

Arylation of Olefins by *N*-Nitroso-*N*-arylacetylides under Palladium(0) Catalysis: A New Precursor of Arylpalladium Species

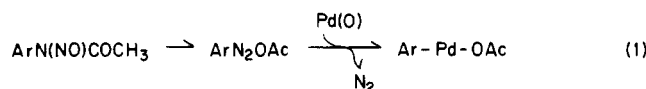
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Olefins (styrene, octene-1, cycloheptene, ethyl acrylate, and vinyl acetate) were easily arylated in good yields with *N*-nitroso-*N*-arylacetylides ($\text{ArN}(\text{NO})\text{COCH}_3$; Ar = Ph, 4-MeC₆H₄, 4-MeOC₆H₄, 4-ClC₆H₄, 4-BrC₆H₄, and 4-IC₆H₄) under palladium(0) catalysis at 40 °C within 40 min.

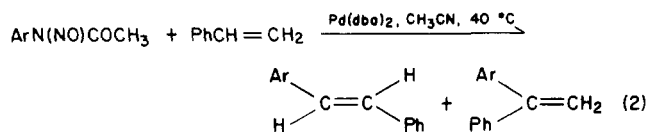
Transformation of arenediazonium salts to alkyl,¹ alkenyl,² acyl,³ and carboxyl⁴ substituted aromatic compounds via aryl-palladium species could be effected by palladium(0) catalysis under mild conditions, room temperature, and short reaction time (~1 h). Since *N*-nitroso-*N*-arylacetylides ($\text{ArN}(\text{NO})\text{COCH}_3$) are known to isomerize easily to diazonium acetates (eq 1),⁵ they can be expected to be another precursor of the aryl-palladium species.



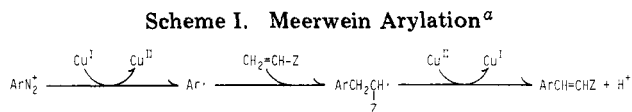
Herein a convenient arylation of olefins by $\text{ArN}(\text{NO})\text{COCH}_3$ under palladium(0) is described.

Results and Discussion

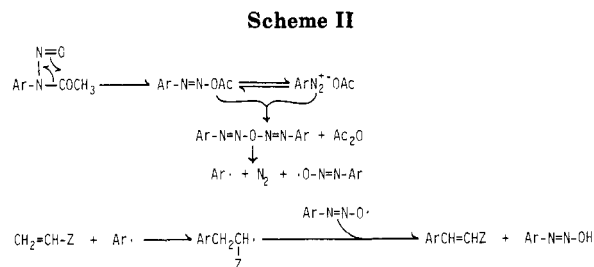
When a mixture of $\text{PhN}(\text{NO})\text{COCH}_3$, styrene, and bis(dibenzylideneacetone)palladium(0) ($\text{Pd}(\text{dba})_2$) in acetonitrile was warmed to 40 °C with stirring, a reaction started with continuous evolution of gas and was completed within 40 min. GC analysis of the reaction mixture showed the formation of (*E*)-stilbene along with a small amount of 1,1-diphenylethylene (eq 2). After the ordinary work up and column chromatography ($\text{SiO}_2\text{-CCl}_4$), (*E*)-stilbene was isolated in a 90% yield based on $\text{PhN}(\text{NO})\text{COCH}_3$ used.



Various $\text{ArN}(\text{NO})\text{COCH}_3$ prepared in situ could be used directly in this arylation. Gaseous N_2O_3 (10 times excess) was introduced into an acetonitrile solution of PhNHCOCH_3 at 0 °C and anhydrous K_2CO_3 was added and then filtered. The phenylation with the filtrate instead of isolated $\text{PhN}(\text{NO})\text{COCH}_3$ proceeded under smooth gas evolution and 60% of (*E*)-stilbene was isolated based on PhNHCOCH_3 used. Table I shows the arylation of styrene with various in situ prepared $\text{ArN}(\text{NO})\text{COCH}_3$. Results



^a Z = Ar, CN, COOR, COR, etc.



with some isolated $\text{ArN}(\text{NO})\text{COCH}_3$ are also included in the Table. Good results were obtained for para-substituted $\text{ArN}(\text{NO})\text{COCH}_3$, but ortho substitution decreased the yields drastically. The chemoselective formation of halo-substituted stilbene shows the higher reactivity of the *N*-nitrosoacetamide group than that of the halogen group to zero valent palladium.

The reaction mixture should be warmed to 40 °C to obtain a reasonable rate and yield. At room temperature, the reaction hardly proceeded. The decomposition temperature of $\text{ArN}(\text{NO})\text{COCH}_3$ varies considerably with the substituent on the aromatic ring from 51 °C (Ph) to 84 °C (4-Cl-C₆H₄). Since the decomposition of $\text{ArN}(\text{NO})\text{COCH}_3$ is supposed to proceed through $\text{ArN}=\text{NOAc}$ and/or ArN_2^+OAc ,⁵ the reaction with zero valent palladium (eq 1) is presumably expected to depend on the decomposition temperature. However, the rates of gas evolution, which should reflect the rate of the arylation, were not affected materially with the nature of the substituents in the present catalyzed reactions. These results suggest that palladium catalyst not only reacts with diazonium acetates isomerized to give arylpalladium acetates (eq 1), but also promotes the isomerization process.

Cycloheptene, octene-1, and ethyl acrylate were also phenylated in good yields under the same reaction conditions as Table II shows. However, the isomer distribution of the products obtained here were considerably different from those of related phenylation with PhN_2BF_4 ,² where octene-1 gave more than eight isomers of phenyloctenes including 1-, 2-, 3-, and 4-phenyloctenes, and cycloheptene produced a mixture of phenylcycloheptenes. These results reveal that relatively stable palladium hydride species, $[\text{H-Pd}]^+\text{BF}_4^-$, which is assumed as an in-

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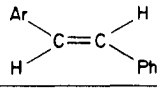
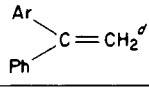
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
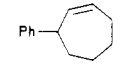

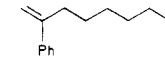
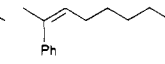
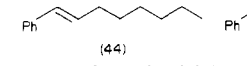
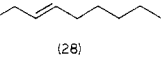
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Table I. Arylation of Styrene by in Situ Prepared ArN(NO)COCH₃^a

Ar in ArN(CO)COCH ₃	reactn time, min	yields, % ^b	product compositn, % ^c	
				
Ph	40	60 (90)	97	3
2-MeC ₆ H ₄	25	9	94	6
4-MeC ₆ H ₄	35	59 (90)	96	4
4-MeOC ₆ H ₄	30	40	<i>e</i>	
2-ClC ₆ H ₄	25	1	<i>e</i>	
4-ClC ₆ H ₄	30	35 (65)	96	4
4-BrC ₆ H ₄	30	68	<i>e</i>	
4-IC ₆ H ₄	30	39	94	6
3-pyridyl	30	30	<i>e</i>	


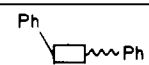

^a The reactions were performed with a solution of in situ prepared ArN(NO)COCH₃ (1 mmol as ArNHCOCH₃) and N₂O₃ gas, styrene (2 mmol), and Pd(dba)₂ (0.1 mmol) in CH₃CN (5 mL) at 40 °C. ^b Isolated yields based on ArNHCOCH₃ used. Values in parentheses are isolated yields with isolated ArN(NO)COCH₃. ^c Determined by GC analysis. ^d Involved a trace of (Z)-ArCH=CHPh. ^e Not determined.

Table II. Phenylation of Olefins by PhN(NO)COCH₃^a

olefins	reactn time, min	yields ^b %	product compositn, % ^c
	40	70	
	45	72	 (23)  (5)
CH ₂ =CHCOOEt	30	56	 (44)  (28) (E)-PhCH=CHCOOEt

^a The reactions were performed with a solution of PhN(NO)COCH₃ (1 mmol), an olefin (2 mmol), and Pd(dba)₂ (0.1 mmol) in CH₃CN (5 mL) at 40 °C. ^b Isolated yields were based on PhN(NO)COCH₃ used. ^c Determined by GC analysis.

Table III. Phenylation of Vinyl Acetate with Ph-Pd Species Derived from Various Sources

precursor of Ph-Pd species	solvent	temp, °C	time, h	total yield, % ^a	% yield of product ^b				
								Ph-Ph	ref
PhN(NO)COCH ₃ -Pd(dba) ₂	CH ₃ CN	40	0.5	53	43 ^c	10	<i>d</i>	0	<i>f</i>
PhN ₂ BF ₄ -Pd(dba) ₂ -NaOAc	CH ₃ CN	25	0.5	<i>t</i> ^g	0	<i>t</i> ^g	<i>d</i>	0	<i>f</i>
PhI-Pd(OAc) ₂ (PPh ₃) ₂ -Et ₃ N	neat	130	2	47	12	21	14	1	10
PhI-Pd(OAc) ₂ -2PPh ₃ -Et ₃ N	CH ₃ CN	100	8	67 ^e	12	52	<i>d</i>	3	16

^a Isolated yields based on Ph-X. ^b Determined by GC analysis. ^c E:Z = 62:38. ^d Not determined. ^e GC yield based on PhI. ^f This work. ^g Trace.

intermediate in the catalytic cycle,² may work as an efficient isomerization catalyst in the case of PhN₂BF₄. While in the present phenylation, the intermediate palladium hydride, H-Pd-OAc, may decompose to zero valent palladium and acetic acid rapidly. It should be noted that phenylation of octene-1 with PhNH₂-*t*-BuONO-CH₃COOH, which presumably proceeded through phenylpalladium acetate as a key intermediate,⁶ gave very similar isomer distribution with that of present phenylation.

ArN(NO)COCH₃ have been known as good precursors of aryl radicals via isomerization to ArN₂OAc.⁷ Since the Meerwein arylation,⁸ copper-catalyzed arylation of olefins with ArN₂X (Scheme I), involves aryl radical as a key intermediate, a radical pathway should be considered in the present arylation (Scheme II). In the absence of palladium catalyst, however, the reaction of PhN(NO)COCH₃ with styrene gave only 2% of (E)-stilbene along with various decomposition products (more than ten compounds including a small amount of phenyl acetate). In the presence of palladium catalyst, the reaction gave ex-

clusively arylated products which were almost free from the above decomposition products. Furthermore the radical pathway may require activated olefins with an electron-withdrawing group to obtain good results as in the Meerwein arylation. However, octene-1 and cycloheptene (poor substrates in the Meerwein arylation) also gave good results in the present arylation. Thus, the palladium catalyst plays a very important role in this arylation.

The present arylation showed substantially similar results as those of palladium-catalyzed arylation with ArX (X = Br, I)⁹ and ArN₂BF₄,² in which the arylpalladium species is a key intermediate. However, a considerably different feature was observed in the phenylation of vinyl acetate as shown in Table III. The phenylation with PhN(NO)COCH₃ produced (E)- and (Z)-phenylvinyl acetates as main products, whereas other methods gave (E)-stilbene as the main product.^{10,16} The extremely low yields of the phenylvinyl acetates with PhN₂BF₄ might be

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caused by the decomposition of vinyl acetate and/or phenylvinyl acetates under acidic conditions which resulted from the liberation of HBF_4 and/or BF_3 . The mild conditions of the present phenylation afforded the formation of primary phenylated products, (*E*)- and (*Z*)-phenylvinyl acetates.

Consequently a combination of zero valent palladium and $\text{ArN}(\text{NO})\text{COCH}_3$ or $\text{ArNHCOCH}_3\text{-N}_2\text{O}_3$ provides a new source of arylpalladium acetate under mild conditions, although ortho substituents cause some difficulty in the present arylation.

Experimental Section

Materials. Acetonitrile was refluxed over P_2O_5 (twice) and CaH_2 , and distilled under nitrogen. ArNHCOCH_3 were prepared from ArNH_2 and acetic anhydride and recrystallized from ethanol. $\text{ArN}(\text{NO})\text{COCH}_3$ were prepared by introducing N_2O_3 (10 times excess) generated from $\text{NaNO}_2\text{-H}_2\text{SO}_4$ to a solution of ArNHCOCH_3 in $\text{Ac}_2\text{O-AcOH}$ (1/4 (v/v)) with ice cooling.¹¹ The resulting green solution was poured into ice water to obtain a yellow solid. The solid was collected and dried under vacuum. $\text{Pd}(\text{dba})_2$ was prepared by the published method.¹² Olefins were used as received.

Procedure for Arylation. Into a 100-mL three-necked flask equipped with gas buret were placed an $\text{ArN}(\text{NO})\text{COCH}_3$ (1 mmol), an olefin (2 mmol), $\text{Pd}(\text{dba})_2$ (0.1 mmol), and CH_3CN (5 mL). Smooth evolution of gas started by heating the solution to 40 °C. After completion of the gas evolution, the mixture was diluted with 100 mL of diethyl ether and filtered to remove precipitated palladium. GC analysis of the filtrate was used to determine the products composition. The solvent was removed directly from the filtrate under reduced pressure to dryness except for the reaction with vinyl acetate. For the reaction with vinyl acetate, the filtrate was washed with aqueous NaHCO_3 and brine and dried over MgSO_4 .

Arylation with in Situ Prepared $\text{ArN}(\text{NO})\text{COCH}_3$. An excess of N_2O_3 gas was introduced to a solution of ArNHCOCH_3 (1 mmol) in CH_3CN (5 mL) with ice cooling. To the resulting green solution was added anhydrous K_2CO_3 (2 g) and the solution was then filtered. The filtrate was used to prepare a 1 mmol solution of $\text{ArN}(\text{NO})\text{COCH}_3$, the same workup was used as in the preceding section.

Stilbene Derivatives. The residue was chromatographed on $\text{SiO}_2\text{-CCl}_4$. Concentration of the first fraction gave (*E*)-stilbene derivatives along with a trace of $\text{Ar}(\text{Ph})\text{C}=\text{CH}_2$. The structure of (*E*)- $\text{ArCH}=\text{CHPh}$ was assigned by comparison of IR, NMR, and retention time on GC with those of authentic samples prepared from arylation of styrene by $\text{ArNH}_2\text{-}t\text{-BuONO-CCl}_2\text{COOH-Pd}(\text{dba})_2$.⁶ All the melting points in parentheses shown below were cited from "Beilstein Handbuch der Organischen Chemie". (*E*)-Stilbene, mp 122.5–124.5 °C (mp 124 °C). (*E*)-4-Methylstilbene, mp 117.8–119.6 °C (mp 119.5–120 °C). (*E*)-4-Chlorostilbene, mp 126.2–128.3 °C (mp 129 °C). (*E*)-4-Bromostilbene, mp 136.5–139 °C (mp 139 °C). (*E*)-4-Iodostilbene, mp 148.3–150.2 °C (mp 152 °C). (*E*)-4-Methoxystilbene, mp 133.0–136.0 °C (mp 136 °C). (*E*)-3-Styrbazole, mp 80.0–82.5 °C (mp 81.4–83.0 °C).⁶ Since the formation of $\text{Ar}(\text{Ph})\text{C}=\text{CH}_2$ was too little for isolation, the structure of $\text{Ar}(\text{Ph})\text{C}=\text{CH}_2$ was assumed by comparison of their retention times

on GC with that of authentic samples.¹³

3-Phenylcycloheptene. Column chromatography of the residue on $\text{SiO}_2\text{-hexane}$ gave a colorless liquid as the first fraction with a single peak on GC analysis: NMR (CCl_4) δ^6 1.0–2.8 ($\text{H}^4\text{-H}^7$) (m, 8 H), 3.40 (H^3) (m, 1 H), 5.63 (H^1) (dt, $J_{1,2} = 11.9$ Hz, $J_{1,7} = 1.9$ Hz, 1 H), 5.65 (H^2) (dd, $J_{2,3} = \sim 3$ Hz (not clear), 1 H), 7.05 (Ph) (s, 5 H).

Phenylacetenes. A colorless liquid was obtained from the first fraction of $\text{SiO}_2\text{-hexane}$. The structures of the products were determined by comparison of the retention times on GC with those of authentic samples prepared from phenylation of octene-1 with $\text{PPh}_3\text{-Pd}(\text{OAc})_2$ in CH_3CN .^{14,15} The NMR spectrum of the isomer mixture showed reasonable area ratios among the aliphatic, olefinic, and aromatic protons. Hydrogenation of the products under atmospheric hydrogen (Pd/C) gave 1- and 2-phenyloctanes. For comparison, octene-1 was phenylated with PhN_2BF_4 by the published method.² The first fraction of column chromatography ($\text{SiO}_2\text{-hexane}$) showed 8 major peaks with several small peaks on GC analysis. Hydrogenation of the mixture gave four isomers of phenyloctanes.

(E)-Ethyl Cinnamate. The residue was distilled under reduced pressure. GC analysis of the distillate showed 98% purity. IR, NMR, and GC analyses were compared with those of the authentic sample of commercial origin.

(E)- and (Z)-Phenylvinyl Acetates. The residue was separated by medium-pressure column chromatography (Fuji-Gel CQ-3, $\text{CCl}_4/\text{CHCl}_3$). The NMR spectrum was identical with those of the *E* and *Z* isomers reported previously.^{10,14} (*E*)- $\text{PhCH}=\text{CH}^b\text{OCOCH}_3^c$, 2.11 (H^c) (s), 6.26 (H^b) (d, $J_{ab} = 12.5$ Hz), 7.73 (H^a) (d). *Z* isomer, 2.20 (H^c) (s), 5.56 (H^b) (d, $J_{ab} = 7.3$ Hz), the resonance of H^a was obscure by overlap with phenyl protons.

Registry No. $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{Ph}$ -(*E*), 103-30-0; 2-Me- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{Ph}$ -(*E*), 22257-16-5; 4-Me- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{Ph}$ -(*E*), 1860-17-9; 4-MeO- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{Ph}$ -(*E*), 1694-19-5; 4-Cl- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{Ph}$ -(*E*), 1657-50-7; 4-Br- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{Ph}$ -(*E*), 13041-70-8; 4-I- $\text{Ph}(\text{H})\text{C}=\text{C}(\text{H})\text{Ph}$ -(*E*), 17404-86-3; 3-pyridyl($\text{H})\text{C}=\text{C}(\text{H})\text{Ph}$ -(*E*), 2633-06-9; $\text{Ph}(\text{Ph})\text{C}=\text{CH}_2$, 530-48-3; 2-Me $\text{Ph}(\text{Ph})\text{C}=\text{CH}_2$, 947-77-3; 4-Me $\text{Ph}(\text{Ph})\text{C}=\text{CH}_2$, 948-55-0; 4-Cl $\text{Ph}(\text{Ph})\text{C}=\text{CH}_2$, 18218-20-7; 4-IPh($\text{Ph})\text{C}=\text{CH}_2$, 94089-31-3; PhNHAc , 103-84-4; 2-Me PhNHAc , 120-66-1; 4-Me PhNHAc , 103-89-9; 4-MeO PhNHAc , 51-66-1; 4-Cl PhNHAc , 539-03-7; 4-Br PhNHAc , 35920-23-1; 4-IPh NHAc , 622-50-4; (3-pyridyl) NHAc , 5867-45-8; $\text{PhN}(\text{NO})\text{COCH}_3$, 938-81-8; 2-Me $\text{PhN}(\text{NO})\text{COCH}_3$, 90557-56-5; 4-Me $\text{PhN}(\text{NO})\text{COCH}_3$, 10557-67-2; 4-MeO $\text{PhN}(\text{NO})\text{COCH}_3$, 14839-81-7; 4-Cl $\text{PhN}(\text{NO})\text{COCH}_3$, 13014-92-1; 4-Br $\text{PhN}(\text{NO})\text{COCH}_3$, 35920-23-1; 4-IPh $\text{N}(\text{NO})\text{COCH}_3$, 19260-02-7; (3-pyridyl) $\text{N}(\text{NO})\text{COCH}_3$, 94089-32-4; $\text{Pd}(\text{dba})_2$, 32005-36-0; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_5\text{CH}_3$, 111-66-0; $\text{H}_2\text{C}=\text{CHCOOEt}$, 140-88-5; $\text{H}_2\text{C}=\text{C}(\text{Ph})(\text{CH}_2)_5\text{CH}_3$, 5698-49-7; $\text{H}_3\text{C}(\text{Ph})\text{C}=\text{CH}(\text{CH}_2)_4\text{CH}_3$ -(*E*), 53109-17-4; $\text{PhCH}=\text{CH}(\text{CH}_2)_5\text{CH}_3$ -(*E*), 29518-72-7; $\text{PhCH}_2\text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}_3$ -(*E*), 42079-83-4; (*E*)- $\text{PhCH}=\text{CHCOOEt}$, 4192-77-2; PhN_2BF_4 , 369-57-3; (*E*)- $\text{PhCH}=\text{CHOAc}$, 1566-65-0; (*Z*)- $\text{PhCH}=\text{CHOAc}$, 1566-67-2; $\text{PhCH}=\text{CHPh}$, 588-59-0; N_2O_3 , 10544-73-7; styrene, 100-42-5; cycloheptene, 628-92-2; 3-phenylcycloheptene, 19217-54-0; vinyl acetate, 108-05-4.

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