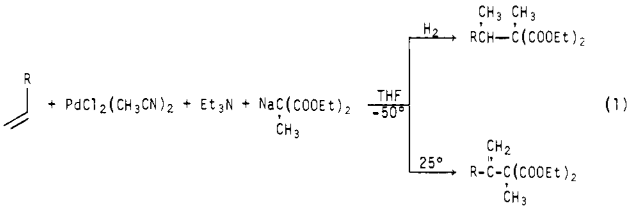
Palladium(II) Assisted Alkylation of Olefins with Stabilized Carbanions

Sir:

We wish to report the facile alkylation of simple monoolefins by the stabilized carbanions of diethyl methylmalonate, dimethyl hexylmalonate, dimethyl malonate, *tert*-butyl acetoacetate, and phenylacetone in the presence of $PdCl_2$ and triethylamine (eq 1). Unsaturated products were obtained by simply allowing the reaction mixture to warm to room temperature to facilitate β-elimination of "PdH" from the intermediate σ-alkylpalladium complex, while exposure of the cold reaction mixture to an atmosphere of hydrogen followed by warming to room temperature produced saturated (reduced) products. Both types of products were obtained in fair to excellent overall yield (Table I). Thus sodium diethyl methylmalonate reacted with ethene, propene, 1-butene, and 1-hexene to give excellent yields of alkylation product, while cyclopentene reacted only in low yield. With substituted olefins alkylation occurred predominantly at the *most* substituted position.[1] Small amounts (<10%) of reduced product were obtained with this carbanion, even when the β-elimination isolation procedure was used. Similar results were obtained in the reaction between dimethyl hexylmalonate and ethene. The behavior of sodium dimethyl malonate was slightly more complex. While the reductive isolation procedure resulted in good yields of desired product, the β-elimination procedure always resulted in production of some dialkylation products with a ~10% lowering of the yield. These dialkylation products are thought to arise from a base (or "PdH") catalyzed rearrangement of the initially formed olefinic product to the conjugated ester, followed by 1,4-addition of another dimethyl malonate anion (Scheme I). The best substrate with this anion was the enamide N-vinylacetamide which alkylated at the carbon α to nitrogen in excellent yield. The less basis *tert*-butyl acetoacetate anion reacted with ethylene in fair yield, as did the considerably more basic phenylacetone anion. Thus, this reaction proceeded well with both normal and electron-rich olefins and with carbanions of pK_a 10 to ~17.



Scheme I

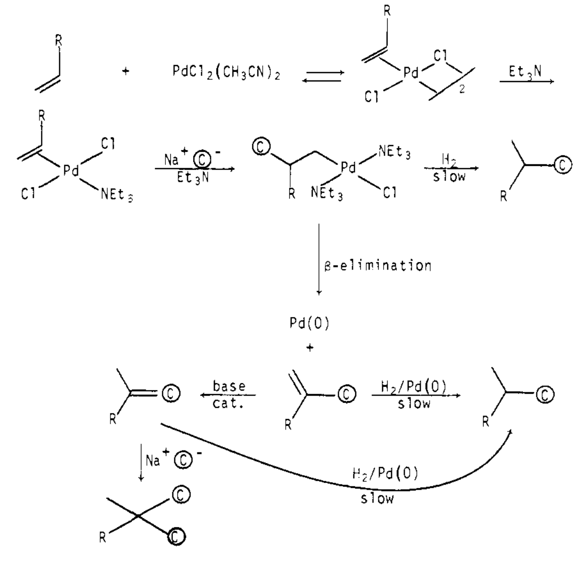
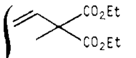
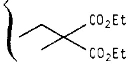
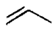
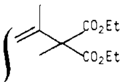
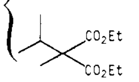
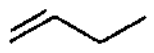
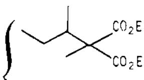
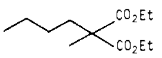
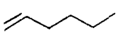
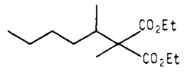
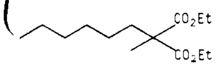
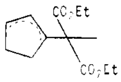
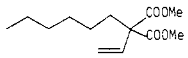
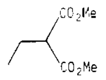
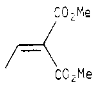
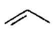
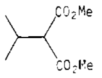
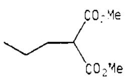
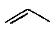
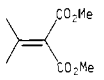
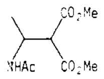
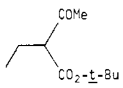
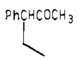


Table I. Alkylation of Olefins

OLEFIN	ANION	ISOLATION	PRODUCT	YIELD, %[a]
	$NaCMe(CO_2Et)_2$	β-elimination		92%
				7%
	$NaCMe(CO_2Et)_2$	β-elimination		90%
				9%
	$NaCMe(CO_2Et)_2$	H_2		61%
				24%
	$NaCMe(CO_2Et)_2$	H_2		55%[b]
				24%
	$NaCMe(CO_2Et)_2$	β-elimination		31%
	$NaC(COOMe)_2$ C_6H_{13}	β-elimination		87%[d]
	$NaCH(CO_2Me)_2$	H_2		65%
	$NaCH(CO_2Me)_2$[c]	β-elimination		53%
	$NaCH(CO_2Me)_2$	H_2		63%
				3%
	$NaCH(CO_2Me)_2$[c]	β-elimination		58%
	$NaCH(CO_2Me)_2$	H_2		88%[b]
	$NaCH(COMe)CO_2$-$\underline{t}$-Bu	H_2		60%
	$NaCH(Ph)COCH_3$	H_2	 PhCHCOCH$_3$	72%[b]

[a] Yields, based on $PdCl_2(CH_3CN)_2$ employed, were determined by GLC using appropriate internal standards. [b] Isolated yield. [c] 1.1 equiv of the nucleophile was used. [d] A minor amount of reduced material was also obtained.

The reactions were run in the following way. The appropriate olefin[1] (2-5 mmol) was added to a suspension of $PdCl_2(CH_3CN)_2$ (1.0 mmol) in 20 mL of THF and the resulting solution was cooled to -78 °C. Triethylamine (2.0 mmol) was added dropwise over 0.2 h, the mixture stirred for 0.25 h, and a solution of the nucleophile (2.0 mmol) in 10 mL of THF was added over 0.2 h. The reaction mixture was stirred for 1 h at -50 °C, then allowed to warm to room temperature (β-elimination), or exposed to an atmosphere of hydrogen (balloon) while warming (reduction). The resulting black suspension was filtered, the filtrate passed through a short silica gel column, and the solvent evaporated; the products were isolated by preparative GLC or silica gel column chromatography.

The procedure illustrates several interesting features of the reaction. Optimum results required the use of 2 equiv of triethylamine and 2 equiv of carbanion. With no added amine the yield of alkylation product was <1%, with 1 equiv it jumped to 30%, and with 2 equiv it was essentially quantitative. Triethylamine was the reagent of choice. Use of pyridine, diethylamine, trimethylamine, or ethyldiisopropylamine resulted in very low yields. Use of only 1 equiv of carbanion resulted in yields 10-20% lower than those obtained with 2 equiv. With dimethyl malonate anion, only 1 equiv of anion could be used when the β-elimination isolation was used, since excess anion led to 1,1-dialkylation of the olefin in ~80% yield. The probable course of the reaction is outlined in Scheme I and is similar to other palladium-assisted nucleophilic attack on olefins.[2-4]

Although stabilized carbanions have long been known to alkylate *chelate* diolefin palladium and platinum complexes,[5-7] prior to the work reported in this communication, alkylation of simple monoolefins complexed to palladium had not been achieved in usable yield.[8-10] Very recently dimethyl ethylmalonate was produced in 68% yield by the reaction of sodium dimethyl malonate with (ethylene)iron tetracarbonyl, followed by oxidation to remove the metal.[11] Similarly, stabilized carbanions alkylated the olefin in cationic (carbonyl)(olefin)-cyclopentadienyliron complexes. Again oxidative removal of the metal was required.[12,13] In contrast, the method presented in this communication requires neither prior synthesis of the metal-olefin complex nor chemical removal of metal from the desired organic products. Rather, it is a direct, one-pot procedure resulting in the alkylation of olefins primarily at the 2 position, under very mild conditions. It is quite complementary to the recently reported *allylic* alkylations of olefins via their π-allylpalladium complexes,[14-25] which lead to alkylation at the 1 and/or 3 position of the potential allyl system.

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References and Notes

(1) With liquid olefins, 2 equiv was used. With gaseous olefins, a balloon filled with olefin was affixed to the stopcock of the flask to ensure the presence of adequate olefin.

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(8) The reaction of styrene with dimethyl malonate in the presence of $Pd(acac)_2$ has recently been reported, with no yields or experimental details: S. Murahashi, M. Yamamura and K. Yanagisawa, 34th Annual Meeting of the Chemical Society of Japan, 3 G 40, 1976, cited in a review by J. Tsjui, *Yuki Gosei Kagaku Kyokai Shi*, **35**, 10 (1977).

(9) The alkylation of styrene-palladium complexes with Grignards in low yield has been reported: H. Okada and H. Hashimoto, *Kogyo Kagaku Zasshi*, **70**, 2152 (1967). This reaction was thought to proceed via a mechanism similar to the Heck arylation, rather than simple nucleophilic attack of the olefin by the carbanion.

(10) After submission of this paper, the alkylation of allylamines and allyl sulfides with stabilized carbanions in the presence of Na_2PdCl_4 was reported. These authors were unable to alkylate 1-octene under their conditions: R. A. Holton and R. A. Khonaas, *J. Am. Chem. Soc.*, **99**, 4177 (1977). The final cyclization in the Pd catalyzed synthesis of deethylibogamine is now thought to involve nucleophilic attack of an enamine anion on an olefin: B. M. Trost and J. P. Genet, *ibid.*, **98**, 8516 (1976).

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Tamio Hayashi, Louis S. Hegedus*
Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

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Photoinduced Redox Reactions of Hydrophobic Ruthenium(II) Complexes

Sir:

In several cases, it has been shown that light-induced electron-transfer reactions in solution can result in efficient energy conversion.[1-5] However, usually the practical utility of these reactions is limited by the subsequent occurrence of energy-wasting back-electron-transfer reactions which produce the ground states of the starting reagents.[2,4,5] Our studies involving photoreactions occurring in organized media have led to the synthesis of several surfactant molecules including a number of ruthenium(II) complexes which are surfactant analogues of the widely studied tris(2,2′-bipyridine)ruthenium(II)$^{2+}$ ($Ru(bipy)_3{}^{2+}$, **1**).[6] We have recently synthesized a series of water-insoluble complexes **2-9** in which the polar, charged $Ru(bipy)_3{}^{2+}$ core is surrounded by aliphatic groups of varying size. These "hydrophobic" complexes appeared to be attractive candidates for solution studies of photoinduced electron-transfer reactions owing both to their high solubility in relatively nonpolar solvents where to date relatively few studies have been carried out and further to the possibility that the "shielding" of the reactive core by the hydrophobic sheath might impart a selectivity to electron-transfer reactions. In the present paper, we report results which suggest that such selectivity can indeed occur; more importantly, we find indications that substantial energy conversion and storage in the form of high energy redox products can be accomplished with these complexes.

Hydrophobic complexes **2-9** exhibit relatively intense absorption (Figure 1) and luminescence in the visible region in acetonitrile solution, similar but slightly red shifted compared to **1**. Lifetimes and λ_{max} for the luminescence in degassed acetonitrile are listed in Table I. Electrochemical oxidations and reductions of several of the complexes were also carried out in acetonitrile. As might be anticipated on the basis of substitution of the bipyridine ligand with electron-withdrawing carboxyl groups, the potentials for oxidation of hexacarboxy complexes **2-4** were shifted by ~0.3 V more anodic while the corresponding potentials for the reduction of the dication were shifted 0.4 V more anodic. Interestingly, it was found that acetonitrile solutions of **5**, **6**, **8**, and **9** were electrochemically