Table I. CD Data of Allylic Alcohol Benzoates in Ethanol

benzoate	chirality	CD λ_{ext}, nm ($\Delta\epsilon$)
5α-cholest-2-en-1α-yl (1)	(+)	228.2 (+12.7)
5α-cholest-1-en-3β-yl (2)	(+)	228.2 (+11.5)
cholest-4-en-3β-yl (3)	(–)	229.5 (–8.7)
cholest-4-en-3α-yl (4)	(+)	229.0 (+11.5)
6β-hydroxycholest-4-en-3β-yl (5)	(–)	229.5 (–8.9)
3β-hydroxycholest-5-en-4β-yl (6)	(+)	230.0 (+6.4)
3β-hydroxycholest-4-en-6β-yl (7)	(–)	233.0 (–4.7)
3β-acetoxy-5α-cholest-7-en-6α-yl (8)	(+)	231.0 (+3.0)
3β-acetoxy-5α-cholest-7-en-6β-yl (9)	(–)	230.6 (–11.8)
3β-hydroxycholest-5-en-7α-yl (10)	(–)	229.0 (–11.8)
3β-hydroxycholest-5-en-7β-yl (11)	(+)	229.5 (+7.3)
3β-acetoxycholest-5-en-7β-yl (12)	(+)	229.5 (+4.9)

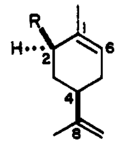
and/or skeletal strain of the double bond, overlap of additional Cotton effects complicates the CD curve of the double-bond chromophore. On the other hand, since the benzoate chromophore is strain-free, the 230-nm benzoate transition is mainly affected by the 195-nm allowed $\pi \rightarrow \pi^*$ transition of the double bond as a result of the dipole–dipole coupling mechanism in nondegenerate systems.

The CD spectra of cholest-4-en-3β-yl benzoate (3) is shown in Figure 2. In the region of the benzoate $\pi \rightarrow \pi^*$ transition around 229 nm, the spectrum exhibits a negative Cotton effect, the sign of which is in accordance with the negative chirality between the benzoate and double-bond chromophores. The negative CD ellipticity observed below 210 nm is in apparent disagreement with the theoretical expectation that the signs of the first and second Cotton effects should be opposite to each other.[7] This intense ellipticity is presumably due to the participation of the benzenoid ^{1}B transition (~200 nm) of the benzoate chromophore and/or the CD activity of the double-bond moiety as discussed above. Other pertinent examples are listed in Table I.

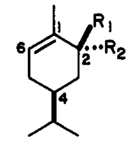
As in the case of the dibenzoate chirality method,[1] para-substituted benzoate chromophores (Me, Cl, Br, OMe, NO_2, and NMe_2) can also be used in the present method. Table II lists the examples of the *p*-nitrobenzoates of monoterpene alcohols. The fact that the sign of the exciton chirality between the benzoate and double-bond chromophore is not affected by conformational change greatly simplifies application of the present method. For instance, in the case of (*R*)-2-cyclohexen-1-yl benzoate, the cyclohexene ring can adopt two half-chair conformations (quasi-equatorial and -axial benzoates). In both conformers, the exciton chirality between the benzoate and double-bond chromophores is positive *irrespective of the cyclohexene conformation*; this is in contrast to the case of cyclohexenone systems where conformational inversions lead to reversal in enone helicity. Thus, in the present case, a positive benzoate Cotton effect leads to an *R* configuration in a straightforward manner.

All chiroptical data including the case of monocyclic compounds are in agreement with the exciton chirality between the benzoate and double-bond chromophores. The present CD exciton method for determining the absolute stereochemistry of *allylic alcohols* is based on theoretical grounds and covers the empirical Mills' rule,[8] Brewster's rule,[9] and the benzoate sector rule.[10] It is extendable to larger rings and acyclic systems where conformations of the allylic benzoates are known.

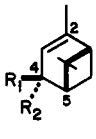
Table II. CD Data of Allylic Alcohol *p*-Nitrobenzoates in Ethanol



14, R = OBz-p-NO_2



15, R_1 = OBz-p-NO_2
R_2 = H
16, R_1 = H
R_2 = OBz-p-NO_2



17, R_1 = OBz-p-NO_2
R_2 = H
18, R_1 = H
R_2 = OBz-p-NO_2

p-nitrobenzoate	chirality	CD λ_{ext}, nm ($\Delta\epsilon$)
cholest-4-en-3β-yl (13)	(–)	263.0 (–3.22)
(2*R*,4*R*)-1(6),8-*p*-menthadien-2-yl (14)	(+)	262.0 (+5.84)
(2*S*,4*S*)-1(6)-*p*-menthen-2-yl (15)	(–)	261.0 (–5.64)
(2*R*,4*S*)-1(6)-*p*-menthen-2-yl (16)	(+)	258.0 (+7.39)
(1*S*,4*S*,5*S*)-2-pinen-4-yl (17)	(+)	264.4 (+5.11)[a]
(1*S*,4*R*,5*S*)-2-pinen-4-yl (18)	(–)	262.0 (–5.45)[a]

[a] The $\Delta\epsilon$ values are corrected on the basis of the optical purity (72.6%) of samples.

Acknowledgment. This investigation was supported in part by grants from the Ministry of Education, Japan (No. 447018), and NIH (CA-11572).

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(6) (a) Yogev, A.; Amar, D.; Mazur, Y. *Chem. Commun.* **1967**, 339. (b) Scott, A. I.; Wrixon, A. D. *Tetrahedron* **1970**, *26*, 3695.

(7) In the case of conjugated diene–benzoate systems, both exciton split Cotton effects are clearly observable. Harada, N., to be published.

(8) Mills, J. A. *J. Chem. Soc.* **1952**, 4976.

(9) Brewster, J. H. *Tetrahedron* **1961**, *13*, 106. See also: Brewster, J. H. *J. Am. Chem. Soc.* **1959**, *81*, 5475, 5483, 5493.

(10) Harada, N.; Ohashi, M.; Nakanishi, K. *J. Am. Chem. Soc.* **1968**, *90*, 7349. Harada, N.; Nakanishi, K. *Ibid.* **1968**, *90*, 7351.

Additivity Relation Found in the Amplitudes of Exciton-Split Circular Dichroism Curves of Pyranose Benzoates

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When two or more chromophores absorbing strongly around the same wavelength are closely located in space, the system gives rise to a Davydov-split[1] circular dichroism (CD) curve, the sign of which reflects the chiralities of the interacting transition moments. This splitting is due to the so-called coupled oscillator theory[2] and is the only means other than the X-ray Bijvoet method for determining the absolute configuration or conformation of molecules in a nonempirical manner.

The exciton chirality method,[3] an extension of the dibenzoate chirality method,[4] is based on this coupled oscillator theory and has been applied to a wide variety of compounds.[5] A systematic investigation of the CD of over 40 sugar benzoates, an extension

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(1) Davydov, A. S. "Theory of Molecular Excitons"; McGraw-Hill: New York, 1962.

(2) (a) Rosenfeld, V. L. *Z. Phys.* **1928**, *52*, 161. (b) Kauzmann, W. J.; Walter, J. E.; Eyring, H. *Chem. Rev.* **1940**, *26*, 339. (c) Moscowitz, A. *Adv. Chem. Phys.* **1962**, *4*, 67. (d) Tinoco, I., Jr. *Ibid.* **1962**, *4*, 113. (e) Schellman, J. A. *J. Chem. Phys.* **1966**, *44*, 55. (f) Mason, S. F. *J. Chem. Soc. B* **1966**, 370. (g) Mason, S. F.; Schofield, K.; Wells, R. J.; Whitehurst, J. S.; Vane, G. W. *Tetrahedron Lett.* **1967**, 137. (h) Gottarelli, G.; Mason, S. F.; Torre, G. *J. Chem. Soc. B* **1970**, 1349.

(3) (a) Harada, N.; Nakanishi, K. *Acc. Chem. Res.* **1972**, *5*, 257. (b) Harada, N.; Chen. S. M. L.; Nakanishi, K. *J. Am. Chem. Soc.* **1975**, *97*, 5345. (c) Harada, N.; Takuma, Y.; Uda, H. *Ibid.* **1978**, *100*, 4029.

(4) Harada, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1969**, *91*, 3989.

(5) Harada, N.; Nakanishi, K. "Circular Dichroic Spectroscopy—Exciton Coupling in Organic and Bioorganic Stereochemistry"; University Science Books: Mill Valley, CA, in press.

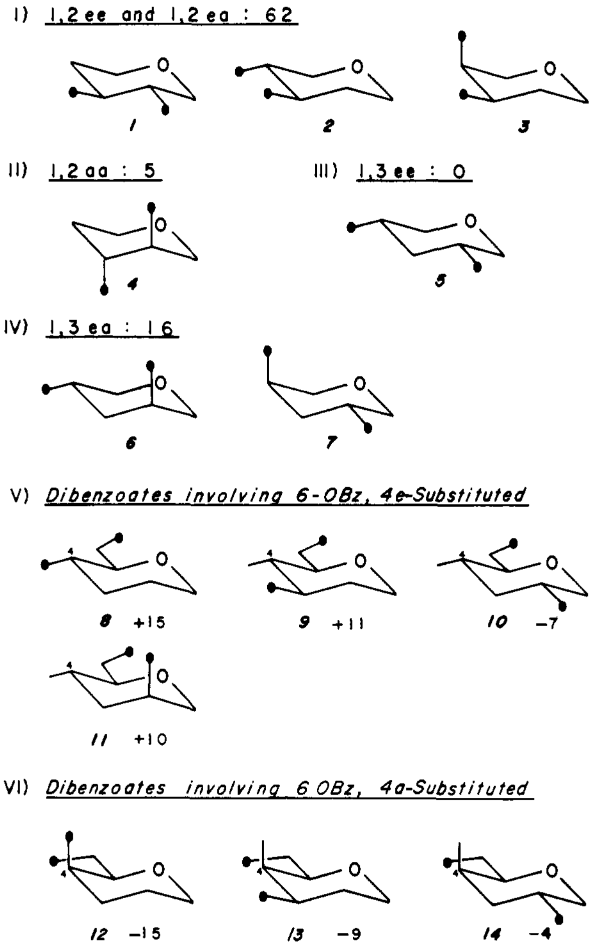

Figure 1. A values (in MeOH) of various pyranose p-bromobenzoates. The signs of A values are dependent on chiralities of benzoate groups. Benzoate groups are indicated by hatched circles. The anomeric carbon is normally α-OMe but occasionally β-OMe; the "unsubstituted" carbons at other locations are either methylenes or substituted with nonchromophoric groups, e.g., OAc, OMe, CH_2OH, Me, etc. However, in the 6-benzoates (units **9–11**, **13**, **14**), the nonbenzoate substituents at C-4 are also depicted because the 6-benzoate conformation is affected by the C-4 substituent (see text).

Table I. Observed and Calculated A Values of Tri- and Tetra-p-bromobenzoates

entry	compd	236/253 nm	A- (obsd)	A- (calcd)[a]
1	β-Xyl-2e,3e,4e-	−1/+1	+2	0
2	β-Ara-2e,3e,4a-	−32/+101	+133	+140
3	α-Gal-2e,3e,4a-	−42/+95	+137	+140
4	α-Man-6-O-TBDMS[b]-2a,3e,4e-	+29/−91	−120	−140
5	α-Glu-3-OMe-2e,4e,6-	−1/+8	+9	+8
6	α-Glu-2e,3e,6-	−22/+47	+69	+66
7	α-Glu-2-OMe-3e,4e,6-	+11/−22	−33	−36
8	α-Glu-2-OAc-3e,4e,6-	+10/−22	−32	−36
9	α-Gal-3-OAc-2e,4a,6-	0/+6	+6	−3
10	α-Gal-2e,3e,6-	−14/+31	+45	+49
11	β-Gal-2e,3e,6-	−16/+30	+46	+49
12	β-Glu-2e,3e,4e,6-	−7/+25	+32	+19
13	α-Glu-2e,3e,4e,6-	−4/+20	+24	+19
14	β-Gal-2e,3e,4a,6-	−26/+74	+100	+112
15	α-Gal-2e,3e,4a,6-	−29/+70	+99	+112
16	α-Man-2a,3e,4e,6-	+23/−66	−89	−104

[a] Estimated A value from sum of component dibenzoate units 1–14 (Figure 1). [b] *tert*-Butyldimethylsilyl.

of earlier studies,[6] has shown that an additivity relation exists in the A values[7] of split CD curves resulting from multiple (≥3) interacting chromophores. *For example, in the case of a molecule containing three interacting chromophores I, II,* and *III, the A value can be approximated by the summation of component A values*: $A \simeq A(I/II) + A(II/III) + A(III/I)$.

p-Bromobenzoates which have their UV maxima and split CD curves centered at 244 nm were used for the present studies because of the relatively large CD amplitudes and ease of preparation. The specific benzoylations were carried out on the methyl glycosides (mostly α), the hydroxyl groups of which had been appropriately blocked or derivatized as acetonides, benzylidenes, acetates, methyl ethers, etc. An alternative method for preparing a mixture of various benzoates was to reflux the glycosides with bis(tributylstannyl) oxide[8] in toluene for 2 h with continuous removal of water; evaporation of the solvent gave partially stannylated products which were then acetylated with 3 equiv of acetyl chloride. This usually gave one major acetate accompanied by several other minor acetates. These were separated by high-performance liquid chromatography, μ-Porasil, 3% MeOH in $CHCl_3$, and the respective acetates were then benzoylated by treatment with p-bromobenzoyl chloride in pyridine at 60 °C for 12 h. All benzoates were fully characterized by CI-MS (CH_4 carrier gas) and ^1H NMR spectroscopy. Measurements of 3–4 samples of respective p-bromobenzoates led to the following standard UV ϵ values: mono- ϵ 21 300, di- ϵ 38 200, tri- ϵ 57 200, and tetrabenzoate ϵ 76 400. These ϵ values were employed for deriving the concentrations of the solutions submitted to UV and CD measurements. Only a few micrograms of the sample was necessary because of the large CD amplitudes. The methyl pyranosides (mostly α-OMe) employed in this study were derivatives of glucose, galactose, mannose, xylose, arabinose, altrose, etc.

The A values for six classes of dibenzoates are summarized in Figure 1. When more than two dibenzoates belonging to the same class were measured, the A values usually agreed within ±3.[9]

Class I. In 1,2-ee and 1,2-ea dibenzoates (Figure 1, units **1–3**), which have dihedral angles of ca. 60°, the A values are 62. In **class II** (unit **4**), i.e., 1,2-aa dibenzoates, the fact that a split CD is observed with small amplitudes is not surprising because 1,3-diaxial interactions with 1α-OMe, 4β-H, and 5α-H would tend to decrease the dihedral angle between the two axial benzoate groups.

Class III (1,3-ee, Unit 5). Since the two C–O bonds are coplanar, no split CD should result. In **class IV** (1,3-ea, units **6**,**7**), the A value of 16 is smaller than the A value for the 1,2-ee and -ea units (A = ±62); this is to be expected since the A value is inversely proportional to the square of the interchromophoric distance,[3b] provided the angle and other factors remain unchanged.

Class V (Units 8–11). The signs of the A values clearly show that the 6-benzoate is pointing toward the "right" or as depcited. In contrast, in **class VI** benzoates (units **12–14**) which carry 4a substituents, the 6-benzoates must be directed toward the left as depicted. These conclusions can be readily rationalized by inspection of space-filling CPK models.

The data for tri- and tetrabenzoates are summarized in Table I. The 1,2,3-eee tribenzoate (entry 1) shows only a very weakly split CD because the 1,2 and 2,3 chiralities cancel out, and the 1,3 chirality is "nil". In the 1,2,3-eea tribenzoates (entries 2–4), the readings are large (A = 140) because the three interactions, 1,2, 1,3, and 2,3, all have the same chiralities. In all four cases, it was found that the A values could be estimated from the sum of the three-component dibenzoate units; i.e., an additivity relationship exists. For example, for entry 2 (2e,3e,4a-): +62 (2e,3e;

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[6] Harada, N.; Sato, H.; Nakanishi, K. *J. Chem. Soc., Chem. Commun.* **1970**, 1691.

[7] The amplitude A is taken as a difference in $\Delta\epsilon$ of the split extrema; the sign is defined positive when the first Cotton effect (longer wavelength) is positive and vice versa.

[8] Ogawa, T.; Matsui, M. *Carbohydr. Res.* **1977**, *56*, C1.

[9] Summation of the integrated areas of the split CD curves would have represented a more accurate measurement of the intensities because the shapes of the curves do not necessarily follow a Gaussian distribution pattern.[3b] However, while A values based on $\Delta\epsilon$ values are readily measurable, this is not the case for integrated areas. In Figure 1, the A values rather than the more accurate integrated areas are thus given as the constants.

or unit **1**) + 62 (3e,4a; or unit **3**) + 16 (2e,4a; or unit **7**) = +140 (observed +133).

Entries 5–11 in Table I are tribenzoates involving 6-OBz. As in classes V and VI, the conformations of the 6-benzoates are oriented toward the right or left depending on whether the 4 substituent is equatorial or axial. That this is so was supported by the good agreement between the observed and calculated *A* values in all cases; e.g., for entry 6 (2e,3e,6-): +62 (2e,3e; or unit **1**) – 7(2e,6; or unit **10**) + 11 (3e,6; or unit **9**) = +66 (observed +69).

The additivity relation still holds satisfactorily for the tetrabenzoates (entries 12–16) despite the fact that there are now *six component interactions* (involving also the 6-OBz group), e.g., for entry 14 (2e,3e,4a,6-): +62 (2e,3e; or unit **1**) + 16 (2e,4a; or unit **7**) – 4 (2e,6; or unit **14**) + 62 (3e,4a; or unit **3**) – 9 (3e,6; or unit **13**) – 15(4a,6; or unit **12**) = +112 (observed +100). Although the *A* values for the two anomeric methyl glycosides are usually in good agreement (entries 10/11 and 14/15), this was not so for the methyl glucosides, entries 12/13, in which the ratio of *A* values was 1.33; however, the ratio of the integrated values was satisfactory and was 1.1.[9]

The values summarized in Figure 1 for the various units can be regarded as *constants which are dependent only on the benzoate substitution pattern and are independent of the nature of the pyranose or other substituents.* This aspect together with the fact that only microgram quantities of the sugar derivatives are required forms the basis of a new method for determining oligosaccharide structures currently under investigation. The *A* value additivity relation, which has been found to hold for as many as six interacting units, and which is not confined to the benzoate chromophore, greatly simplifies the interpretations of CD data and also has general applicabilities in the studies of complex natural products.[10,11]

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(10) It has been applied to structural studies of trichilin, a limonoid insect antifeedant (by Dr. M. Nakatani) and a new compound related to ecdysteroids (by Dr. D. A. Trainor): manuscripts in preparation.

(11) The work was supported by NIH Grant CA 11572.

Allylic Rearrangements in the Thermal Decarbonylation of (2-Cyclopropene-1-carbonyl)rhenium Compounds; Nonfluxional η^1-Cyclopropenylrhenium Compounds

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Two examples of fundamental organometallic reaction pathways which have stimulated the attention of synthetic and theoretical chemists involve (a) the migration of σ-bonded organic ligands to and from an adjacent coordinated carbon monoxide ligand[1] and (b) the migration of metals around the periphery of coordinated cyclic polyenyl ligands.[2] The former area is of intense interest because of its crucial role in many homogeneously catalyzed organometallic reactions;[3] in every defined case reported to date such migrations proceed via simple 1,2 shifts. The latter area has generated some controversy concerning the mechanism of metal migrations; the question of whether they are sigmatropic rearrangements which are subject to the constraints of conservation of orbital symmetry[4] or whether a simple least-motion migration pathway for the metal is operative has been raised.[5] η^1-Cyclopentadienyl compounds have been studied extensively; metal migrations around the periphery of the ring are invariably fast on the ^{1}H NMR time scale and have been shown to occur by a sequence of 1,2 shifts for both main group[6] and transition-metal derivatives.[2,5] Unfortunately the 1,2 shift of least motion is indistinguishable from an allowed [1,5]-sigmatropic shift in these molecules. Two examples of such metal migrations in η^1-cycloheptatrienyl compounds have been studied. The main group derivative $SnPh_3(\eta^1\text{-}C_7H_7)$ has been shown to undergo a 1,5 shift,[7] which is not the least motion pathway but which is consistent with an orbital-symmetry-allowed [1,5]-sigmatropic rearrangement. In contrast, $Re(CO)_5(\eta^1\text{-}C_7H_7)$ undergoes a 1,2 shift of the metal,[8] which appears to be consistent with a least motion pathway but which would correspond to a formally forbidden [1,7]-sigmatropic rearrangement were orbital symmetry the sole controlling factor. η^1-Cyclopropenyl compounds represent a class of molecule in which the least motion 1,2 shift pathway for metal migration corresponds to an orbital-symmetry-forbidden [1,3]-sigmatropic rearrangement; yet no studies of the dynamic behavior of such compounds have been reported.[9] This communication details the synthesis and characterization of *nonfluxional* η^1-cyclopropenyl compounds of rhenium; these are formed by clean, quantitative thermal decarbonylations of (2-cyclopropene-1-carbonyl)(pentacarbonyl)rhenium compounds, which proceed exclusively with *allylic rearrangement* of the migrating group.

We have reported previously the reaction of the acyl chloride **1** with $Co(CO)_4^-$ to afford η^3-cyclobutenonyl complexes of cobalt; an unstable acyl(tetracarbonyl)cobalt intermediate was detected in these reactions.[10] A similar reaction of **1** with $Re(CO)_5^-$ (THF, –78 °C), followed by warming to –20 °C and removal of the solvent at this temperature, allows the isolation of the rhenium acyl compound **2**.[11] In contrast to its cobalt analogue, **2** undergoes a smooth thermal decarbonylation in solution at 20 °C[12] to afford quantitatively the η^1-cyclopropenyl compound **3**.[11] Similarly, reaction of the deuterium labeled acyl chloride **4** with $Re(CO)_5^-$ under identical conditions affords the thermally unstable acyl complex **5a**,[11,13] which undergoes rapid decarbonylation at 20 °C to give exclusively **6a**;[11] the analogous conversion of **4b** → **5b** →

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† Alfred P. Sloan Research Fellow, 1980–1982.

(1) For reviews of the CO insertion/extrusion reaction, see: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87–145. (b) Kuhlmann, E. J.; Alexander, J. J. *Coord. Chem. Rev.* **1980**, *33*, 195–225.

(2) For a review, see: Cotton, F. A. In "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; Chapter 10.

(3) For leading references, see ref 1b.

(4) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1971.

(5) Fabian, B. D.; Labinger, J. A. *J. Organomet. Chem.* **1981**, *204*, 387–392 and references cited therein. Free energies of activation for transition-metal migrations in η^1-C_5H_5 systems usually lie in the range of 8–11 kcal·mol^{-1}.[2]

(6) Holmes-Smith, R. D.; Stobart, S. R. *J. Am. Chem. Soc.* **1980**, *102*, 382–384 and references cited therein.

(7) Larrabee, R. B. *J. Am. Chem. Soc.* **1971**, *93*, 1510–1512. Mann, B. E.; Taylor, B. F.; Taylor, N. A.; Wood, R. *J. Organomet. Chem.* **1978**, *162*, 137–144.

(8) Heinekey, D. M.; Graham, W. A. G. *J. Am. Chem. Soc.* **1979**, *101*, 6115–6116. The free energy of activation for this process is $\Delta G^{\ne} = 19.8 \pm 0.1$ kcal·mol^{-1} at 300 K.

(9) Some η^1-cyclopropenyl compounds of iron have been characterized: Gompper, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 456–457. Gompper, R.; Bartmann, E.; Noth, H. *Chem. Ber.* **1979**, *112*, 218–233.

(10) Chidsey, C. E.; Donaldson, W. A.; Hughes, R. P.; Sherwin, P. F. *J. Am. Chem. Soc.* **1979**, *101*, 233–235.

(11) Compound **2** is isolated as pale yellow crystals (30%) after recrystallization: mp 92–94 °C; ν_{CO} (hexane) 2122 w, 2054 w, 2009 vs, 1984 s, 1592 w cm^{-1} ($\nu_{C=C}$ is too weak to be observed); ^{1}H NMR (60 MHz, CDCl$_3$, 20 °C) δ 2.98 (s, CH), 7.37–7.72 (m, Ph); mass spectrum *m/e* 546 (P$^+$, using ^{187}Re). **3**: mp 100–103 °C; ν_{CO} (hexane) 2137 w, 2045 w, 2025 vs, 1993 s cm^{-1}; $\nu_{C=C}$ 1730 cm^{-1}; ^{1}H NMR (CDCl$_3$, 20 °C) δ 6.43 (s, C=CH), 6.98–7.61 (m, Ph); mass spectrum, *m/e* 518 (P$^+$, using ^{187}Re). **5a**: ^{1}H NMR (CDCl$_3$, 20 °C) δ 2.92 (s, CH), 1.15 (s, *t*-Bu). **6a**: ^{1}H NMR (CDCl$_3$, 20 °C) δ 6.20 (s, C=CH), 1.20 (s, *t*-Bu). **6b**: ^{1}H NMR (CDCl$_3$, 20 °C) δ 2.20 (d, *J* = 1.2 Hz, CH), 6.20 (d, *J* = 1.2 Hz, C=CH), 1.20 (s, *t*-Bu). IR and mass spectral data for compounds **5** and **6** are compatible with those quoted for **2** and **3**. Satisfactory microanalysis data have been obtained for all compounds reported.

(12) The rate of decarbonylation is qualitatively faster in more polar solvents. If THF solutions of **2** are warmed to 20 °C the rate of conversion of **2** → **3** is sufficiently fast so as to preclude isolation of pure **2**; **2** is moderately stable in C_6H_6 solution at 20 °C.

(13) Compounds **5** are much more labile toward decarbonylation than is **2**.

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