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ALKYLATION OF OLEFINS WITH "ALKYLPALLADIUM ACETATES" LACKING β HYDROGEN SUBSTITUENTS. OBSERVATION OF AN INTRAMOLECULAR SHIFT OF AN ACETATOPALLADIUM GROUP IN NEOPHYLPALLADIUM ACETATE

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SUMMARY

Methyl-, benzyl-, neopentyl- and (2-methyl-2-phenylpropyl)palladium acetates, prepared *in situ* by exchange reactions of the corresponding mercurials with palladium acetate, alkylate monosubstituted ethylene derivatives in fair to good yields. The "(2-methyl-2-phenylpropyl)palladium acetate" apparently underwent an unusual rearrangement during reaction with methyl acrylate. The palladium acetate group was partially transferred from the side-chain to the *ortho* position of the aromatic ring and produced methyl *o*-tert-butylcinnamate in 49% yield. The "normal product", methyl 5-methyl-5-phenyl-2-hexenoate was also obtained, in 16% yield. A similar rearrangement occurred in the reaction with styrene.

INTRODUCTION

Previous work demonstrated that some olefins could be methylated with "methylpalladium chloride", prepared *in situ* by the exchange reaction of methylmercury chloride, methyltin or lead derivatives, with palladium chloride[1]. The use of mercury, tin or lead alkyls with β hydrogen groups in the reaction, however, resulted in only elimination of metal hydride from the alkyl, producing olefin. The methylation and arylation of olefins with organopalladium salts[1], of course, only succeeds because this hydride elimination occurs much more rapidly than the addition to a second olefin molecule[1]. The alkylation of olefins with other groups lacking β hydrogens should be possible since β-hydride elimination cannot occur. The reactions would be synthetically useful and, therefore, we have undertaken a brief investigation of this area.

RESULTS AND DISCUSSION

Four different "alkyl" groups were investigated. Methylation was studied further and reactions of benzyl, neopentyl and neophyl (2-methyl-2-phenyl-1-propyl) groups were carried out. Preliminary experiments established, as noted previously

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** Contribution No. 1575.

TABLE 1

OLEFIN ALKYLATIONS WITH ORGANOPALLADIUM COMPLEXES[a]

Alkylating agent	*Olefinic compound*	*Palladium salt*	*Solvent*	*Product*
5 mmoles CH_3HgOAc	2 ml $C_6H_5C(CH_3)=CH_2$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	78% $CH_2=C(C_6H_5)CH_2CH_3$
1.67 mmoles $(CH_3)_3PbOAc$	2 ml $C_6H_5C(CH_3)=CH_2$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	91% $CH_2=C(C_6H_5)CH_2CH_3$
1.67 mmoles $(CH_3)_3PbOAc$	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	44% *trans*-$CH_2CH=CHCOOCH_3$
5 mmoles CH_3HgOAc	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	84% *trans*-$CH_3CH=CHCOOCH_3$
1.25 mmoles $Sn(CH_3)_4$	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	10 ml CH_3CN	94% *trans*-$CH_3CH=CHCOOCH_3$
5 mmoles $C_6H_5CH_2HgOAc$	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	8 ml CH_3CN	20% $C_6H_5CH_2OAc$
				13% *trans*-$C_6H_5CH_2CH=CHCOOCH_3$
50 mmoles $C_6H_5CH_2HgOAc$	100 ml $CH_2=CHCOOCH_3$	50 mmoles $Pd(OAc)_2$		10% $C_6H_5CH_2OAc$
				60% (41%)[b] *trans*-$C_6H_5CH_2CH=CHCOOCH_3$
5 mmoles $C_6H_5CH_2HgOAc$	2 ml $CH_2=CHCH_2OAc$	5 mmoles $Pd(OAc)_2$	8 ml CH_3CN	78% $C_6H_5CH_2OAc$
				8% $C_6H_5CH_2CH=CHCH_2OAc$
5 mmoles $C_6H_5CH_2HgOAc$	10 ml $CH_2=CHCH_2OAc$	5 mmoles $Pd(OAc)_2$		18% $C_6H_5CH_2OAc$
				23% $C_6H_5CH_2CH=CHCH_2OAc$
5 mmoles $(CH_3)_3CCH_2HgOAc$	2 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$	8 ml CH_3CN	94% *trans*-$(CH_3)_3CCH_2CH=CHCOOCH_3$
5 mmoles $(CH_3)_3CCH_2HgOAc$	10 ml $CH_2=CHCOOCH_3$	5 mmoles $Pd(OAc)_2$		68% $(CH_3)_3CCH_2CH=CHCOOCH_3$
50 mmoles $C_6H_5C(CH_3)_2CH_2HgOAc$	20 ml $CH_2=CHCOOCH_3$	50 mmoles $Pd(OAc)_2$	100 ml CH_3CN	41% *trans*-$(CH_3)_2C(C_6H_5)CH_2CH=CHCOOCH_3$
				19% *trans*-2-$(CH_3)_3CC_6H_4CH=CHCOOCH_3$
20 mmoles $C_6H_5C(CH_3)_2CH_2HgOAc$	8 ml $C_6H_5CH=CH_2$	20 mmoles $Pd(OAc)_2$	40 ml CH_3CN	46% $C_6H_5CH=CHOAc$
				50% *trans*-2-$(CH_3)_3CC_6H_4CH=CHC_6H_5$

[a] Reactions carried out at room temperature for about 15 h.

[b] Yield of isolated product.

in the carbomethoxylation and arylation reactions[1,2], that acetate salts gave higher yields and purer products than chlorides. Mercurials were generally used as the source of the alkyl groups except in the methylation experiments where lead and tin compounds were also employed. Indications are that the lead and tin derivatives react about as well as the corresponding mercurials and there seems to be no reason to choose one over the others. The results obtained are summarized in Table 1.

The methylation reaction has been found to be more limited in its applicability than we had expected on the basis of the related carboalkoxylation and arylation reactions. Not only are there practical problems in separating the starting olefin from the methylated derivative because of their similar properties but the reaction appears limited to terminal, monosubstituted olefins or aryl conjugated olefins. While α-methylstyrene and methyl acrylate undergo methylation in good yields, dipentene* and methyl methacrylate do not. This is in contrast to carboalkoxylation and arylation where internal double bonds react readily. The other "alkylpalladium acetate" reagents studied also suffer the same limitation. Nevertheless, a number of useful reactions can be carried out with them.

Benzylation with "benzylpalladium acetate" occurred in low to moderate yields with methyl acrylate and allyl acetate. A major side reaction in the benzylation reaction is the formation of benzyl acetate presumably by reductive elimination from "benzylpalladium acetate". The use of the olefin as solvent tends to reduce the amount of side reaction and reasonable yields can probably be obtained this way with most monosubstituted ethylene derivatives. The position of the double bond in the reaction product is probably dependent upon the structure of the olefin. Benzylation of allyl acetate gave 4-phenyl-2-butyl acetate as the main product. Although elimination to produce the 4-phenyl-1-butenyl acetate might have been expected to be a major

$$[C_6H_5CH_2PdOAc] + CH_2{=}CHCH_2OAc \rightarrow \left[\begin{array}{c} PdOAc \\ | \\ C_6H_5CH_2CH_2CHCH_2OAc \end{array}\right]$$

$$\rightarrow [HPdOAc] + C_6H_5CH_2CH{=}CHCH_2OAc$$

product on the basis of previous results[3]; the acetate substituent apparently inhibits the loss of hydrogen from the same carbon atom. This effect has been noted previously in the palladium acetate reaction with 2-butene where 1-buten-3-yl acetate is formed in preference to 2-buten-3-yl acetate[4]. With other substituents than acetate, the benzylation probably would give substantial amounts of the other double bond isomer.

Alkylation with neopentyl type palladium compounds provides a new method of preparing quaternary carbon compounds. Thus, "neopentylpalladium acetate" prepared, in situ, from neopentylmercury acetate and palladium acetate, reacted with methyl acrylate in acetonitrile solvent to form methyl-5,5-dimethyl-*trans*-2-hexenonate in 94% yield.

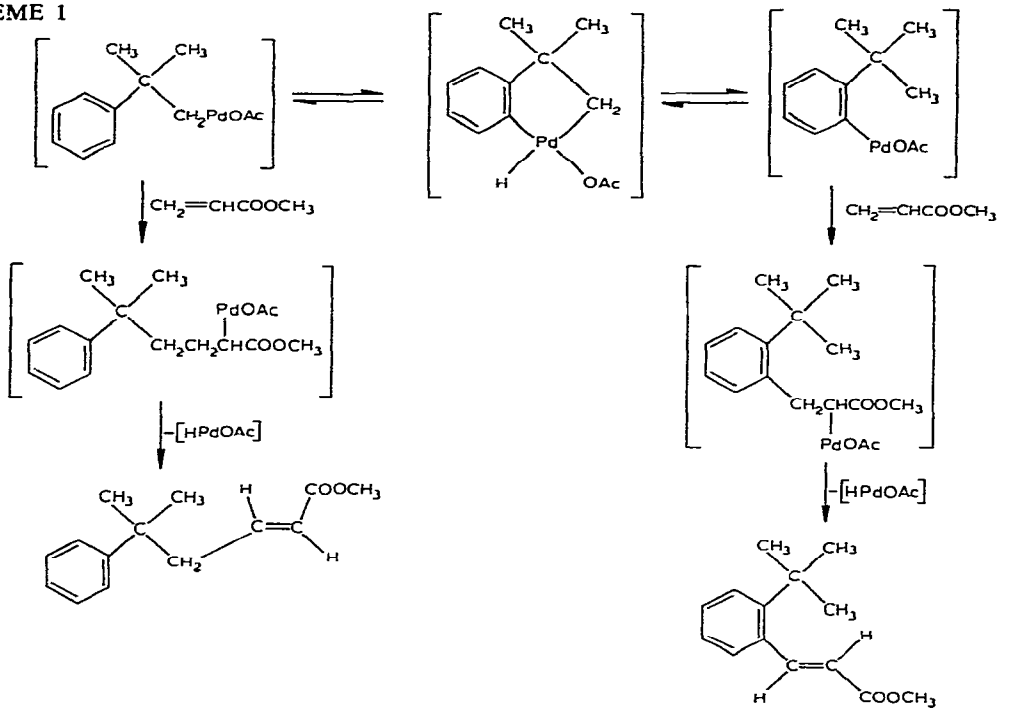
$$[(CH_3)_3CCH_2PdOAc] + CH_2{=}CHCOOCH_3 \rightarrow$$

$$(CH_3)_3CCH_2CH{=}CHCOOCH_3 + [HPdOAc]$$

The use of methyl acrylate as solvent in place of acetonitrile offered no advantage in

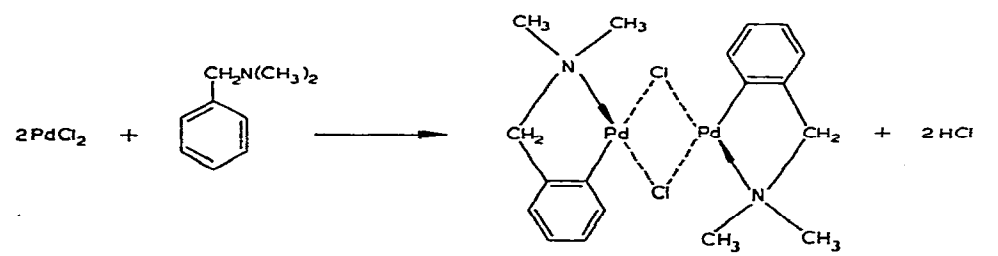
* I thank Drs. E. Van Tamelen and P. M. McCurry for pointing out this limitation to me in a personal communication.

SCHEME 1



this reaction, in fact, a lower yield was obtained in the absence of the solvent.

Another neopentyl-type compound, (2-methyl-2-phenylpropyl)mercury acetate was also reacted with palladium acetate and methyl acrylate. The product consisted of a 35/65 mixture of two isomeric materials. The major product was clearly the expected methyl 5-methyl-5-phenyl-*trans*-2-hexenoate by NMR and mass spectral analyses. The second product was found to be methyl *o*-tert-butyl-*trans*-cinnamate. Since the reaction also produced traces of tert-butylbenzene, presumably by cleavage of the palladium compound, the second product could have arisen by *ortho* mercuration of the tert-butylbenzene with product mercuric acetate followed by reaction with palladium acetate and methyl acrylate. A separate experiment, however, showed that tert-butylbenzene mercurated in the *para* position and subsequent reaction of the mercurial with palladium acetate and methyl acrylate gave, in 49% yield, methyl *p*-tert-butyl-*trans*-cinnamate which was clearly different from the above product. The *ortho* product very likely arises from a rearrangement of the intermediate palladium alkyl since the NMR spectrum of the starting mercurial shows it to have the

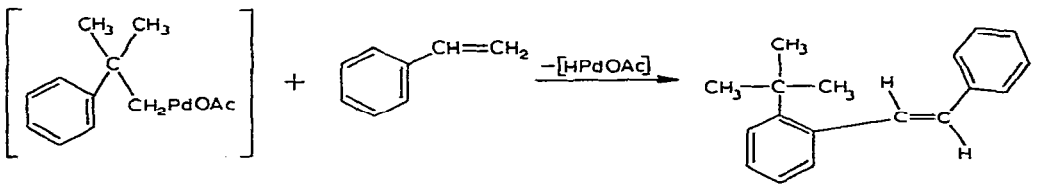


expected structure. The shift of the acetatopalladium group from the alkyl chain to the *ortho* aryl position is apparently without precedent but it is no doubt closely related to the many known *ortho* metalation reactions. The reaction of *N*,*N*-dimethylbenzylamine with palladium chloride[5], for example, is probably a similar reaction.

Coordination of the amine group to the palladium chloride is likely the first step, and this is probably followed by an oxidative addition-type reaction of the palladium group with the *ortho* carbon–hydrogen group to produce, at least, a transient Pd^{IV} complex. Finally, hydrogen chloride is lost. A similar mechanism could explain the formation of methyl *o*-tert-butylcinnamate in the above reaction (Scheme 1).

It is not clear from the data obtained where the equilibrium lies in the rearrangement step. A similar reaction takes place when "2-methyl-2-phenyl-1-propylpalladium acetate" is reacted with styrene. The major product is *o*-tert-butyl-*trans*-stilbene formed in about 50% yield along with the palladium acetate oxidation product of styrene, 2-acetoxystyrene and a few percent of an unknown which may have been the unrearranged product, 4-methyl-1,4-diphenyl-1-pentene.

Obviously, there are many more metal alkyls lacking β-hydrogen groups which probably could be used successfully in the alkylation reaction. The few examples reported illustrate that reasonable yields can be obtained in several cases under mild conditions but that there are limitations and side reactions which may be important.



EXPERIMENTAL SECTION

Methylmercury acetate

This material was obtained from Alfa Inorganics and used without further purification.

Benzylmercury acetate

A mixture of 3.8 g (10 mmoles) dibenzylmercury (Alfa Inorganics) and 3.2 g (10 mmoles) mercuric acetate with 50 ml methanol was heated to boiling for a few minutes on the steam bath. A small amount of dark solid which did not dissolve was removed by hot filtration through celite. Addition of water to the filtrate until it just became cloudy and cooling gave crystals of benzylmercury acetate. There was obtained 5.39 g of colorless solid, m.p. 118–119°. The compound was stored in the dark at 0°.

Neopentylmercury acetate

A mixture of 6.14 g (20 mmoles) neopentylmercury chloride (Orgmet, Inc.), 4.0 g (20 mmoles) powdered silver acetate and 50 ml acetonitrile was stirred magnetic-

ally at room temperature, overnight. The mixture was then heated on the steam bath and filtered hot through celite and rinsed several times with methylene chloride. The filtrate was evaporated to dryness at room temperature under reduced pressure and the crude product was crystallized from hexane. There was obtained 5.03 g of colorless crystals, m.p. 66–67°.

The product was found to contain 60.3% mercury (calcd. for $C_7H_{14}O_2Hg$, 60.65%). The NMR spectrum in deuterochloroform had bands at 2.11 ppm [singlet, J(Hg–H) = 103 Hz, 2 protons], 2.00 [singlet J(Hg–H) = 24 Hz, 3 protons], and 1.09 [singlet, J(Hg–H) = 7 Hz, 9 protons].

Neophylmercury acetate

In a 500 ml round bottomed flask with a stirring motor, a condenser with a nitrogen inlet and mercury bubbler, and a dropping funnel was placed 4.86 g (0.2 mole) of magnesium turnings and 100 ml of dry ether. The mixture was stirred under nitrogen and about a third of 34.9 g (0.2 mole) of neophyl chloride[6] was added from the dropping funnel and the reaction mixture was heated to boiling on a steam bath. The reaction did not start until a few drops of methyl iodide were added. The remainder of the neophyl chloride was added and the reaction mixture was heated under reflux for 3 h. When the magnesium had practically all dissolved, the mixture was cooled in an ice bath and 55.0 g (0.2 mole) mercuric chloride was added in small portions. The reaction mixture was stirred at room temperature for about an hour and the ether was removed by distillation. The residue was extracted several times with 200 ml portions of warm methylene chloride. The extracts were filtered and the solvent was removed under reduced pressure. The solid remaining was crystallized twice from aqueous methanol. There was obtained 27 g of neophylmercury chloride as nearly colorless, long needles, m.p. 80–81°. Another 3 g was recovered from the solution. The m.p. reported was 80.6–81.3° [7].

The acetate was obtained from the chloride by stirring 3.2 g of the chloride with 20 g of powdered silver acetate in 25 ml of acetonitrile overnight as in the neopentylmercury acetate preparation described above. There was obtained, after crystallization from hexane, 2.5 g of fine colorless needles, m.p. 67–68°. (Found: H, 51.57. $C_{12}H_{16}HgO_2$ calcd.: Hg, 51.06%.) The NMR spectrum is deuterochloroform had bands at 7.34 ppm (multiplet, 5 protons), 2.43 (singlet, J(Hg–H) = 99 Hz, 2 protons), 1.96 (singlet, 3 protons) and 1.49 [singlet, J(Hg–H) = 7 Hz, 6 protons].

General procedure for alkylation of olefins

Reactions were generally carried out in Erlenmeyer flasks with magnetic stirring. The mercury, tin, or lead compound was placed in the Erlenmeyer; the olefin and solvent, if any, were added; and the flask was stirred in an ice bath while the palladium acetate was added. After the addition, stirring was continued at 0° for 30 min and then at room temperature overnight. Products from small scale runs were isolated by gas chromatography of the filtered and concentrated reaction mixtures. In larger scale reactions, products were isolated by diluting the reaction mixtures with 200 ml of ether and pouring onto 200 g of ether-wet alumina in a chromatographic column. The products were rinsed through with 2 l of ether. The eluates were concentrated by distillation and the higher boiling residues distilled under reduced pressure. The properties of the products isolated, analyses and NMR spectra are given in Table 2.

TABLE 2

ANALYTICAL DATA FOR REACTION PRODUCTS

Compound	B.p.[a] [°C(mm)]	Analyses found (calcd.) (%)		NMR data (δ) (ppm)
		C	H	
$CH_2=C(C_6H_5)CH_2CH_3$	[b]	90.42 (90.85)	9.07 (9.15)	7.32 (multiplet, 5 protons) 5.28 (multiplet, 1 proton) 5.08 (multiplet, 1 proton) 2.53 (quartet, $J=7$, 2 protons) 1.09 (triplet, $J=7$, 3 protons)
$C_6H_5CH_2CH=CHCOOCH_3$	80–150(5)	74.89 (74.97)	7.09 (6.87)	7.20 (multiplet, 6 protons) 5.79 (double triplet, $J=15.5$ and 1.5) 3.65 (singlet, 3 protons) 3.42 (double doublet, $J=7$ and 1.5)
$C_6H_5CH_2CH=CHCH_2OAc$	[b]	74.55 (74.76)	7.54 (7.42)	7.18 (singlet, 5 protons) 5.75 (multiplet, 2 protons) 4.52 (doublet, $J=5$, 2 protons) 3.36 (doublet, $J=5$, 2 protons) 2.01 (singlet, 3 protons)
$(CH_3)_3CCH_2CH=CHCOOCH_3$	[b]	69.07 (69.19)	10.31 (10.33)	6.93 (multiplet, 1 proton) 5.80 (doublet, $J=15.5$, 1 proton) 3.71 (singlet, 3 protons) 2.07 (doublet, $J=7.5$, 2 protons) 2.07 (doublet, $J=7.5$, 2 protons) 0.92 (singlet, 9 protons)
$C_6H_5C(CH_3)_2CH_2CH=CHCOOCH_3$	115–125(2)[c]	77.02[c] (77.03)	8.29[c] (8.31)	7.32 (singlet, 5 protons) 6.78 (multiplet, 1 proton) 5.75 (doublet, $J=16$, 1 proton) 3.68 (singlet, 3 protons) 2.52 (doublet, $J=7$, 2 protons) 1.33 (singlet, 6 protons)
$C_6H_4(C(CH_3)_3)CH=CHCOOCH_3$				8.48 (doublet, $J=16$, 1 proton) 7.35 (multiplet, 4 protons) 6.12 (doublet, $J=16$, 1 proton) 3.80 (singlet, 3 protons) 1.42 (singlet, 9 protons)
$C_6H_4(C(CH_3)_3)CH=CHC_6H_5$	[d]	91.48 (91.47)	8.40 (8.53)	7.82 (doublet, $J=17$, 1 proton) 7.38 (multiplet, 9 protons) 6.79 (doublet, $J=17$, 1 proton) 1.48 (singlet, 9 protons)

[a] Boiling range of crude product. Analytical samples isolated by GLC. [b] Sample collected directly from concentrated reaction mixture and b.p. not determined. [c] Mixture of both isomers. [d] M.p. 48–50°.

Reaction of "neophylpalladium acetate" with methyl acrylate

A reaction mixture consisting of 19.6 g (50 mmoles) of (2-phenyl-2-methylpropyl)mercury acetate, 20 ml of methyl acrylate and 100 ml acetonitrile was stirred at 0° and 11.2 g (50 mmoles) of powdered palladium acetate was added. After stirring at 0° for 30 min, stirring was continued at room temperature overnight. The reaction mixture was diluted with 200 ml of ether and poured onto 200 g of alumina and washed through with one liter of ether. The eluate was concentrated and distilled under reduced pressure to give 3.6 g of colorless liquid, b.p. 115–125° (2 mm). This fraction was

82% two products; 59% methyl 5-phenyl-5-methyl-*trans*-2-hexenoate and 33% methyl *o*-tert-butyl-*trans*-cinnamate. The compounds were separated by gas chromatography on a 1/4" × 12', 5% diethyleneglycol succinate on Chromosorb W column at 175°. Both compounds showed molecular weights of 218 by mass spectrometry. NMR spectra and analyses are given in Table 2.

Reaction of "neophylpalladium acetate" with styrene

A combination of 7.84 g (20 mmoles) of (2-phenyl-2-methyl-propyl)mercury acetate, 8 ml of styrene and 40 ml of acetonitrile was stirred at 0° and 4.48 g powdered palladium acetate was added. The mixture was stirred for one hour at 0° and at room temperature overnight. The products were isolated as in the previous example. The first fraction, b.p. 58–100° (2 mm), weighing 2.0 g was mainly 2-styryl acetate as indicated by its NMR spectrum while a fraction b.p. 128–145° (3 mm) contained 85–90% of a single product by GLC on the above mentioned diethyleneglycol succinate column at 200°. This fraction slowly crystallized on cooling and two recrystallizations from methanol gave 0.884 g (18%) of colorless prisms of *o*-tert-butyl-*trans*-stilbene, m.p. 48–50°. The UV spectrum of the compound in isooctane showed peaks at 285 nm (ε 22,650) and at 220 nm (ε = 15,250). NMR spectra and analyses are given in Table 2.

Methyl p-tert-butyl-trans-cinnamate

tert-Butylbenzene was mercurated by heating 80 g (0.6 mole) in 200 ml of acetic acid with 63 g (0.2 mole) of mercuric acetate on a steam bath overnight. The mixture was cooled, diluted with water and filtered. Excess tert-butylbenzene was removed by washing the solid with hexane. After drying, there was obtained about 30 g of the crude mercurial.

The ester was prepared by stirring 3.9 g (10 mmoles) of the mercurial, 20 ml of acetonitrile, and 4 ml of methyl acrylate at 0° and adding 2.24 g (10 mmoles) of palladium acetate. After 30 min at 0° the mixture was stirred at room temperature overnight. It was then filtered and distilled under reduced pressure to give 1.56 g of product, b.p. 70–160° (2 mm). This fraction contained methyl *p*-tert-butyl-*trans*-cinnamate in 49% yield. A sample collected by GLC on the above described diethyleneglycol succinate column at 175° had the following analyses: (Found; C, 76.40; H, 8.29. $C_{14}H_{18}O_2$ calcd.: C, 77.03; H, 8.31%.) The retention time of this compound by GLC was different from the *ortho* isomer prepared above.

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