

Chloropalladation of 2-Phenyl-1,2,3-triazoles as a Means of Selective *o*-Chlorination

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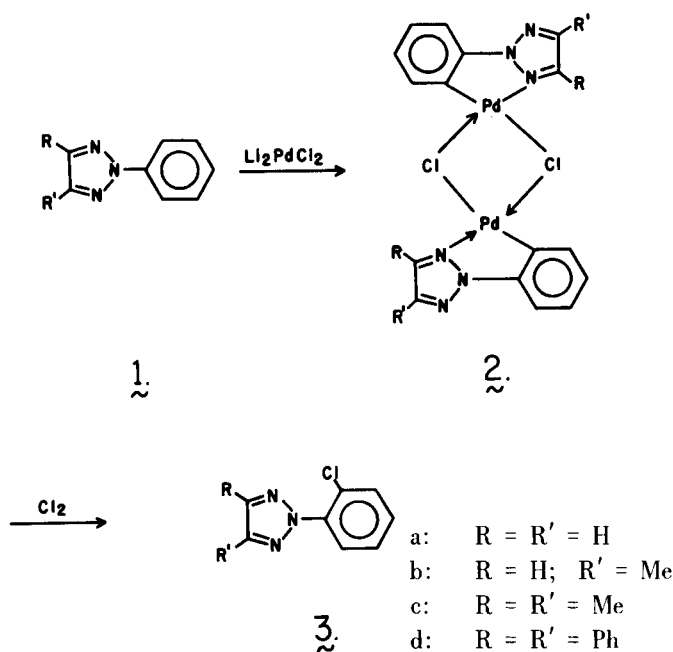
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The phenyl ring of 2-phenyl-1,2,3-triazoles undergoes electrophilic substitution mainly in the 4-position (1,2). Accordingly, substituted 2-(*p*-chlorophenyl)-1,2,3-triazoles can be prepared either by chlorinating a 2-phenyl-1,2,3-triazole or by cyclizing a bis-*p*-chlorophenylhydrazone with an oxidant (1). Since halogenation is of little use in preparing 2-(*o*-halogenophenyl)-1,2,3-triazoles and 2-(*m*-halogenophenyl)-1,2,3-triazoles, the latter triazoles were prepared by cyclizing bis *m*-halogenophenylhydrazones (1). The 2-(*o*-halogenophenyl)-1,2,3-triazoles except for the *o*-fluorophenyl derivatives (3) are unknown because when the corresponding bis-*o*-chloro-, bis-*o*-bromo- and bis-*o*-iodophenylhydrazones undergo cyclizations, they lose their *o*-halogen atom (4,5).

It has been shown some that 2-(*m*-chlorophenyl)-1,2,3-triazoles and some 2-(*p*-chlorophenyl)-1,2,3-triazoles exhibited insecticidal properties (6). It was therefore thought interesting to synthesize some substituted 2-(*o*-chlorophenyl)-1,2,3-triazoles for screening. If active, the *o*-halogenated insecticides would readily lose their halogen atoms by hydrolysis and undergo degradation.

1-Phenylpyrazole has recently been shown to react with palladium (II) chloride to form 2-(1'-pyrazolyl)-phenyl palladium (II) chloride which was readily cleaved by halogens to give 1-(*o*-chlorophenyl)pyrazole (7,8). We therefore attempted to prepare analogous palladium (II) chloride complexes by refluxing 2-phenyl-1,2,3-triazole (1a) in methanol with Li₂PdCl₄. The light-yellow green di- μ -chloro-bis[2-[2'-H-(1',2',3'-triazolyl)]-phenyl]dipalladium (II), precipitated in nearly quantitative yield. This compound was given a dimeric structure (2a) similar to that of the pyrazole derivative. Similar reactions were carried out with 4-methyl-2-phenyl-1,2,3-triazole (1b), 4,5-dimethyl-1-phenyl-1,2,3-triazole (1c) and 2,4,5-triphenyl-1,2,3-triazole (1d) which gave the corresponding palladium (II) chloride complexes (2b), (2c) and (2d). All the palladium chloride complexes were obtained in near quantitative yields, were yellow green, and melted with decomposition at about 280°.

The infrared spectra of the palladium chloride complexes (see Table I), showed weaker triazole ring-breathing absorption at ν 976-951 cm⁻¹ than those of the parent



triazoles at ν 974-946 cm⁻¹ (9-11). This is consistent with the assumption that chelation of the palladium was involved with one of the nitrogen atoms of the triazole rings as in structures 2a-d, which would affect their ring breathing mode. The complexes also showed absorptions between ν 432 and 425 cm⁻¹ and ν 365 to 324 cm⁻¹ attributed to C-Pd stretching and Pd-Cl stretching, respectively (12-15).

Cleavage of the carbon palladium bond in the metallated 2-phenyl-1,2,3-triazoles (2a-d) could be readily carried out by bubbling chlorine in a suspension of the complex in *p*-dioxane-water. The palladium chloride complex of 2,4,5-triphenyl-1,2,3-triazole (2d) afforded 2(*o*-chlorophenyl)-2,4-diphenyl-1,2,3-triazole in 60% yield. The other chloropalladium complexes gave mixtures of mono-, di- and polychlorinated derivatives which were difficult to separate and were of little synthetic value.

The mass spectrum of 2-(*o*-chlorophenyl)-4,5-diphenyl-1,2,3-triazole was quite similar to that of the known 2-(*p*-chlorophenyl)-4,5-diphenyl-1,2,3-triazole (16) (see Figure 1). The position of the chlorine was established

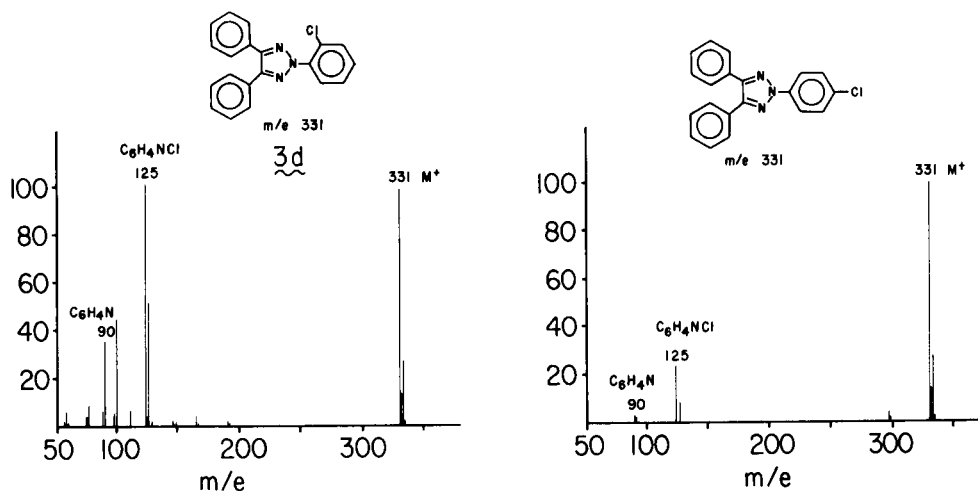


Figure 1. Mass spectra of 2-(*o*-chlorophenyl)-4,5-diphenyl-1,2,3-triazole (**3d**) and 2-(*p*-chlorophenyl)-4,5-diphenyl-1,2,3-triazole.

Table I

Palladium Chloride Complexes of Substituted 2-Phenyl-1,2,3-triazoles (**2a-d**)

Compound	R	R'	Formula	C	H	N	C	H	N	Triazole breathing	ν cm ⁻¹ Pd-Cl	Pd-Cl
2a	H	H	C ₈ H ₆ N ₃ PdCl	33.60	2.11	14.70	33.54	2.31	14.69	951	425	344
2b	Me	H	C ₉ H ₈ N ₃ PdCl	36.03	2.66	14.01	36.00	2.65	13.85	962	426	324
2c	Me	Me	C ₁₀ H ₁₀ N ₃ PdCl	38.24	3.21	13.38	38.17	3.19	13.35	954	430	340
2d	Ph	Ph	C ₂₀ H ₁₄ N ₃ PdCl	54.82	3.22	9.59	54.55	3.28	9.71	976	432	365

from: (a) The fact that compound **3d** was a monochloro derivative, different from the known 2-(*m*- and 2-(*p*-chlorophenyl)-4,5-diphenyl-1,2,3-triazoles and (b) A comparison of its nmr spectrum in the phenyl proton region with the nmr spectrum of the parent 2,4,5-triphenyl-1,2,3-triazole and of 4,5-diphenyl-2-(*o*-fluorophenyl)-1,2,3-triazole we prepared earlier (3). The parent 2,4,5-triphenyl-1,2,3-triazole showed three multiplets; one between δ 8.3 and 8.0 which corresponded to the *o*-protons of the 2-phenyl ring, which is attached to the 2-nitrogen atom; one at δ 7.7-7.4 corresponding to the *ortho* protons of the 4 and 5-phenyl ring; and one between δ 7.3 and 7.1 for the *meta* and *para* protons of the three phenyl ring. The integration of these 3 peaks was found to be in the ratio 2:4:9 for the parent 2,4,5-triphenyl-1,2,3-triazole and 1:4:9 for both the 4,5-diphenyl 2-(*o*-fluorophenyl)-1,2,3-triazole and the prepared 2-(*o*-chlorophenyl)-4,5-diphenyl-1,2,3-triazole (**3d**). The last two compounds also showed an upfield shift of the 6' proton due to the halogen substituent in the *o*-position of the 2-phenyl ring.

In conclusion, it can be stated that chloropalladation of substituted 2-phenyl-1,2,3-triazoles occurs quantitatively and that chlorination of the palladium complexes is of synthetic use for the preparation of 2-(*o*-chlorophenyl)-4,5-diphenyl-1,2,3-triazole.

EXPERIMENTAL

Melting points were determined using a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer 621 spectrophotometer; nmr spectra were recorded on a Varian T-60 spectrometer, and mass spectra were determined with a Varian M-66 recording spectrometer. Elemental analyses were determined by Spang Micro-analytical Laboratory of Ann Arbor, Michigan and by M. Gilles, Department of Chemistry and Chemical Engineering, Michigan Technological University, on a Perkin-Elmer 240 elemental analyser.

The 2-phenyl-1,2,3-triazoles needed for this study were prepared by methods described in the references cited: 2-phenyl-1,2,3-triazole (1,5); 4-methyl-1-phenyl-1,2,3-triazole (5); 4,5-dimethyl-2-phenyl-1,2,3-triazole (5); 2,4,5-triphenyl-1,2,3-triazole (17,18).

Preparation of the Palladium (II) Chloride Complexes (**2a-d**).

The desired 2-phenyl-1,2,3-triazole (**1a-d**) (3.4 mmoles) was stirred in methanol (50 ml.) and refluxed with 3.4 mmoles of Li_2PdCl_4 . Separation of the complexes began in about 30 minutes. After 2 hours, refluxing was stopped and the reaction mixture containing the complex slurry was filtered to remove the complex and the filtrate was refluxed for an additional 48 hours. The complex was removed from the solution several more times until the reaction mixture was nearly colorless. The complex was washed several times with 50 ml. portions of methanol and dried under reduced pressure. All the complexes were yellow-green powders which melted with decomposition at about 280° , and were obtained in more than 95% yield. For the analyses see Table I.

Preparation of 2-(*o*-Chlorophenyl)-4,5-diphenyl-1,2,3-triazole (**3d**).

A suspension of 0.81 g. (0.4 mmole) of di- μ -chloro-bis-[2-[2'-H-(4',5'-diphenyl-1',2',3'-triazolyl)]phenyl]dipalladium (II) (**2d**) in 125 ml. of a 3:1 *p*-dioxane-water solution was warmed with stirring for about 10 minutes. Chlorine was then bubbled into the reaction mixture. The suspension cleared up after 10 minutes, and chlorination was continued for 20 more minutes. The red brown solution was treated with 50 ml. of water and extracted four times with 25 ml. portions of light petroleum ether (b.p. $37-49^\circ$). The petroleum ether solution was concentrated to about 50 ml. and extracted three times with 100 ml. portions of water to remove *p*-dioxane. The solution was then evaporated to dryness under reduced pressure and the residue recrystallized from absolute ethanol. Compound **3d** was obtained as light yellow crystals, m.p. $105-106^\circ$ in 60% yield. Major infrared absorption bands were at ν 1488, 1464, 1456, 1440, 1298, 1049, 987, 975, 787, 863, 755, 697, 681 and 670 cm^{-1} .

Anal. Calcd. for $\text{C}_{20}\text{H}_{14}\text{ClN}_3$: C, 72.40; H, 4.25; N, 12.66. Found: C, 72.07; H, 4.17; N, 12.66.

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