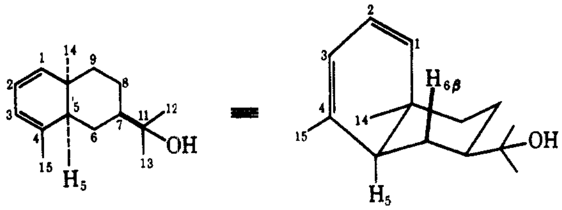
TABLE I

NMR SPECTRAL DATA FOR OCCIDENTALOL[a]

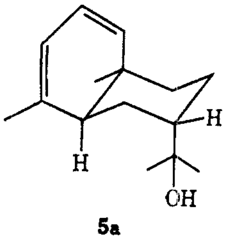


2 **2a**

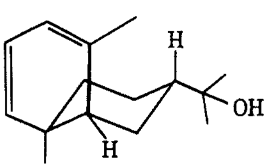
Proton(s)	Chemical shift,[b] δ	Multiplicity[c]	Observed coupling constants,[d] Hz
H-1	5.21	d (br)	$J_{1,2} = 9.6$, $J_{1,3} = 1.0$, $J_{1,5} = 1.0$, $J_{1,15} = 0.8$
H-2	5.74	d, d	$J_{1,2} = 9.0$, $J_{2,3} = 5.1$
H-3	5.49	d, q, d (sl br)	$J_{2,3} = 5.0$, $J_{3,15}$ 1.5, $J_{1,3} = 1.0$
H-5	1.51[e,f]	d, d, d (br)	$J_{5,6\alpha} = 12.5$,[g,h] $J_{5,6\beta} \sim 3.3$,[i] $J_{1,5} = 1.0$
H-6β	~0.97[j]	m (v br)	
H-12,13	1.07	s	
H-14	0.85	s	
H-15	1.79	d, d	$J_{3,15} = 1.5$, $J_{1,15} = 0.8$
H-*x*	1.66[e,f]	d (?)(br)	$J_{x,y} \sim 9$[k,l]
H-*y*	~1.18	m (v br)	

[a] The nmr spectrum was measured in CCl_4 solution (10%) with a Varian HA-100 spectrometer; internal benzene and tetramethylsilane (TMS) were used to provide lock signals; methanol was added to shift the –OH signal out of the upfield region. [b] Chemical shifts are relative to internal TMS at δ 0.00. [c] As observed in the undecoupled spectrum. [d] Assignments indicated by = symbol were confirmed by spin-decoupling experiments; estimated accuracies are 0.1 Hz except were stated otherwise. [e] The downfield half of the pattern due to H-5 partially overlaps the upfield half of the pattern due to H-*x*. [f] In the cases of H-5 and H-*x* (which appeared superimposed on broad absorption signals due to other protons) careful comparisons of estimated δ_5, δ_x, $J_{5,6\beta}$, and $J_{x,y}$ values were made at 60 and 100 MHz; the deviation in $\Delta(\delta_5 - \delta_x)$ was less than 10%. [g] Decoupled by applying a strong irradiating field at δ 0.97 (H-6β); the doublet at δ 1.66 (H-*x*) was unperturbed in this experiment. [h] Estimated accuracy, 1.5 Hz. [i] Not confirmed by spin-decoupling experiments. [j] Significantly perturbed by irradiation at δ 1.51 (H-5). [k] Estimated accuracy, 0.3 Hz. [l] Collapses to a broad peak at δ ~1.68 by irradiation at 1.18 (H-*y*).

sible structures for (+)-occidentalol, **2** and **5**, on the condition that each must exist preferentially in a nonsteroidal conformation, *i.e.*, **2a** and **5a**. However, since there is no reason *a priori* to favor conformer **5a** over **5b**, only structure **2**, in conformation **2a**, is possible for (+)-occidentalol.[11,14]



5a



5b

The apparent discrepancy between these results, which indicate an α orientation of the C-10 methyl group in occidentalol, and those reported earlier, which indicate β orientation,[7] can probably be attributed to the inhomogeneity of **3**.[17]

It is notable that, although the 7β orientation is considered usual for the hydroxypropyl group in naturally occurring eudesmanes, the α orientation of the C-10 methyl group relative to the 7β group, as observed in occidentalol, is very unusual.[3] This fact adds support to the hypothetical biogenetic pathway for **2** mentioned earlier and consequently suggests[19] that further examination of the essential oil of *Thuja occidentalis* L. may also lead to the isolation of **1**.

Registry No.—**2**, 18509-05-2.

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[11] It should be noted, in contrast to our conclusions and those of others[2,6] concerning the preferred conformation of **5**, that the structures I, II, and III in ref 4 exist predominantly in conformers having their C-7 substituents *axially* oriented. This is probably due, in part, to relief of an interaction between H-7 and the C-15 substituents in the alternate conformer and to the smaller effective steric bulk of 7-ethynyl[12] and 7-vinyl groups when compared with that of the 2-hydroxypropyl group in **5**. Further support for these conclusions can be derived from examination of data from base-catalyzed equilibration studies on chamaecynone and its derivatives from hydrogenation (T. Nozoe, *et al.*, cited in ref 4) and on 7α- and 7β-*cis*-tetrahydro-*epi*-α-cyperones.[13]

(12) R. J. Ouellette, *J. Amer. Chem. Soc.*, **86**, 3089 (1964).

(13) C. Djerassi and W. Klyne, *J. Chem. Soc.*, 4936 (1962).

(14) Implicit in our interpretation of the nmr spectrum of occidentalol is the assumption that long-range coupling between H-1 and H-5 occurs exclusively through σ bonds in the coplanar W configuration. However, a comparable coupling, $J_{1,15} = 0.8$ Hz, which could not occur *via* a W configuration, is observed between H-1 and the methyl hydrogens on C-15. This observation has lead a referee to suggest that the coupling interactions responsible for *both* $J_{1,5}$ and $J_{1,15}$ might possibly arise *via* transmission through the π system of the diene since each of the protons on C-5 and C-15 is similarly separated from H-1 by six bonds *via* the diene system. If $J_{1,5}$ did, in fact, arise exclusively as a result of such an allylic σ–π interaction, the structure **1** in its favored conformation (enantiomeric with **5b**) would have to be seriously considered as a possibility for (+)-occidentalol.[15] However, the observations that $J_{5,6\beta} = 12.5$ and $J_{5,6\alpha} \sim 3.3$ Hz, as well as the absence of coupling interactions of the allylic σ–π type[16] between H-3 and H-5 ($J_{3,5} = 0$; carefully ascertained at both δ 1.51 and 5.49) are sufficient to exclude this possibility.[4,10]

(15) This assumes, by analogy with observations recorded for simple allylic systems,[16] that coupling between H-1 and H-5 transmitted *via* the diene system will be at a maximum where H-5 is perpendicular to the coplanar C-5–C-4–C-3–C-2–C-1–H-1 portion of the molecule. Although such an analogy with allylic systems seems reasonable, it should be noted that, to our knowledge, no examples have been recorded which define the limits of significant coupling over six bonds *via* allylic σ–π interactions in diene systems such as those present in **1** and **2**.

(16) N. S. Bhacca and D. H. Williams, "Applications of N.M.R. Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964.

(17) The compound believed to be **3** was obtained[7] by oxidation of tetrahydrooccidentalol (~90% pure) in *ca.* 15% yield; however, this ketone (purified by glpc) yielded no crystalline derivatives and exhibited an ε value (6300) at λ_{max} 242 mμ which was less than half that normally associated[18] with conjugated ketones of this type. The comparable, and often higher, intensities of Cotton effects observed for unconjugated ketones suggests that impurities of this type may have given rise to the relatively low-intensity curve reported[7] for **3**. In addition, the fact that anomalous rotatory dispersion curves are often exhibited[18] by 4-en-3-ones having 6- and 7-alkyl substituents indicates that any ORD data obtained using pure **3** with undetermined configuration at C-6 would result in uncertain conclusions regarding the configuration of C-10 in **3**.

(18) C. Djerassi, O. Halpern, V. Halpern, and B. Riniker, *J. Amer. Chem. Soc.*, **80**, 4001 (1958), and references cited.

(19) *Cf.* footnote 9 in ref 5.

Oxidative Introduction of Alkyloxycarbonyl Groups into Olefins

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It has previously been shown in this laboratory that α,β-unsaturated esters may be prepared directly from

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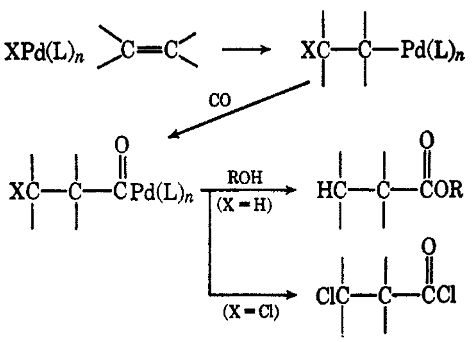
aromatic olefins, carbon monoxide, and methyl alcohol by electrolysis.[2] The present investigation deals with the oxidative displacement of olefinic hydrogen by alkyloxycarbonyl groups using a palladium salt as oxidant.

Palladium salts oxidize olefins to aldehydes or ketones in water,[3] to vinyl ethers or acetals in alcohols,[4] and to vinyl acetates or alkylidene diacetates in acetic acid.[5] Moreover, Moritani and Fujiwara have recently found that the styrene–palladium chloride complex reacts with benzene to yield stilbene.[6] Acrylates, however, have not yet been obtained directly from olefins.

Palladium catalyzes the carbonylation of olefins in alcohol, but the reaction requires a high pressure of carbon monoxide (100 atm) and the products are saturated esters.[7] It is also known that olefin–palladium chloride complexes in benzene afford β-chloro acid chlorides on treatment with 30–50 atm of carbon monoxide.[8] Scheme I explains these reactions.[9]

SCHEME I



L: ligand

Here we wish to report that the styrene–palladium chloride complex, when treated with triethylamine, reacts with methyl alcohol and carbon monoxide at atmospheric pressure to give methyl cinnamate, dimethyl phenylsuccinate, and small amounts of methyl hydrocinnamate, but neither methyl atropate nor methyl hydroatropate is obtained. Not only methyl alcohol but also other alcohols react and the results are summarized in Table I. Table I shows that the yields of phenylsuccinates vary considerably with the alcohols used, but the reason is not clear.

TABLE I

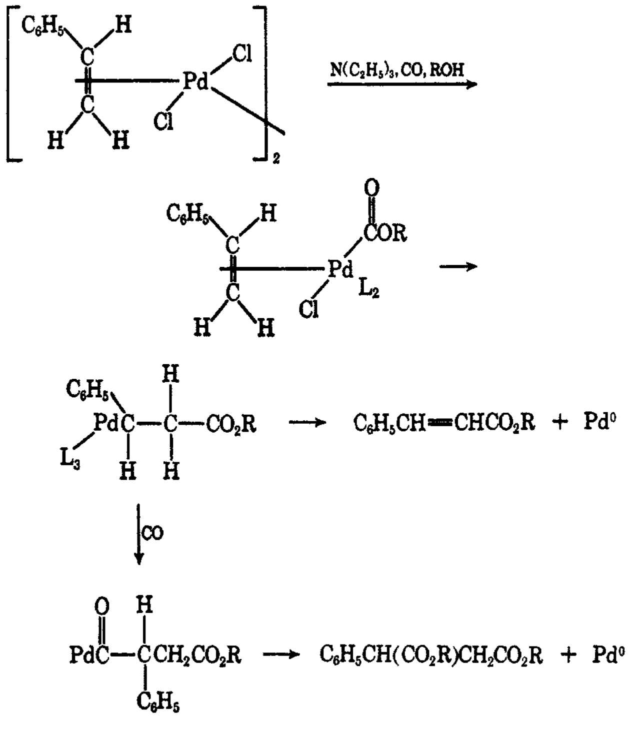
YIELDS OF ESTERS FROM STYRENE–PALLADIUM COMPLEX, CARBON MONOXIDE, AND ALCOHOLS

	Yield, %		
Alcohol	Cinnamate	Phenylsuccinate	Hydrocinnamate
None[a]	0	0	0
Methyl alcohol	41	7	3
Ethyl alcohol	34	2	2
Isopropyl alcohol	21	15	2
t-Butyl alcohol	21	4	0.3

[a] The products were alcoholized after the reaction.

It is known that alcohols in the presence of amine react upon transition metal halides to produce transition metal alkoxides,[10] and that carbon monoxide inserts into metal–oxygen bonds to form alkyloxycarbonyl metal derivatives.[9,11] Therefore, it is not unreasonable to assume that the reaction which we report here involves the insertion of carbon monoxide into the palladium–oxygen bond. The whole reaction most simply can be represented as in Scheme II, supposing that cinnamate and phenylsuccinate are derived from the same intermediate.

SCHEME II



L: ligand

The possibility that cinnamates are dehydrochlorination products of β-chlorohydrocinnamoyl chloride[7] seems excluded by results in the absence of alcohol (see Table I) or triethylamine. Namely, acid derivatives were not detected in both cases.

Ethylene–palladium chloride complex reacts with ethyl alcohol and carbon monoxide to yield ethyl acrylate (5%), ethyl propionate (5%), and acetaldehyde diethyl acetal (10%).

Experimental Section

Materials.—Alcohols were dried over Drierite before use. Olefin–palladium chloride complexes were prepared according to known procedures.[12] Triethylamine was refluxed in the presence of potassium hydroxide and was purified by fractional distillation. Benzene, chloroform, and potassium carbonate were commercial products.

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[2] T. Inoue and S. Tsutsumi, *J. Amer. Chem. Soc.*, **87**, 3525 (1965); *Bull. Chem. Soc., Jap.*, **38**, 2122 (1965).

[3] J. Smidt, *et al.*, *Angew. Chem.*, **71**, 176 (1965).

[4] I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960).

[5] W. Kitching, Z. Rappoport, S. Winstein, and W. C. Young, *J. Amer. Chem. Soc.*, **88**, 2054 (1966); E. W. Stern and M. L. Spector, *Proc. Chem. Soc.*, 111 (1963).

[6] I. Moritani and Y. Fujiwara, *Tetrahedron Lett.*, 1119 (1967).

[7] J. Tsuji and M. Morikawa, *ibid.*, 1437 (1963).

[8] J. Tsuji, M. Morikawa, and J. Kiji, *J. Amer. Chem. Soc.*, **86**, 4851 (1964).

[9] R. F. Heck, Advances in Chemistry Series No. 49, American Chemical Society, Washington, D. C., 1965.

[10] D. C. Bradley, R. K. Multini, and W. Wardlaw, *J. Chem. Soc.*, 126 (1958).

[11] J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition Metal Complexes," Elsevier Publishing Co., Amsterdam, The Netherlands, 1968, p 135; J. Halpern and S. F. A. Kette, *Chem. Ind.* (London), 668 (1961); R. F. Heck, *J. Organometal. Chem.*, **2**, 195 (1964).

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Reaction of Styrene–Palladium Chloride Complex.—Typically, 1.4 ml (0.01 mol) of triethylamine in 10 ml of benzene was slowly added to a mixture of 2.8 g (0.005 mol) of styrene–palladium chloride complex and 1 g of potassium carbonate in 250 ml of dry benzene. (Potassium carbonate is not always necessary for the reaction, but the filtration of the reaction mixture from palladium metal which deposited on potassium carbonate is much more easy then in the case without it.) The whole was warmed to 70° quickly, and 4 ml (0.156 mol) of methyl alcohol was added. At the same time, carbon monoxide was bubbled into the mixture and the bubbling was continued for 10 min. After cooling, the reaction mixture was filtered and benzene was distilled from the filtrate on a steam bath. Distillation of the condensed mixture under reduced pressure gave 890 mg of the product. Infrared, nmr, and vpc analyses showed that it consisted of methyl cinnamate (0.0041 mol, 41%), dimethyl phenylsuccinate (0.0007 mol, 7%), and methyl hydrocinnamate (0.0003 mol, 3%).

In the case of the ethylene–palladium chloride complex, chloroform was used instead of benzene and the reaction was carried out at 45°.

Registry No.—Styrene–palladium chloride complex, 12313-39-2; triethylamine, 75-50-3; carbon monoxide, 630-08-0.

An Improved Preparation of Specifically Deuterated Methyl Acrylate[1]

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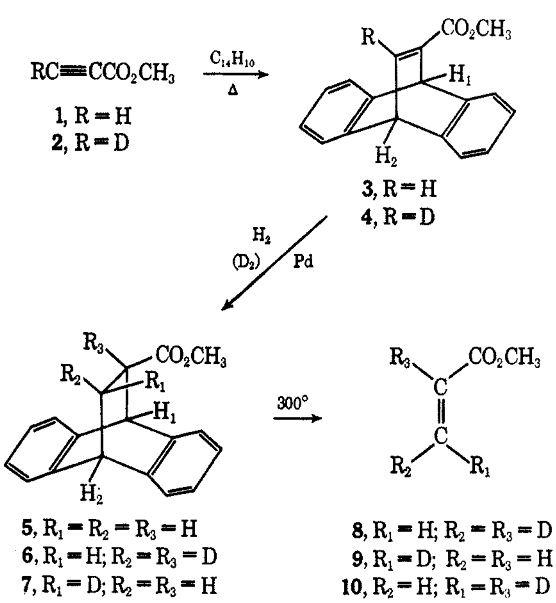
Received July 31, 1968

Samples of methyl acrylate stereospecifically deuterated at the β position were required for the preparation of 6α- and 6β-deuterioshikimic acids,[4] necessary for an investigation of the stereochemistry of chorismate formation. A number of β-deuterated acrylates have been prepared recently[5,6] for nmr studies of the conformations of their polymers and bromine adducts. Generally two methods of preparation have been employed: (1) catalytic deuteration of propiolic esters or hydrogenation of deuteriopropiolic esters using the Lindlar catalyst,[5] or (2) homogeneous reduction of propiolic esters with chromous ion in D_2O.[6] A third method, addition of DCl to acetylene followed by conversion to the Grignard reagent and carbonation gave β-deuterioacrylic acid with low (3:2) stereospecificity.[5b]

The chromous ion reduction of acetylenes in D_2O gives exclusive *trans* addition of deuterium,[6,7] but suffers from low yields obtained in reduction of propiolate esters and in the necessity for anhydrous chromous chloride when carrying out reactions in D_2O. We were unable to obtain yields above 10% in reducing methyl propiolate by Schuerch's procedure. Though hydrogenation of acetylenes with the Lindlar catalyst is predominantly *cis*, reduction of propiolate esters has given mixtures of *cis* and *trans* isomers in ratios of 3:1,[5a] 6:1,[5b] and 87:13.[5c] An added difficulty with this method, in our experience, is overreduction to propionates.

We have been able to circumvent both the problems of unsatisfactory stereospecificity and overreduction in the catalytic deuteration of propiolates by the simple expedient of using the anthracene–methyl propiolate Diels–Alder adduct **3**. The increased bulk of the substrate leads to complete stereospecificity in its reduction, while overhydrogenation is impossible. Reduction of **3** with deuterium gas over palladium gave the dideuterio ester **6**, in which the exclusive *cis* configuration of the deuterium atoms was shown by comparison of the nmr spectrum with that of the anthracene–methyl acrylate adduct **5**. The aliphatic protons of **5** are easily differentiated (see Experimental Section); in particular, the hydrogen at R_1 can be distinguished from that at R_2 by the magnitude of the coupling with the hydrogen at R_3 (4 and 12 Hz, respectively). In the spectrum of **6**, the only signal upfield of the methoxy singlet corresponded exactly to the position of R_1, while the clean singlet for H_1 and simple doublet for H_2 further testified to the absence of hydrogens at R_2 and R_3. Pyrolysis of **6** at 290–300° effected retro Diels–Alder dissociation[8] to anthracene and methyl α-*trans*-β-dideuterioacrylate **8**, isolated in 94% yield (Scheme I).

SCHEME I



Comparison of the relative areas of the methyl and olefinic proton signals showed that **8** contained greater than 98% of two deuteriums. The nmr spectrum was identical with that described[5a] for **8**, showing in the olefinic region *only* the 1:1:1 triplet at δ 6.3 due to the β hydrogen *cis* to carbomethoxyl.

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[3] Public Health Service Postdoctoral Fellow, 1967–1968.

[4] R. K. Hill and G. R. Newkome, *Tetrahedron Lett.*, 1851 (1968).

[5] (a) T. Yoshino, J. Komiyama, and M. Shinomiya, *J. Amer. Chem. Soc.*, **86**, 4482 (1964)· (b) T. Yoshino and K. Kuno, *ibid.*, **87**, 4404 (1965); (c) R. J. Jablonski and E. I. Snyder, *ibid.*, **90**, 2316 (1968).

[6] (a) C. Schuerch, W. Fowells, A. Yamada, F. A. Bovey, F. P. Hood, and E. W. Anderson, *ibid.*, **86**, 4481 (1964); (b) W. Fowells, C. Schuerch, F. A. Bovey, and F. P. Hood, *ibid.*, **89**, 1396 (1967).

[7] C. E. Castro and R. D. Stephens, **86**, 4358 (1964).

[8] For other examples of retro Diels–Alder reactions, see J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **5**, 211 (1966). The present case provides one of the few clear examples of retention of configuration in the reverse Diels–Alder reaction.