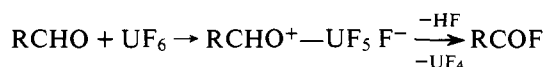**Table III.** Oxidation and Oxidative Fluorination of Alcohols and Aldehydes

| Alcohol or aldehyde	Products	Yield, %
Benzyl	Benzaldehyde (benzoyl fluoride)	40
4-Methylbenzyl	p-Tolualdehyde (p-toluoyl fluoride)	38
1-(4-Fluorophenyl)ethanol	4-Fluoroacetophenone	64
Benzhydryl	Benzophenone	45
Benzaldehyde	Benzoyl fluoride	40
Heptanal	Heptanoyl fluoride	47
Pentanal	Pentanoyl fluoride	29
2-Bromobenzaldehyde	2-Bromobenzoyl fluoride	35

Table IV. Oxidative Cleavage of Hydrazones

Carbonyl product	Yield, %
N,N-Dimethylhydrazone	
Propiophenone	49
Cyclohexanone	46
4-tert-Butylcyclohexanone	50
2-Heptanone	56
2-Methylcyclohexanone	69
Benzaldehyde	41
Tosylhydrazone	
Acetophenone	96
Isobutyrophenone	95
Cycloheptanone	95
Cyclooctanone	76
2-Norbornanone	56
4-Heptanone	66

carbonyl compounds. In the case of aldehydes transformation into aroyl fluorides can also take

$$RCHO + UF_6 \rightarrow RCHO^+—UF_5 \ F^- \xrightarrow[-UF_4]{-HF} RCOF$$

place with excess UF_6. Oxidative fluorination of aliphatic and aromatic aldehydes with UF_6 to the corresponding acyl fluorides indeed can be carried out as a general reaction. The results of the reaction of benzylic alcohols and aliphatic, as well as aromatic aldehydes are summarized in Table III.
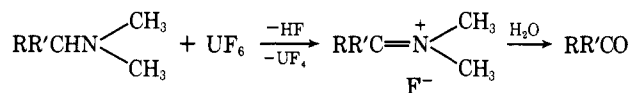
Oxidative cleavage of protected carbonyl compounds, such as tosylhydrazones and N,N-dimethylhydrazones, also takes place with ease upon aqueous quenching of the initially formed UF_6 adducts.

$$RR_1C{=}NN(CH_3)_2 \xrightarrow[2. \ H_2O]{1. \ UF_6} RR_1C{=}O$$
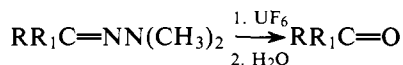
Data of the studied hydrazones are summarized in Table IV.

The oxidation of carboxylic acid hydrazides with UF_6 appears to be more complex, as the corresponding acids were isolated in only fair yield (benzoic acid 30%, m-nitrobenzoic acid 25%, phenylacetic acid 34%, and cyclohexanecarboxylic acid 55%).

N,N-Dimethylalkyl(cycloalkyl)amines are also oxidized by UF_6, yielding on aqueous quench the corresponding carbonyl compounds in fair yield. We are presently extending our

$$RR'CHN{\Large<}^{CH_3}_{CH_3} + UF_6 \xrightarrow[-UF_4]{-HF} RR'C{=}\overset{+}{N}{\Large<}^{CH_3}_{CH_3} \ \overset{H_2O}{\longrightarrow} RR'CO$$
$$F^-$$

investigation of the utility of UF_6 in oxidizing such varied organic systems as benzoins, hydroquinones, aromatic hydrocarbons, epoxides, alkenes, sulfur compounds, and the like.

Our studies have shown that UF_6 is a new, convenient oxi-

dizing agent for organic synthesis. The surprisingly limited fluorinating ability of UF_6 in solution does not interfere with most reactions. In addition, many organic functional groups are unaffected under our reaction conditions. These include, inter alia, ketone, ester, amide, nitrile, and nitro groups.

References and Notes

(1) Part 16. G. A. Olah, H. C. Lin, and A. Serianz, *Synthesis*, 42 (1976).
(2) UF_6 was obtained from the U.S. Energy Research and Development Administration in its depleted form. This material can be safely handled with normal laboratory techniques and care, considering its ease of hydrolysis giving hydrogen fluoride, and its low radioactivity.

George A. Olah,* John Welch, Tse-Lok Ho

Department of Chemistry, Case Western Reserve University
*Cleveland, Ohio 44106*

Received May 10, 1976

Mercury in Organic Chemistry. 9. A Novel Synthesis of π-Allylpalladium Compounds

Sir:

π-Allylpalladium compounds have been known since 1957.[1] They have recently found increasing utility in organic synthesis due to the ease with which they undergo stereocontrolled carbon–carbon bond formation.[2] Today the most widely employed methods of preparing these compounds involve either the direct allylic hydrogen substitution of alkenes[3,4] or palladium insertion into allylic halides.[5,6] We wish to report a novel new route to π-allylpalladium compounds which has a number of advantages over previous methods.
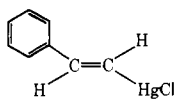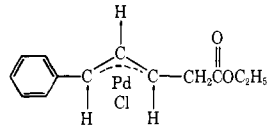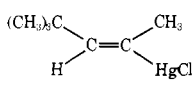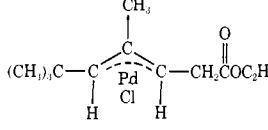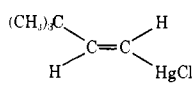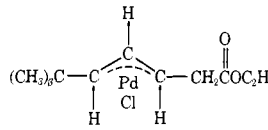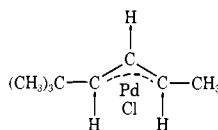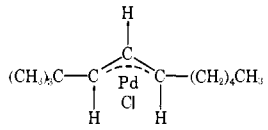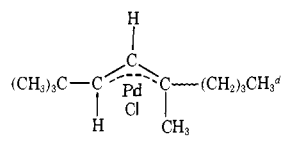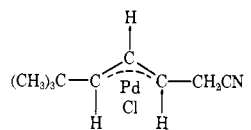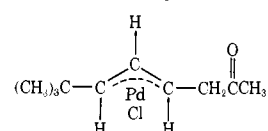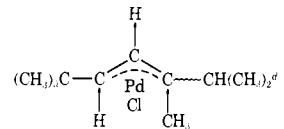
During studies directed towards the development of new synthetic methods employing organomercurials, we chose to examine the reaction of vinylmercuric chlorides, palladium salts, and simple alkenes. It was anticipated that conjugated 1,3-dienes would be obtained in a fashion similar to that previously reported.[7] To our surprise we obtained excellent yields of π-allylpalladium compounds instead (eq 1). An examination
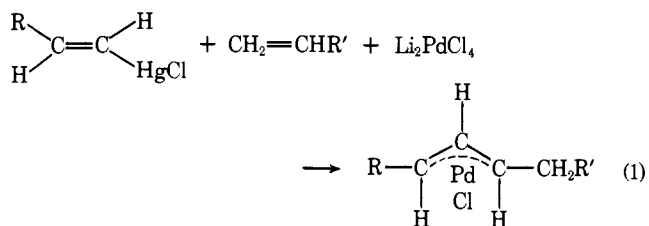
of Table I indicates the full scope of this reaction. Excellent yields are obtained from vinylmercurials derived from both internal and terminal acetylenes.[8,9] Especially rewarding is the ability of the reaction to accommodate not only simple olefins such as ethylene and 1-hexene, but a wide variety of functionally substituted olefins including α,β-unsaturated esters, nitriles, and ketones. Internal olefins also undergo reaction, although the yield decreases with increasing substitution.

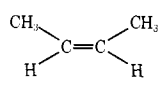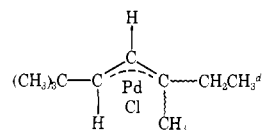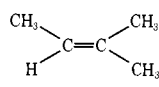The following procedure for the preparation of di-μ-chlorodi(1-carboethoxy-5,5-dimethylhex-2-enyl)dipalladium(II) (entry 3) is representative. Anhydrous lithium chloride (20 mmol) and palladium chloride (10 mmol) were added to a well-dried round-bottom flask containing a nitrogen inlet tube and septum inlet. After flushing with nitrogen, 100 ml of tetrahydrofuran (THF) and 10 g of ethyl acrylate (100 mmol) were added by syringe. After cooling to 0 °C, 3.19 g of *trans*-3,3-dimethyl-1-butenylmercuric chloride (10 mmol) was added while backflushing with nitrogen. The well-stirred reaction

Table I. Synthesis of π-Allylpalladium Compounds

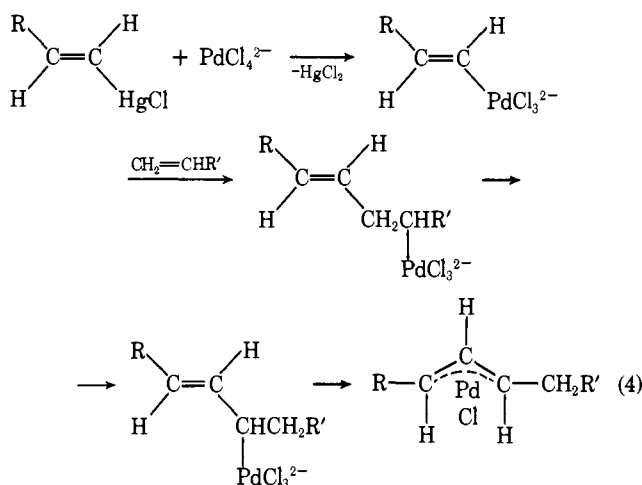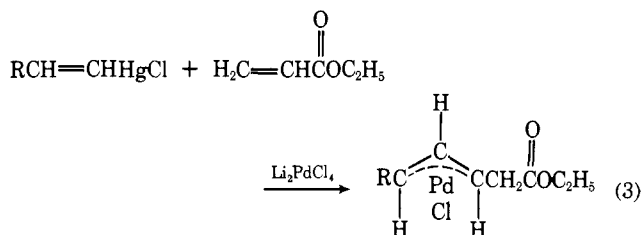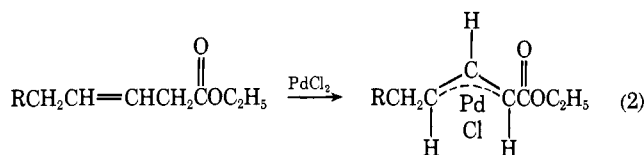| Entry	Vinylmercurial	Olefin	π-Allylpalladium compound[a]	% yield[b]
1	(phenyl)CH=CH–HgCl	$H_2C=CHCOC_2H_5$ (with C=O)	phenyl–CH···C(H)···C(H)–Pd(Cl)–CH_2COC_2H_5	100 (58)
2	$(CH_3)_3C$–C(H)=C(CH_3)–HgCl		$(CH_3)_3C$–CH···C(CH_3)···CH–Pd(Cl)–$CH_2COC_2H_5$	97 (83)
3	$(CH_3)_3C$–C(H)=C(H)–HgCl		$(CH_3)_3C$–CH···CH···CH–Pd(Cl)–$CH_2COC_2H_5$	90 (82)
4		$H_2C=CH_2$	$(CH_3)_3C$–CH···C(H)···CH–Pd(Cl)–CH_3	92
5a		$H_2C=CH(CH_2)_3CH_3$	$(CH_3)_3C$–CH···C(H)···CH–Pd(Cl)–$(CH_2)_4CH_3$	67 (63)[c]
5b			$(CH_3)_3C$–CH···C···CH–Pd(Cl)···C–$(CH_2)_3CH_3$[d] (CH_3)	
6		$H_2C=CHCN$	$(CH_3)_3C$–CH···C(H)···CH–Pd(Cl)–CH_2CN	87 (71)
7		$H_2C=CHCOCH_3$ (with C=O)	$(CH_3)_3C$–CH···C(H)···CH–Pd(Cl)–CH_2CCH_3 (with C=O)	100 (67)
8	CH_3(H)C=C(CH_3)H (cis)		$(CH_3)_3C$–CH···C···CH–Pd(Cl)···C–CH_2CH_3[d] (CH_3)	59 (37)
9	CH_3(H)C=C(CH_3)(CH_3)		$(CH_3)_3C$–CH···C···CH–Pd(Cl)···C–$CH(CH_3)_2$[d] (CH_3)	19 (7)

[a]NMR, ir, and elemental analysis data are in complete agreement with the assigned structures. [b]Crude yield (recrystallized yield). [c]Approximate ratio 5a:5b is 5:1; [d]Mixture of syn and anti isomers.

mixture was allowed to slowly warm to room temperature and stirred overnight. Ether and activated carbon were added to the reaction mixture which was filtered and washed with saturated aqueous ammonium chloride. The combined washings were reextracted with ether and the combined ether extractions dried over anhydrous sodium sulfate. Removal of the solvent provided 2.92 g (90%) of bright yellow π-allylpalladium compound. Recrystallization provided an 82% overall yield (hexane-ethanol): mp 125 °C dec; ir (KBr) 1730 cm^{-1}; NMR δ 1.17 (s, 9 H, Me$_3$C), 1.25 (t, 3 H, J = 7 Hz, Me), 2.57 (d, 1 H, J = 8 Hz, CHC=O), 2.69 (d, 1 H, J = 4 Hz, CHC=O), 3.4–3.9 (m, 1 H, π-allyl), 3.78 (d, 1 H, J = 11 Hz, π-allyl), 4.12 (q, 2 H, J = 7 Hz, OCH$_2$), 5.18 (t, 1 H, J = 11 Hz, π-allyl); Anal. Calcd for $C_{11}H_{19}ClO_2Pd$: C, 40.64; H, 5.89.

Found: C, 40.50; H, 5.80.

This procedure offers a number of advantages over previous methods employed in the preparation of π-allylpalladium compounds. It proceeds under very mild reaction conditions, tolerates considerable functionality, and employs very simple starting materials. It utilizes carbon–carbon bond formation to rapidly build up complex carbon structures thus avoiding the initial preparation of complicated olefinic starting materials. Unlike the direct palladation of olefins, this procedure allows one to predictably control the position of the π-allyl system, while also generating regioisomers not previously available (compare eq 2[4] and 3).

The mechanism of this unusual reaction almost certainly involves the generation and subsequent addition of a vinyl-

$$RCH_2CH=CHCH_2COC_2H_5 \xrightarrow{PdCl_2} \quad (2)$$

$$RCH=CHHgCl + H_2C=CHCOC_2H_5$$

$$\xrightarrow{Li_2PdCl_4} \quad (3)$$

$$+ PdCl_4^{2-} \xrightarrow{-HgCl_2}$$

$$\xrightarrow{CH_2=CHR'} \longrightarrow$$

$$\longrightarrow \longrightarrow \quad (4)$$

palladium species to the olefin, followed by a palladium hydride rearrangement as suggested below (eq 4).

The formation of π-allylpalladium compounds in these reactions is at first surprising in view of previous reports that vinylboronic acids and palladium acetate, as well as vinyl halides and palladium catalysts, react with olefins in the presence of organic bases to give 1,3-dienes.[7] However, it has been suggested previously that π-allylpalladium compounds may be involved in these reactions.[7] Indeed, we have observed that π-allylpalladium compounds possessing neighboring electron withdrawing groups like those generated in our reactions readily react with bases to give 1,3-dienes (eq 5). We are

$$\xrightarrow{base} C_6H_5CH=CHCH=CHCO_2C_2H_5 \quad (5)$$
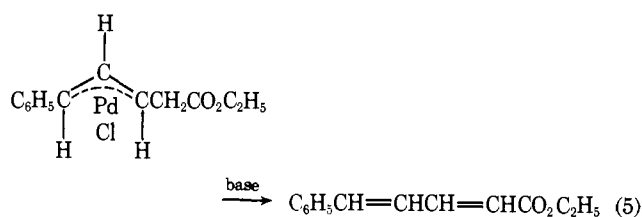
presently examining this approach to unsymmetrical 1,3-dienes from vinylmercurials, as well as the possibility that other π-allyl transition metal complexes may be prepared in this same manner.

Acknowledgments. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the National Science Foundation (NSF-URP Grant No. EPP75-04944) for generous financial support, and Matthey Bishop, Inc. for a large loan of palladium chloride.

References and Notes

(1) P. E. Slade, Jr., and H. B. Jonassen, J. Am. Chem. Soc., **79**, 1277 (1957).

(2) B. M. Trost and T. R. Verhoeven, J. Am. Chem. Soc., **98**, 630 (1976), and earlier references cited therein.
(3) B. M. Trost and P. E. Strege, Tetrahedron Lett., 2603 (1974).
(4) J. Tsuji, S. Imamura, and J. Kiji, J. Am. Chem. Soc., **86**, 4491 (1964).
(5) W. T. Dent, R. Long, and A. J. Wilkinson, J. Chem. Soc., 1585 (1964).
(6) M. Sakakibara, Y. Takahashi, S. Sakai, and Y. Ishii, Chem. Commun., 396 (1969).
(7) H. A. Dieck and R. F. Heck, J. Org. Chem., **40**, 1083 (1975).
(8) R. C. Larock and H. C. Brown, J. Organomet. Chem., **36**, 1 (1972).
(9) R. C. Larock, S. K. Gupta, and H. C. Brown, J. Am. Chem. Soc., **94**, 4371 (1972).
(10) DuPont Young Faculty Scholar, 1975–1976.
(11) NSF–URP participant, summer 1975.

Richard C. Larock,[*10] **Mark A. Mitchell**[11]

Department of Chemistry, Iowa State University
Ames, Iowa 50011

Received June 1, 1976

Alkylation of Polyguanylic Acid at the 2-Amino Group and Phosphate by the Potent Mutagen (±)-7β,8α-Dihydroxy-9β,10β-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene

Sir:

We recently described the stereoselective synthesis of (±)-7β,8α-dihydroxy-9β,10β-epoxy-7,8,9,10-tetrahydrobenzo[a]pyrene (**1**) and established that anchimeric assistance by the benzylic 7-hydroxy group greatly enhances its reactivity toward nucleophiles[1,2] when compared to the isomeric 9α,10α-epoxide (**2**).[3,4] Both diol expoxides (**1** and **2**) are formed on metabolism of the environmental carcinogen benzo[a]pyrene (BP) via oxidation of the 7,8-dihydrodiol.[5] The remarkably high mutagenicity of **1** and **2** toward bacterial and mammalian cells,[6] the indications that **1** and **2** are responsible for most of the binding of metabolities of BP to DNA,[3,7] and the high carcinogenicity of benzo[a]pyrene 7,8-oxide[8] (precursor of **1** and **2**) suggest **1** and **2** as ultimate carcinogens from BP. Since the guanine base (**3**, R = H) in DNA is generally the best nucleophile toward alkylating agents,[9] we have established the structures of the products formed when the highly reactive **1** ($t_{1/2} \sim$ 30 s at pH 7, 37 °C; solvolysis to tetraols by cis and trans addition of water at C-10)[5,10] covalently binds to polyguanylic acid (poly G).

In a typical binding experiment, tritiated **1** (0.4 mg/ml)[5] was added to a solution of poly G (1.7 mg/ml) in 50% aqueous acetone at 37 °C. Tetraols resulting from solvolysis of **1** were completely removed by three extractions with ethyl acetate. Precipitation of the polymer with ethanol followed by further extraction of aqueous solutions of the precipitate failed to release any of the bound hydrocarbon. Examination of the extent of binding as a function of pH and time established that optimum modification (10%) occurred near pH 6 and was complete within 1 h. The rate of binding was at least 30 times faster at pH 4 compared to pH 7, which required 2 h to reach completion. The uv spectrum of the modified poly G (Figure 1) showed the characteristic pyrene absorption pattern near 340 nm with a bathochromic shift which is typical of stacked chromophores.[11]

Acid hydrolysis of the modified poly G in ^{18}O-enriched (18%) 0.1 N HCl at 100 °C for 1 h released essentially all of the hydrocarbon as tetraols of **1** which had incorporated 0.96 atom % solvent water. The experiment provides little structural information since the tetraols incorporate 0.86 atom % solvent water under these conditions. Two classes of polymer-adducts were, however, identified by their differences in chemical stability. The minor and chemically labile products (type I adducts), 10–15% of the bound hydrocarbon, were released as tetraols with 0.95 atom % incorporation of solvent water on heating of modified polymer at 85 °C for 15 min at pH 7.0, conditions under which tetraols do not exchange.[12] Alkaline hydrolysis of the modified polymer (1 N KOH, 24 h, 37 °C)