nmr ($CDCl_3$) τ 3.46 (d, J = 3.2 Hz, 1, C_9 H), 4.70 (s, 1, NH), 7.14 and 7.32 (m, 2, C_7 and C_1 H), 7.90 (broad s, 1, C_6 H), 8.22 (m, 1, C_4 H), 8.49 (m, 2, C_2 and C_3 H), and 8.60 (s, 11, C_5 H and CH_3).

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.12; H, 8.83; N, 6.68.

8-Cyano-9-chloro-δ-cyclene (3c), *exo*-3-Cyano-4-chlorotricyclo[4.2.1.0^{2,5}]nona-3,7-diene (4), and 2-Chloro-3-cyanotricyclo[4.3.0.0^{4,9}]nona-2,7-diene (5).—The reaction product of **1** with **2c** could not be extensively pruified by a fractional distillation under reduced pressure, and hence preparative vpc separation was performed at 150° on a silicone SE-30 column (20 ft × 0.375 in.). The first peak afforded **4** in 6% yield as a colorless oil which on standing crystallized: mp 36–37°; ir (KBr) 2260 and 1610 cm^{-1}; uv max (EtOH) 228 (infl) and 248 nm (ϵ 1700); mass spectrum m/e (rel intensity) 179 (0.3, M + 2), 177 (1, M$^+$), 142 (16, M − Cl), 115 (46, M − HCN), 66 (57, cyclopentadiene), and 51 (100, cyanoacetylene).

Anal. Calcd for $C_{10}H_8NCl$: C, 67.62; H, 4.54; N, 7.88. Found: C, 67.52; H, 4.67; N, 7.70.

The second peak afforded **3c** in 40% yield as colorless crystals: mp 40–42°; ir (KBr) 2250 and 1585 cm^{-1}; uv max (EtOH) 240 nm (ϵ 9100); mass spectrum m/e (rel intensity) 179 (20, M + 2), 177 (61, M$^+$), 142 (99, M − Cl), and 115 (100, M − HCN).

Anal. Calcd for $C_{10}H_8NCl$: C, 67.62; H, 4.54; N, 7.88. Found: C, 67.52; H, 4.67; N, 7.70.

The third peak was very weak and was not resolved well with the fourth peak, and therefore, pure material could not be obtained.

The fourth peak gave **5** in 20% yield as a colorless oil: $n^{16.5}$D 1.5524; ir (neat) 2300 and 737 cm^{-1}; uv max (EtOH) 227 and 238 nm (ϵ 800 and 490); mass spectrum m/e (rel intensity) 179 (0.3, M + 2), 177 (1, M$^+$), 142 (16, M − Cl), 115 (46, M − HCN), 66 (57, cyclopentadiene), and 51 (100, cyanoacetylene).

Anal. Calcd for $C_{10}H_8NCl$: C, 67.62; H, 4.54; N, 7.88. Found: C, 67.85; H, 4.59; N, 7.60.

Reaction of 1 with Methylenebisurethane.—To a refluxing mixture of methylenebisurethane (9.5 g, 0.05 mol) and 47% boron trifluoride etherate (1.81 g) in dry benzene (50 ml) was added a solution of **1** (4.6 g, 0.05 mol) in dry benzene (20 ml) slowly over a period of 3 hr and the mixture was further refluxed for 3 hr. The cooled mixture was washed with water several times and dried over sodium sulfate. Removal of the solvent gave a dark brownish residue (*ca.* 6 g) which was purified on a silica gel column eluting with chloroform–methanol to give ***N*-ethoxycarbonyl-8-aza-δ-cyclane (10)** as a colorless oil. This was also obtained by distillation of the crude product: bp 88–90° (0.4 mm); n^{20}D 1.5179; ir (neat) 1700, 800, and 770 cm^{-1}.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.40; H, 7.82; N, 7.22.

Further elution gave ***N*-ethoxycarbonylamino-5-*N*-ethoxycarbonylaminomethyltricyclo[2.2.1.0^{2,6}]heptane (11)** as colorless crystals: mp 130–131°; ir (KBr) 3260, 1700, 805, and 782 cm^{-1}.

Anal. Calcd for $C_{14}H_{22}N_2O_4$: C, 59.55; H, 7.85; N, 9.92. Found: C, 59.69; H, 7.84; N, 9.76.

Reaction of 1 with Benzalbisurethane.—The reaction was carried out as above. Work-up afforded only **3-nortricyclylurethane (12)** in *ca.* 50% yield as colorless crystals, mp 61–64° (lit.[15] mp 64°); there was no depression of the mixture melting point with an authentic sample.

Reaction of 1 with Anhydrochloralurethane (9c).—An equimolar mixture of **1** and **9c**[16] in dry benzene was heated at 80° for 6 hr. After removal of the solvent, the residue was dissolved in chloroform and was purified on a silica gel column ($CHCl_3$–MeOH). The major product was an adduct of chloralurethane to **9c**, which was isolated in 23% yield as needles: mp 164–166° (lit.[17] mp 163–164°); nmr ($CDCl_3$) τ 3.95–4.70 (broad m, 4, two -NHCH), 5.78 (q, 4, two $CO_2CH_2CH_3$), and 8.70 (t, 6, two $CO_2CH_2CH_3$).

Further elution gave only unidentified oily minor products.

Registry No.—**1**, 121-46-0; **2a**, 1070-71-9; **2b**, 22237-84-9; **2c**, 2003-31-8; **2d**, 536-74-3; **2e**, 33064-30-1; **2f**, 28112-07-4; **3a**, 34627-34-4; **3b**, 34627-35-5; **3c**, 34627-36-6; **4**, 34627-45-7; **5**, 34627-37-7; **9a**, 34627-38-8; **9b**, 27593-62-0; **9c**, 16723-30-1; **10**, 34627-41-3; **11**, 34627-42-4.

Palladium-Catalyzed Vinylic Hydrogen Substitution Reactions with Aryl, Benzyl, and Styryl Halides

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Aryl, benzyl, and styryl halides react with olefinic compounds in the presence of a hindered amine and a catalytic amount of palladium metal to form vinylic derivatives in which the aryl, benzyl, or styryl group has replaced a vinylic hydrogen of the original olefin. The reactions occur readily at 100° and yields are generally good.

Mizoroki[1] and coworkers have recently reported a palladium-catalyzed arylation reaction of olefinic compounds with aryl iodides and potassium acetate in methanol at 120°. We have independently discovered this reaction and find that it can be carried out under much more convenient laboratory conditions than were used by Mizoroki and that the reaction provides an extremely convenient method for preparing a variety of olefinic compounds.

The reaction is undoubtedly closely related to the known olefinic arylations and alkylations achieved at room temperature or below with palladium salts[2,3] using organomercury, -tin, or -lead compounds rather than organic halides. While the known reactions are very useful, they suffer from two major difficulties. There is often a problem of obtaining the necessary organomercury, -lead, or -tin compounds and there is the problem of working with thick slurries of salts, particularly if the reaction is carried out catalytically in palladium. This new method eliminates both difficulties.

Results and Discussion

It is well known that $Pd[P(C_6H_5)_3]_4$ reacts readily with a variety of organic halides to form oxidative addition products of the type $[P(C_6H_5)_3]_2Pd(X)R$.[4,5] In the reaction reported herein, a similar oxidative addition apparently occurs between palladium metal (formed by an *in situ* reduction of the palladium acetate initially

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[1] T. Mizoroki, K. Mori, and A. Ozaki, *Bull. Chem. Soc. Jap.*, **44**, 581 (1971).

[2] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).

[3] R. F. Heck, *ibid.*, **91**, 6707 (1969).

[4] P. Fitton and E. A. Rick, *J. Organometal. Chem.*, **28**, 287 (1971).

[5] P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, 6 (1968).

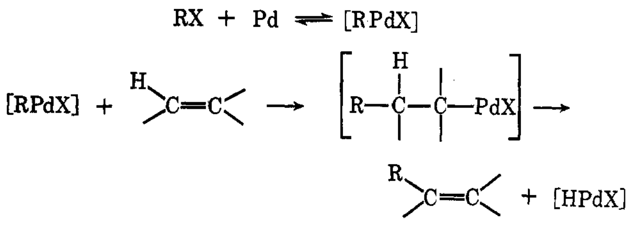
TABLE I

OLEFIN SUBSTITUTION REACTIONS WITH ORGANIC HALIDES[a]

Organic halide	Registry no.	Olefinic compd	Registry no.	Reaction time at 100°, hr	Product (yield, %)[b]	Registry no.	Mp of product, °C (reported)
Iodobenzene	591-50-4	Styrene	100-42-5	2	*trans*-Stilbene (75)	103-30-0	123–124 (124)[c]
Iodobenzene		4-Nitrostyrene	100-13-0	2	*trans*-4-Nitrostilbene (85)	736-31-2	153–155 (155–156)[d]
Iodobenzene		*cis*-1-Phenyl-1-propene	766-90-4	2	*cis*-1,2-Diphenyl-1-propene (7)	1017-22-7	*e*
					trans-1,2-Diphenyl-1-propene (12)	833-81-8	*e*
					1,2-Diphenyl-2-propene (4)		*e*
Iodobenzene		*trans*-1-Phenyl-1-propene	873-66-5	2	*cis*-1,2-Diphenyl-1-propene (21)		*e*
					trans-1,2-Diphenyl-1-propene (26)		*e*
Iodobenzene[f]		Methyl acrylate	96-33-3	1	*trans*-Methyl cinnamate (81)	1754-62-7	*e*
4-Iodoanisole	696-62-8	Methyl acrylate		5	*trans*-Methyl-*p*-methoxycinnamate (68)	3901-07-3	89–90 (90)[g]
Methyl 4-iodobenzoate	619-44-3	Styrene		2	*trans*-4-Carbomethoxystilbene (74)	34541-73-6	158–160 (158–159)[h]
1,4-Diiodobenzene	624-38-4	Styrene		15	*trans,trans*-*p*-Distyrylbenzene (67)	1608-41-9	266–267 (265)[i]
1,2-Diiodobenzene	615-42-9	Styrene		72	*trans,trans*-*o*-Distyrylbenzene (37)	27164-48-3	117–118 (117–119)[j]
Benzyl chloride	100-44-7	Methyl acrylate		15	*trans*-Methyl-4-phenyl-3-butenoate (67)	34541-74-7	*e*
					trans-Methyl-4-phenyl-2-butenoate (9)	34541-75-8	*e*
trans-β-Bromostyrene[l]	588-72-7	Methyl acrylate		72	*trans,trans*-Methyl-5-phenyl-2,4-pentadienoate (47)	24196-29-2	70–71 (71)[k]

[a] Except as noted, all reactions were carried out with 20 mmol of halide, 25 mmol of olefin, 20 mmol of tri-*n*-butylamine, and 0.2 mmol of palladium acetate with magnetic stirring in a steam bath with a water cooler condenser for the time indicated. [b] Yields were based upon the halide used and were of isolated, recrystallized products except where noted. [c] C. Hell, *Ber.*, **37**, 453 (1904). [d] C. Weygand and R. Gabler, *ibid.*, **71**, 2474 (1938). [e] Yields determined by gas chromatography. Products were not isolated. [f] Reaction mixture consisted of 10 mmol of iodobenzene, 20 mmol of methyl acrylate, 10 mmol of tri-*n*-propylamine, 0.1 mmol of palladium acetate, and 9 ml of 1-methyl-2-pyrrolidinone. [g] I. Heilbron, "Dictionary of Organic Compounds," Vol. 4, Oxford University Press, New York, N. Y., 1965. [h] R. C. Fuson and H. G. Cooke, Jr., *J. Amer. Chem. Soc.*, **62**, 1180 (1940). [i] J. Dale, *Acta Chem. Scand.*, **11**, 972 (1957). [j] D. H. Wadsworth, O. E. Schupp, III, E. J. Seus, and J. A. Ford, Jr., *J. Org. Chem.*, **30**, 680 (1965). [k] G. Kresze, J. Firl, and H. Braun, *Tetrahedron*, **25**, 4481 (1969). [l] The use of *cis*-β-bromostyrene also gave *trans,trans*-methyl-5-phenyl-2,4-pentadienoate, but only in 27% yield.

added by olefin) and certain organic halides, presumably producing very reactive solvated organopalladium(II) halides. These are probably the same compounds produced previously in the exchange reaction between palladium halides and organomercury compounds.[1,2] When prepared in the presence of olefinic compounds these organopalladium halides undergo an addition reaction with the olefin, and then the adduct decomposes by eliminating a hydridopalladium halide, forming the substituted olefinic compound.



The hydridopalladium halide product finally decomposes into hydrogen halide and palladium, which is then available to go through another reaction cycle. The accumulation of hydrogen halide in the reaction mixture has a very detrimental effect and must be neutralized by inclusion of a base. Mizoroki used potassium acetate, but we find a hindered amine to be better; tri-*n*-butylamine was generally used. Mizoroki carried out the reaction in methanol solution at 120°, which required pressurized reaction vessels. We find that the reaction can be carried out easily at steam bath temperatures in an open flask with a condenser, without use of a solvent. The reaction proceeds well in solvents such as 1-methyl-2-pyrrolidinone at 100° and atmospheric pressure also, but there seems to be no advantage to using them. The reactions we have carried out are listed in Table I.

Three types of halides were found to undergo the reaction: aryl, benzyl, and styryl. In the aryl examples, only the iodides reacted rapidly. Some product formed with bromobenzene, but the reaction was very slow even at 150°. Benzyl chloride and β-bromostyrene were less reactive than the aryl iodides but did give reasonable yields with longer reaction times. As with the reactions employing organomercury compounds,[1,2] these reactions tolerate a variety of functional groups such as nitro, methoxyl, and carbomethoxyl. Relatively low yields are obtained with olefinic compounds having methylene groups adjacent to the double bond. The low yields are apparently the result of the olefinic materials present forming inert, π-allylpalladium iodide derivatives with the catalyst, since, contrary to reactions with other types of olefins, the palladium metal formed initially dissolves, and addition of more palladium acetate increases the yields of olefin substitution products substantially.

We have arbitrarily used 1 mol % palladium acetate as catalyst relative to the halide. Smaller amounts, no doubt, would be effective with the more reactive halides. Palladium metal deposited on charcoal may also be used as the catalyst but the reactions are slower and yields lower than with the finely divided metal obtained from *in situ* palladium acetate reduction.

This new vinylic substitution reaction is clearly an improvement over the mercurial reaction in many instances, particularly for preparing larger quantities of material. It does have some limitations, however, which the mercurial method does not have. The loss of stereochemistry in the phenylation of *cis-* and *trans*-1-phenyl-1-propene is one limitation. The isomerization appears to occur internally, probably through hydridopalladium halide–olefin π complexes, since neither starting olefin is isomerized to a detectable extent under the reaction conditions. In general, at the higher temperatures of the halide reactions, double bond migrations would be expected to be more serious. The benzyl chloride reaction showed this effect in producing a rearranged olefinic compound as the major product with methyl acrylate. The corresponding reaction

$$C_6H_5CH_2Cl + CH_2{=}CHCOOCH_3 + n\text{-}Bu_3N \xrightarrow{Pd} C_6H_5CH{=}CHCH_2COOCH_3 + C_6H_5CH_2CH{=}CHCOOCH_3 + n\text{-}Bu_3NH^+Cl^-$$

with benzylmercuric acetate and palladium acetate at room temperature gave only the expected *trans*-methyl-4-phenyl-2-butenoate.[6]

Other limitations include not being able to use base-sensitive compounds such as acrolein in the reaction and not being able to methylate by the halide reaction. Surprisingly, methyl iodide and methyl iodoacetate do not react with styrene under the usual conditions.

In spite of some limitations, the organic halide–olefinic substitution reaction should prove to be a useful synthetic reaction.

Experimental Section

Materials.—All reagents were commercially available and used without further purification.

Gas Chromatography.—Samples were analyzed on a 6-ft silicon rubber on firebrick column at 175°. Known samples of the products were available from previous work.[1,2]

General Procedure for Vinylic Substitution with Organic Halides.—In a 25-ml round-bottomed flask containing a magnetic stirring bar was placed 0.2 mmol of anhydrous palladium acetate, 20 mmol of the organic halide, 20 mmol of tri-*n*-butylamine, and 25 mmol of the olefinic compound. A water-cooled condenser was placed on the flask and the mixture was stirred magnetically on a steam bath for the required length of time. On cooling the reaction mixtures often solidify. Several different product isolation procedures can be used. If the product is a high-melting solid, addition of water to the reaction mixture generally will give the product as a solid which can be separated and recrystallized with hot filtration to remove palladium metal present. Alternatively, if the reaction product is soluble in hot hexane, it may be extracted from the reaction mixture with boiling hexane several times. The extracts are then concentrated and either distilled or cooled to crystallize the product if it is a solid. A more general isolation procedure is to dilute the reaction mixture with cold dilute hydrochloric acid, extract the product with ether in the usual way, and distil the extracts. Two examples of the reaction are given in detail below.

***trans*-4-Carbomethoxystilbene.**—A mixture of 0.045 g (0.2 mmol) of palladium acetate, 5.24 g (20 mmol) of methyl *p*-iodobenzoate, 2.86 ml (25 mmol) of styrene, and 4.74 ml (20 mmol) of tri-*n*-butylamine was stirred with a magnetic stirring bar in a steam bath under a water-cooled condenser for 2 hr. After cooling the reaction mixture was broken up with a spatula and stirred with about 100 ml of water in a beaker. After the lumps were thoroughly mashed, the insoluble product was separated by filtration. Recrystallization from 225 ml of boiling absolute ethanol with hot filtration through Celite gave 3.50 g (74%) of shiny plates, mp 158–160°.

***trans,trans-p*-Distyrylbenzene.**—A mixture of 0.045 g (0.2 mmol) of palladium acetate, 3.30 g (10 mmol) of *p*-diiodobenzene, 2.86 ml (25 mmol) of styrene and 4.74 ml (20 mmol) of tri-*n*-butylamine was stirred magnetically in a steam bath under a water-cooled condenser for 15 hr. The mixture solidified during the heating. The solid reaction mixture was broken up with a spatula and stirred with water. The solid was filtered, washed several times with fresh water, and recrystallized from about 50 ml of hot dimethylformamide by filtering through Celite hot and adding water until crystals began to appear in the hot filtrate. After cooling, the pale yellowish product was isolated by filtration. After air drying, there was obtained 1.90 g (67%) of pale yellow crystals, mp 266–267°.

Registry No.—Palladium, 7440-05-3.

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(6) R. F. Heck, *J. Organometal. Chem.*, **37**, 389 (1972).