR spectra (KBr disk and $CHCl_3$

solution) indicates the ionic character of VI. The reaction of VI with carbon monoxide in methanol and ethanol produced 2-methoxycarbonyl- (VIIa)[10] and 2-ethoxycarbonyltropone (VIIb), in 65% and 33% yields, respectively, indicating that VI also has a carbon-palladium σ-bond at 2-position of tropone.

It is remarkable that the tropolonyl-palladium σ-complexes serve as the catalyst of the vinylic substitution as is illustrated by the complex Vc in Table 1.

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7. IR (KBr); 3200 (OH), 1585 and 1575 (C=C, CO), 1470 and 1440 (PPh_3) cm^{-1}. NMR ($CDCl_3$, TMS); 7.65-7.32 (12H, m. Ph), 7.32-7.05 (18H, m. Ph), 6.85 (2H, d, J= 12 Hz), 6.20 (2H, d, J= 12 Hz) ppm.
8. IR (KBr); 3180 (OH), 1605 and 1570 (C=C, CO), 1480 and 1435 (PPh_3) cm^{-1}. NMR ($CDCl_3$, TMS); 7.7-7.4 (12H, m, Ph), 7.3-7.1 (18H, m, Ph), 7.1-6.0 (4H, m, Trpln) ppm.
9. IR (KBr); 1530 (CO), 1470 and 1430 (PPh_3) cm^{-1}. NMR ($CDCl_3$, TMS); 7.8-7.3 (12H, m, Ph), 7.3-7.1 (18H, m, Ph), 7.1-5.4 (5H, m, Trpn) ppm.
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