Transformation of Carbon–Mercury Bonds into Carbon–Carbon Bonds; Chloro-(*exo*-3-acetoxy-*endo*-5-nortricyclyl)dipyridinepalladium and Unsaturated Mercurials

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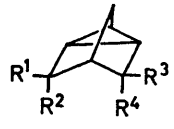
Summary Diphenylmercury and di-isobutenylmercury react with chloro-(*exo*-3-acetoxy-*endo*-5-nortricyclyl)dipyridinepalladium to afford *endo,endo*-3-phenyl-, or -3-isobutenylnortricyclyl-5-mercuric chloride, respectively

WE report an unusual reaction between dialkenyl- or diarylmercury derivatives and the palladium complex (I)[1] to form tricyclic mercurials Thus, treatment of (I) with di-isobutenylmercury in methanol (25°) affords chloro-(3-isobutenyl-5-nortricyclyl)mercury (II) (52%) and palladium metal Similarly, (I) is converted into (III) (67%) by the action of methanolic diphenylmercury Biphenyl is a by-product of this reaction Both (II) and (III) are characterized by correct analyses and the absence of olefinic hydrogens in the n m r spectrum ‡ Also, borohydride reduction of (II) or (III) affords the expected mixture[2] of monosubstituted norbornenes and nortricyclenes The major reduction product obtained from (III) is 3-phenylnortricyclene, while (II) affords similar amounts of 3-isobutenylnotricyclene, 7-isobutenylnortricyclene, and *endo*-2-isobutenylnorborn-5-ene The latter hydrocarbon is identical with an authentic sample prepared from *endo*-2-norbornene-5-carboxaldehyde[3] and isopropylidenetriphenylphosphorane and proves the C-3 *endo* stereochemistry assigned to (II) Direct proof for the C-5 stereochemistry of (II) is not available, but the *endo endo* structure is assigned by analogy to the structure of (III), discussed below



	R^1	R^2	R^3	R^4
(IV)	H	Cl	H	Ph
(V)	Cl	H	H	Ph
(VII)	Cl	H	Ph	H
(VIII)	H	Cl	Ph	H
(X)	H	$ClPd(py)_2$	OMe	H
(XI)	H	ClHg	OMe	H

Chlorination of (III) under conditions which cleave carbon–mercury bonds with retention of stereochemistry[4] affords a single 3-chloro-5-phenylnortricyclene (IV) This compound rearranges partially upon attempted g l p c

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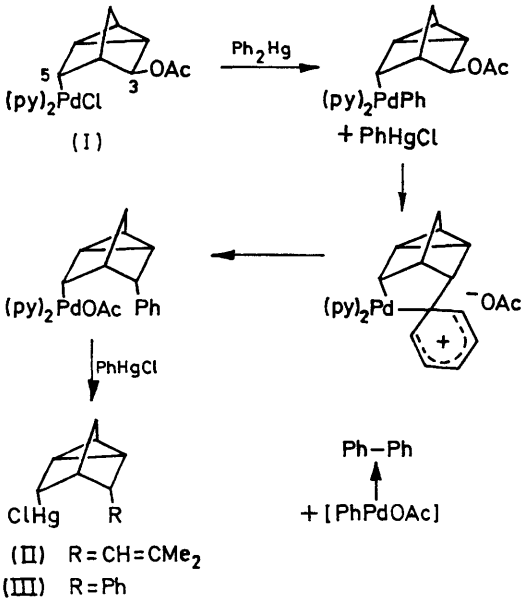
‡ (II) m p 60 5—61 5° n m r ($CDCl_3$) δ 1 08—1 58 (5H, m) 1 73 (3H, br s), 1 85 (3H, br s) 2 12 (1H br s) 2 17—2 50 (2H, m), 5 48 (1H, m), (III) m p 138—140°, n m r ($CDCl_3$) δ 1 17—1 75 (5H, m), 2 10 (1H br s), 2 37 (1H, br s), 3 09 (1H, br s), 7 35 (5H, m)

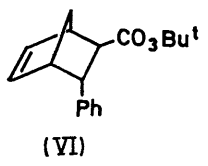
analysis into an isomer (V). Independent synthesis of (V) by free radical decomposition of the perester (VI)[5] in ααα-trichlorotoluene at 140° confirms the C-3 *endo*-phenyl stereochemistry and suggests that (IV) [and therefore, (III)] has the *endo,endo* structure. Final proof for this assignment is provided by the isolation of the remaining possible 3-



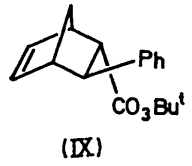
SCHEME.

chloro-5-phenylnortricyclene isomers (VII) and (VIII) from free radical decomposition of the perester (IX)[5] as before. Unidentified bicyclic isomers are also formed as minor products from (VI) and (IX), a result of the equilibration of norbornenyl and nortricyclyl radicals. The isomers (IV), (V), (VII), and (VIII) have similar but readily distinguishable n.m.r. spectra, and all except the hindered isomer (IV) are stable to g.l.p.c. analysis.

Dialkylmercury derivatives, aryl- or alkyl-mercuric salts, and methoxycarbonylmercuric chloride fail to convert (I) into analogues of (II) or (III). Instead, methanolysis occurs to form (X), followed by slower metal exchange with the mercury salt to afford the *exo,endo* compound (XI) (m.p. 134—137°) identified on the basis of spectral and analytical data, and conversion into *endo*-3-chloro-*exo*-5-methoxynortricyclene[6] by chlorination. Treatment of (X) with methanolic diphenylmercury affords (XI) and only traces of (III).



(VI)



(IX)

The experimental evidence indicates that carbon bond formation requires participation by olefinic π-electrons in the nucleophilic displacement of acetate as the leaving group. An ionic mechanism (see Scheme)[7] explains the mercury substituent effects, the contrasting behaviour of (I) and (X), and the stereospecific formation of *endo,endo* products (II) and (III). The ease of acetate displacement by olefinic carbon to form (II) and (III) or by methanol to form (X) suggests that participation by occupied palladium *d*-orbitals is an important factor in these reactions. Similar effects have been noted previously in complexes of palladium and other transition metals.[8]

Initial results indicate that other stable σ-bonded palladium complexes containing α or β leaving groups react similarly with diphenylmercury.

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