

*p*-Toluenesulfonylhydrazide (124 mg, 0.67 mmol) and 30 mg (0.20 mmol) of 10 in 1.5 ml of diglyme were heated in a bath at 160° for 18 hr. After cooling, adding water, and extracting with pentane, glc (XF-1150), showed a 1:2 mixture of 10 and its reduction product, *endo*-2-*tert*-butylnorbornane: ir (CCl<sub>4</sub>) 2960, 1395, 1365 cm<sup>-1</sup> (the fingerprint region is clearly different from that of 15); nmr (CCl<sub>4</sub>) δ 0.92 (s, 9 H, *tert*-butyl), 1.1–2.9 (m, 9 H), 2.22 (broad s, 2 H, C-1,4); mass spectrum *m/e* (rel intensity) 152 (M<sup>+</sup>, 0.6), 137 (2.5), 109 (8), 95 (100), 81 (16), 67 (37), 66 (13), 57 (57), 56 (66), 55 (16). Hydrogenation of 10 in ethanol over 30% Pd/C gave the same compound. Less than 1% of 15 was found. Glc (XE-60, 96°) (*t*): 10 (1.00), 15 (1.36), *endo*-2-*tert*-butylnorbornane (1.55).

**Rearrangement of 4.**—A solution of magnesium bromide in ether was prepared by adding 1.80 g (9.6 mmol) of 1,2-dibromoethane in 25 ml of ether dropwise to 0.25 g (10 mmol) of magnesium in 75 ml of ether at reflux. The solution was filtered, sealed under nitrogen with a "No-Air" stopper, and stored at 5°. Compound 4 (200 μl) was added to 12 ml of the magnesium bromide solution. After 80 min at 25° glc showed that the starting material was absent. Water and pentane were added and the organic layer was separated, washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated by distillation of the solvent through a 26 × 1 cm Vigreux column. Glc analysis (XF-1150, 65°) showed three new peaks (*t*, 4 = 1.00): 17 (58%, 1.09), 18 (38%, 1.18), and 19 (4%, 1.44). The products were collected by glc (Carbowax 20M); spectral data are given below. Preliminary reactions established that the product ratios did not change with time. Aluminum chloride, stannic chloride, and mercuric chloride, all in ether, quickly led to complex mixtures as a consequence of subsequent rearrangement of the initial products.

*endo*-5-*tert*-Butylbicyclo[4.1.0]hept-2-ene (17).—Spectral data: ir (CCl<sub>4</sub>) 3060, 3030, 2960, 1635, 1390, 1365, 1025 cm<sup>-1</sup>; uv λ<sub>max</sub> (ethanol) 198 ± 1 nm (ε 5200); nmr (CCl<sub>4</sub>) δ 0.05–0.27 (m, 1 H, *endo* C-7), 0.98 (s, 9 H, *tert*-butyl) superimposed on 0.75–1.50 (m, 4 H), 1.75–2.03 (m, 2 H, C-4), 5.55 (d of t, 1 H, C-3), 5.85 (br d, 1 H, C-2); mass spectrum *m/e* (rel intensity) 150 (M<sup>+</sup>, 2), 135 (5), 107 (7), 94 (22), 93 (20), 91 (19), 83 (18), 80 (19), 79 (49), 78 (15), 77 (20), 57 (100), 55 (15). *Anal.* Calcd for C<sub>11</sub>H<sub>18</sub>: C, 87.93; H, 12.07. Found: C, 88.07; H, 12.11.

3-*tert*-Butylbicyclo[4.1.0]hept-2-ene (18).—Spectral data: ir (CCl<sub>4</sub>) 3065, 3050, 3000, 2960, 1640, 1390, 1365 (d), 1020 cm<sup>-1</sup>; uv λ<sub>max</sub> (ethanol) 204 ± 1 nm (ε 4300); nmr (CCl<sub>4</sub>) δ 0.35 to ~0.8 (m, ~2 H, C-7), 0.98 (s, 9 H, *tert*-butyl) superimposed on

~1.0–1.4 (m, ~2 H), 1.4–2.15 (m, 4 H), 5.72 (m, 1 H, C-2); mass spectrum *m/e* (rel intensity) 150 (M<sup>+</sup>, 21), 135 (50), 107 (54), 94 (35), 93 (48), 91 (31), 79 (48), 77 (26), 57 (100), 55 (22). *Anal.* Calcd for C<sub>11</sub>H<sub>18</sub>: C, 87.93; H, 12.07. Found: C, 87.95; H, 12.13.

*exo*-5-*tert*-Butylbicyclo[4.1.0]hept-2-ene (19).—Spectral data: ir (CCl<sub>4</sub>) 3065, 3035, 3000, 2960, 1645, 1395, 1365, 1025 cm<sup>-1</sup>; uv λ<sub>max</sub> (ethanol) 202 ± 1 nm (ε 4800); nmr (CCl<sub>4</sub>) δ 0.30 to ~0.9 (m, 2 H, C-7), 0.97 (s, 9 H, *tert*-butyl) superimposed on ~1.0–2.1 (m, 5 H), 5.30 (m, 1 H), 5.90 (m, 1 H); mass spectrum *m/e* (rel intensity) 150 (M<sup>+</sup>, 6), 135 (6), 107 (8), 94 (16), 93 (22), 91 (15), 79 (26), 77 (15), 57 (100).

**Rearrangement of 5.**—Compound 5 (120 μl) was added to 15 ml of 0.1 M magnesium bromide in ether. After 4 days at 25°, the mixture was worked up as above. Glc (XF-1150, 65°) showed the absence of 5 and two new peaks (*t*, 5 = 1.00), 20 (92%, 1.06) and 21 (8%, 1.26), which were collected; spectral data are given below. The same ratios were observed at shorter times when the rearrangement was incomplete.

*exo*-4-*tert*-Butylbicyclo[4.1.0]hept-2-ene (20).—Spectral data: ir (CCl<sub>4</sub>) 3060, 3030, 2995, 2960, 1630, 1395, 1365, 1020 cm<sup>-1</sup>; uv λ<sub>max</sub> (ethanol) 198 ± 1 nm (ε 4800); nmr (CCl<sub>4</sub>) δ -0.15 to +0.05 (m, 1 H, *endo* C-7) 0.83 (s, 9 H, *tert*-butyl) superimposed on ~0.8–1.3 (m, 4 H), 1.6–2.4 (m, 2 H), 5.60 and 5.90 (two d, part of AB q centered at 5.75, 2 H, C-2,3); mass spectrum *m/e* (rel intensity) 152 (M<sup>+</sup>, 2), 135 (1), 107 (4), 94 (20), 93 (100), 92 (16), 91 (25), 79 (19), 77 (27), 57 (68). *Anal.* Calcd for C<sub>11</sub>H<sub>18</sub>: C, 87.93; H, 12.07. Found: C, 88.12; H, 12.21.

*endo*-4-*tert*-Butylbicyclo[4.1.0]hept-2-ene (21).—Spectral data: ir 3065, 3030, 3000, 2960, 1635, 1395, 1365, 1020, cm<sup>-1</sup>; uv λ<sub>max</sub> (ethanol) 203 ± 1 nm (ε 5600); nmr (CCl<sub>4</sub>) δ 0.4–0.8 (m, 2 H, C-7), 0.85 (s, 9 H, *tert*-butyl) superimposed on 0.9–2.2 (m, 5 H), ~5.3 (m, 1 H), ~5.9 (m, 1 H); mass spectrum *m/e* (rel intensity) 150 (M<sup>+</sup>, 1), 135 (2), 107 (2), 94 (16), 93 (100), 92 (11), 91 (26), 79 (22), 77 (29), 57 (93).

**Registry No.**—2, 29339-27-3; 3, 29339-28-4; 4, 29339-29-5; 5, 29339-30-8; 8, 29339-31-9; 9, 29339-32-0; 10, 29339-33-1; 11, 29339-34-2; 15, 1125-54-8; 17, 29339-36-4; 18, 29339-37-5; 19, 29339-38-6; 20, 29339-39-7; 21, 29339-40-0; 2-*tert*-butyl-2-hydroxynorbornane, 29339-41-1.

## Palladium(II)-Catalyzed Aromatic Substitution<sup>1</sup>

P. M. HENRY

Research Center, Hercules Incorporated, Wilmington, Delaware 19899

Received November 5, 1970

Pd(II) salts in the presence of nucleophiles (X<sup>-</sup>) oxidize aromatics or mercurated aromatics to coupled aromatics. With phenylmercury salts the reaction is 2PhHg<sup>+</sup> + Pd<sup>II</sup> + X<sup>-</sup> → Ph<sub>2</sub> + Pd<sup>0</sup> + 2Hg<sup>2+</sup> + X<sup>-</sup>. However, if certain oxidants are added to the reaction mixture, the course of the reaction changes to give substituted aromatics: PhHg<sup>+</sup> + Pd<sup>II</sup> + X<sup>-</sup> (+ Ox.) → PhX + Hg<sup>2+</sup> + Pd<sup>II</sup>. Examples of the reaction were obtained for OAc<sup>-</sup>, N<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, CN<sup>-</sup>, and SCN<sup>-</sup> as nucleophiles; Cr(VI), Pb(OAc)<sub>4</sub>, NaClO<sub>3</sub>, KMnO<sub>4</sub>, NaNO<sub>3</sub>, and NaNO<sub>2</sub> as oxidants; and benzene, toluene, phenyl acetate, and mercurated benzene and toluene as aromatic substrates. Acetic acid was generally used as solvent, but in some cases acetonitrile and nitrobenzene were used. The reaction gives a substitution pattern characteristic of an electrophilic substitution reaction. The reaction most likely proceeds either *via* a Pd(II) aryl or by generation of a Pd(IV) species by the oxidant, followed by attack of the Pd(IV) species on the aromatic substrate.

Although direct hydroxylations or acetoxylation of benzenoid compounds do not occur readily,<sup>2</sup> several metal ion catalyzed direct substitution reactions involving Fe(II)<sup>3</sup> and Pb(IV)<sup>4–6</sup> have recently been

reported. This paper will describe a Pd(II)-catalyzed direct aromatic substitution not only of acetate but of other groups as well.

The possibility that Pd(II) will catalyze the oxidation of aromatic compounds by inorganic oxidants is suggested by our previous work on the Pd(II)-catalyzed oxidation of olefins in the presence of such oxidants. It has been previously reported<sup>7</sup> that Cu(II) changes the nature of olefin oxidations by Pd(II). Thus, in

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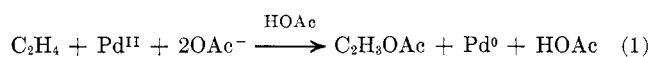
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TABLE I  
 OXIDATION OF BENZENE OR PHENYLMERCURIC ACETATE BY A COMBINATION OF Pd(OAc)<sub>2</sub>  
 AND K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> IN ACETIC ACID AT 90°<sup>a</sup>

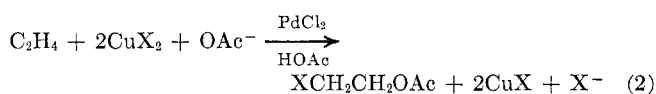
| Expt no. | Pd(OAc) <sub>2</sub> , mmol | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , mmol | Aromatic, (mmol) | Other reagents (mmol)                 | Time, hr | Phenyl acetate, mmol | Biphenyl, mmol |
|----------|-----------------------------|--|------------------|---------------------------------------|----------|----------------------|----------------|
| 1        | 1.0                         | 15   | PhHgOAc (10)     | LiOAc (25)                            | 24       | 0.5                  | 0.06           |
| 2        | 1.0                         | 15   | Benzene (10)     | LiOAc (25)                            | 23       | 1.45                 | <0.015         |
| 3        | None                        | 15   | Benzene (10)     | LiOAc (25)                            | 23       | <0.01                | <0.02          |
| 4        | 1.0                         | None   | PhHgOAc (10)     | LiOAc (25)                            | 23       | <0.05                | 0.95           |
| 5        | 0.5                         | 15   | Benzene (33)     | CH <sub>3</sub> SO <sub>3</sub> H (3) | 16       | 2.03                 | <0.015         |
| 6        | 1.0                         | 15   | Benzene (55)     | Hg(OAc) <sub>2</sub> (3)              | 20       | 1.35                 | <0.02          |
| 7        | 1.0                         | 15   | Benzene (55)     | Hg(OAc) <sub>2</sub> (3)              | 40       | 1.35                 | <0.02          |

<sup>a</sup> All contain 25 ml of acetic acid.

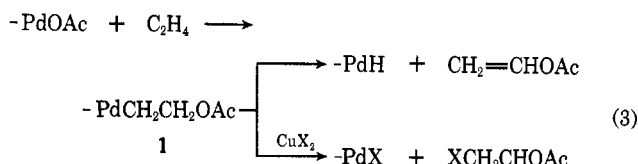
the absence of Cu(II), Pd(II) in acetic acid oxidizes ethylene to vinyl acetate.



However, if Cu(II) is added 1,2-disubstituted ethanes are also formed (X = OAc or Cl).



The most reasonable mechanism for the result<sup>7</sup> is that the reactions producing vinyl acetate and saturated esters proceed through a common acetoxy-palladation adduct, 1, and Cu(II) is capable of changing the mode



of decomposition of the intermediate. It has been demonstrated that NO<sub>3</sub><sup>-</sup><sup>8</sup> as well as other oxidants<sup>9</sup> can be used in place of Cu(II).

If oxidants can cause Pd(II) aryls to decompose with substitution, it seems possible that Pd(II) aryls can also be made to decompose with substitution. Pd(II) aryls have been postulated to be intermediates in several Pd(II)-catalyzed reactions such as carbonylation,<sup>10</sup> olefin arylation,<sup>11</sup> and oxidative coupling.<sup>12,13</sup> This work was undertaken to test this hypothesis.

Under certain conditions, Pd(OAc)<sub>2</sub> is reported to give phenyl acetate.<sup>14</sup> However, this reaction is inhibited by oxygen and apparently has radical character.

One specific example of the general reaction described in this paper, the Pd(II)-catalyzed nitration of benzene, has previously been reported.<sup>15</sup> However, the necessity for an oxidant in order for the reaction to proceed was apparently not recognized.

## Results

In the initial work, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was used as the oxidant. As the results in Table I show, this oxidant in the

presence of Pd(OAc)<sub>2</sub> will indeed give phenyl acetate. Control experiments showed that, in the absence of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, as expected, only biphenyl is produced (expt 4); in the absence of Pd(OAc)<sub>2</sub> (expt 3), neither is formed. Note that the addition of oxidant actually inhibits the formation of biphenyl (compare expt 1 and 4). The benzene was initially introduced as phenylmercuric acetate, but it was later found that benzene itself worked as well. Addition of Hg(OAc)<sub>2</sub> did not improve the yield (expt 2 and 6). Neither did running the reaction for longer periods of time (expt 6 and 7). Control experiments indicated phenyl acetate gradually disappeared under the reaction conditions. The reaction was definitely catalytic in Pd(II). In expt 5, 4 mol of product per mole of Pd(II) was formed. The reaction mixtures of Table I were heterogeneous because of limited solubility of the metal salts.

A number of oxidants other than K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> were tested on benzene. Results are listed in Table II.

TABLE II  
 TEST OF VARIOUS OXIDANTS FOR PHENYL ACETATE  
 PRODUCTION FROM BENZENE<sup>a</sup>

| Pd(OAc) <sub>2</sub> , mmol | Oxidant                         | Phenyl acetate, mmol |
|-----------------------------|---------------------------------|----------------------|
| 1.0                         | Tl(OAc) <sub>3</sub>            | <0.01                |
| 1.0                         | Pb(OAc) <sub>4</sub>            | 0.51                 |
| ...                         | Pb(OAc) <sub>4</sub>            | <0.01                |
| 1.0                         | MnO <sub>2</sub>                | <0.01                |
| 1.0                         | KMnO <sub>4</sub>               | 0.27                 |
| ...                         | KMnO <sub>4</sub>               | <0.01                |
| 1.0                         | CrO <sub>3</sub>                | 0.25                 |
| ...                         | CrO <sub>3</sub>                | <0.01                |
| 1.0                         | V <sub>2</sub> O <sub>5</sub>   | <0.01                |
| 1.0                         | Pb <sub>3</sub> O <sub>4</sub>  | <0.01                |
| 1.0                         | NaNO <sub>3</sub> <sup>b</sup>  | 0.14                 |
| ...                         | NaNO <sub>3</sub>               | <0.01                |
| 1.0                         | NaNO <sub>2</sub> <sup>b</sup>  | 0.08                 |
| ...                         | NaNO <sub>2</sub>               | <0.01                |
| 1.0                         | CuCl <sub>2</sub>               | <0.01                |
| 1.0                         | NaClO <sub>3</sub> <sup>c</sup> | 0.09                 |
| ...                         | NaClO <sub>3</sub>              | <0.01                |

<sup>a</sup> All reaction mixtures contain 25 ml of acetic acid, 10 mmol of the oxidant, 33 mmol of benzenes, and 3 mmol of CH<sub>3</sub>SO<sub>3</sub>H. Run 20 hr at 90°. <sup>b</sup> Nitrobenzene (ca. 0.1 mmol) also present. <sup>c</sup> Chlorobenzene (1.65 mmol) also present.

Pb(OAc)<sub>4</sub>, KMnO<sub>4</sub>, CrO<sub>3</sub>, NaNO<sub>3</sub>, and NaClO<sub>3</sub> gave at least some phenyl acetate while the others gave no detectable amount. Some, such as Pb<sub>3</sub>O<sub>4</sub>, may have failed owing to insolubility in the reaction medium. If Pd(II) plus oxidant gave the reaction, controls were run to show that the oxidant itself did not oxidize benzene to phenyl acetate. When NaNO<sub>3</sub> and NaNO<sub>2</sub>

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TABLE III  
 SUBSTITUTION OF AROMATICS WITH NUCLEOPHILES OTHER THAN ACETATE<sup>a</sup>

| Salt (mmol)  | Nucleophile (mmol)    | Aromatic (mmol) | Oxidant (mmol)                                     | Solvent <sup>b</sup> | Products (mmol)   |
|--|-----------------------|-----------------|--|----------------------|---|
| Pd(OAc) <sub>2</sub> (1.0)                         | LiCl (25)             | PhHgOAc (10)    | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (15) | HOAc                 | PhCl (1.56) <sup>c</sup>  |
|  | LiCl (25)             | PhHgOAc (10)    | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (15) | HOAc                 | PhCl (0.17) <sup>c</sup>  |
| Pd(OAc) <sub>2</sub> (1.0)                         | LiBr (25)             | PhHgOAc (10)    | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (15) | HOAc                 | PhBr (1.2) <sup>c</sup>   |
|  | LiBr (25)             | PhHgOAc (10)    | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (15) | HOAc                 | PhBr (1.07) <sup>c</sup>  |
| Pd(OAc) <sub>2</sub> (1.0)                         | LiF (25)              | PhHgOAc (10)    | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (15) | HOAc                 | PhOAc (0.33),<br>PhF (<0.02)  |
| Pd(OAc) <sub>2</sub> (1.0)                         | LiN <sub>3</sub> (25) | PhHgOAc (10)    | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (15) | HOAc                 | PhOAc (0.19),<br>PhN <sub>3</sub> (0.4)                               |
|  | LiN <sub>3</sub> (25) | PhHgOAc (10)    | K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (15) | HOAc                 | PhN <sub>3</sub> (0.2)  |
| Pd(OAc) <sub>2</sub> (1.0)                         | LiN <sub>3</sub> (25) | PhHgOAc (10)    | Pb(OAc) <sub>4</sub> (10)                          | HOAc                 | PhOAc (0.13),<br>PhN <sub>3</sub> (0.77)                              |
|  | LiN <sub>3</sub> (25) | PhHgOAc (10)    | Pb(OAc) <sub>4</sub> (10)                          | HOAc                 | PhOAc (0.13),<br>PhN <sub>3</sub> (0.015)                             |
| Pd(OAc) <sub>2</sub> (1.0)                         | NaSCN (10)            | PhHgOAc (10)    | Pb(OAc) <sub>4</sub> (10)                          | CH <sub>3</sub> CN   | PhOAc (4.75),<br>PhSCN (0.94),<br>Ph <sub>2</sub> (2.66)              |
| Pd(OAc) <sub>2</sub> (1.0)                         | NaCNO (43)            | PhHgOAc (10)    | Pb(OAc) <sub>4</sub> (10)                          | CH <sub>3</sub> CN   | PhNCO (<0.01)   |
| Pd(OAc) <sub>2</sub> (1.0)                         | NaCN (50)             | PhHgOAc (10)    | Pb(OAc) <sub>4</sub> (10)                          | CH <sub>3</sub> CN   | PhCN (0.18) <sup>c</sup>  |
| Pd(OAc) <sub>2</sub> (1.0)                         |                       | PhOAc (10)      | NaClO <sub>3</sub> (10)                            | HOAc                 | Chlorophenyl<br>acetate (0.79),<br>47% ortho,<br>47% para,<br>6% meta |
| K <sub>2</sub> Pd <sub>2</sub> Cl <sub>6</sub> (5) |                       | PhHgOAc (5)     |  | HOAc                 | PhOAc (0.14), <sup>d</sup><br>PhCl (1.55)                             |

<sup>a</sup> Reaction condition 90° for 18–22 hr when HOAc is solvent. Temperature was 75° when CH<sub>3</sub>CN was solvent. <sup>b</sup> 25 ml of solvent used for all runs but the last run for which 10 ml was used. <sup>c</sup> <0.01 mmol of PhOAc present. <sup>d</sup> Some dichlorobenzenes also present.

 TABLE IV  
 PREPARATION OF CRESOL ACETATES BY OXIDATION OF TOLUENE BY Pd(OAc)<sub>2</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> IN ACETIC ACID<sup>a</sup>

| Pd(OAc) <sub>2</sub> ,<br>mmol | Aromatic (mmol)           | Other reagents<br>(mmol)                 | Reaction<br>conditions | Cresol<br>acetate,<br>mmol | Distribution, % |      |      |
|--------------------------------|---------------------------|--|------------------------|----------------------------|-----------------|------|------|
|                                |                           |  |                        |                            | Ortho           | Meta | Para |
| 0.5                            | Toluene (32)              | 3CH <sub>3</sub> SO <sub>3</sub> H (3.1) | 16 hr at 90°           | 1.0 <sup>b</sup>           | 19              | 62   | 19   |
| 0.5                            | Toluene (32)              | Hg(OAc) <sub>2</sub> (3)                 | 16 hr at 90°           | 1.95 <sup>c,d</sup>        | 12              | 39   | 49   |
| 1.0                            | <i>p</i> -TolylHgOAc (20) | LiOAc (25)                               | 16 hr at 90°           | 0.4 <sup>d</sup>           | 0               | 0    | 100  |
| 0.5                            | Toluene (32)              | CH <sub>3</sub> SO <sub>3</sub> H (3.1)  | 19 hr at 50°           | 0.082 <sup>d</sup>         | 5               | 19   | 76   |
| 0.5                            | Toluene (32)              | Hg(OAc) <sub>2</sub> (3)                 | 22 hr at 50°           | 0.16 <sup>d</sup>          | 6               | 19   | 75   |

<sup>a</sup> K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (15 mmol) and acetic acid (25 ml) used. <sup>b</sup> Benzyl acetate (0.03 mmol) also formed. <sup>c</sup> Bitolyl (0.23 mmol) also formed; mainly 3,3, 3,4, and 4,4. <sup>d</sup> No benzyl acetate detected. Limit of detection 1% of total acetate product.

were used as oxidants, a second product, nitrobenzene, was formed and NaClO<sub>3</sub> gave chlorobenzene. This result suggested other nucleophiles than acetate could be substituted on the aromatic ring. Table III gives the results of experiments using other nucleophiles. LiCl, LiBr, LiN<sub>3</sub>, NaSCN, and NaCN gave substitution while LiF and NaCNO did not. The failure of NaCNO could be due to solubility. LiBr and LiN<sub>3</sub> also gave substitution in the absence of Pd(II) with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as the oxidant; so in these cases substitution was most likely not Pd(II)-catalyzed but results from oxidation of the Br<sup>-</sup> or N<sub>3</sub><sup>-</sup> to radicals or cations. However, when Pb(OAc)<sub>4</sub> was used as oxidant with LiN<sub>3</sub>, only traces of phenyl azide were formed in the absence of Pd(II).

A limited number of aromatics were tested for the substitution reaction. As shown in Table III, phenyl acetate did give chlorophenyl acetates in an isomer ratio characteristic of an electrophilic substitution. Attempts to produce diacetoxybenzenes from phenyl acetate met with little success because the phenyl acetate was consumed in side reactions. Only traces of diacetoxybenzenes, mainly hydroquinone diacetate,

were formed. When equal amounts of benzene and nitrobenzene were oxidized in acetic acid, less than 0.01 mmol of nitrophenyl acetate was formed although 1.43 mmol of phenyl acetate was present.

The results of several experiments aimed at producing cresol acetates from toluene are given in Table IV. At 90°, Pd(OAc)<sub>2</sub> gave a distribution with high amount of meta isomer. Little, if any, benzyl acetate was formed in these reactions. Addition of Hg(OAc)<sub>2</sub>, however, increased the *p*-cresol acetate ratio as well as the conversion. Lowering the temperature also increased the para isomer, and, if pure *p*-tolylmercuric acetate was used as aromatic, only *p*-cresol acetate was formed.

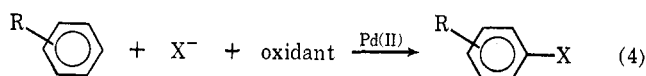
Acetic acid was generally used as solvent because most of the inorganic salts were at least partially soluble in this solvent. Acetonitrile was not quite so effective as acetic acid when K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was the oxidant but was better than acetic acid when Pb(OAc)<sub>4</sub> was the oxidant. Dimethylformamide and nitrobenzene gave little or no reaction.

Finally, Table V gives the results of a study of possible replacements for Pd(II). All the metal salts

gave less than 10% of the conversion to phenyl acetate obtained with PdCl<sub>2</sub> under comparable reaction conditions.

### Discussion

The present work describes a new quite general aromatic substitution reaction (eq 4). Substitution

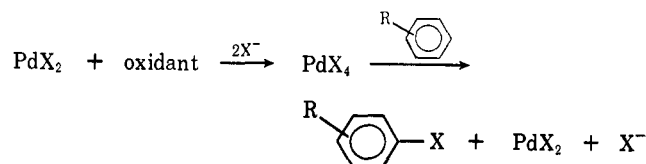


products have been obtained for X<sup>-</sup> = OAc<sup>-</sup>, N<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, CN<sup>-</sup>, and SCN<sup>-</sup> and for K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, Pb(OAc)<sub>4</sub>, KMnO<sub>4</sub>, NaClO<sub>3</sub>, NaNO<sub>3</sub>, and NaNO<sub>2</sub> as oxidants. Benzene, toluene, phenyl acetate, and mercurated benzene and toluene have been used as aromatic reactants. Other combinations of oxidants, nucleophiles, and aromatics very likely will give the reaction, especially if nonhydroxylic solvents which will dissolve all the reagents can be found. Because of its solubility in organic solvents Pb(OAc)<sub>4</sub> appears to be the most generally useful oxidant. Of course Pd(OAc)<sub>4</sub> itself will acetoxylation activated aromatics such as anisole but not benzene or toluene.<sup>4</sup> Control experiments (see Table II) indicated that no acetoxylation of benzene occurred in the absence of Pd(II).

Unfortunately, the usefulness of the reaction is limited by slow rates, side reactions, and the need for expensive oxidizing agents. However, it could be the preferred means of producing substituted aromatics which are not readily available by other means. This is especially true if the substituted aromatic formed in the reaction is deactivated so it will not undergo that further reaction.

The present work does not permit the proposal of a definite mechanism but some observation concerning mechanisms can be made. It does not appear related to the radical-type acetoxylation by Pd(OAc)<sub>2</sub> alone<sup>14</sup> since the present reaction gave cresol acetates with toluene while benzyl acetates were obtained in the radical reaction. Except for Br<sup>-</sup> and N<sub>3</sub><sup>-</sup> with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, the reaction cannot proceed by oxidation of X<sup>-</sup> to reactive X· or X<sup>+</sup> species since control experiments demonstrated that in the other cases Pd(II) is required. The reaction gives substitution patterns consistent with an electrophilic substitution. The lack of reactivity of nitrobenzene is also consistent with an electrophilic reaction.

One of the two most likely mechanisms for the reaction appear to be (1) oxidation of Pd(II) to Pd(IV) followed by attack of the Pd(IV) on the aromatic.



Support for this scheme comes from the fact that Pd(IV) will oxidize aromatics to the observed products. Also HNO<sub>3</sub> is reported to oxidize Pd(II) to Pd(IV) salts.<sup>16</sup> Furthermore, CuCl<sub>2</sub> which causes Pd(II) alkyls to decompose does not give the aromatic sub-

(16) C. C. Addison and B. G. Ward, *Chem. Commun.*, 155 (1966).

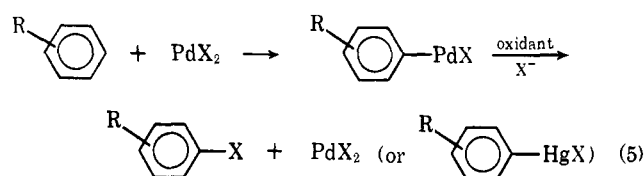
TABLE V  
SUBSTITUTES FOR Pd(II) IN THE AROMATIC  
SUBSTITUTION REACTION<sup>a</sup>

| Metal salt        | PhOAc (mmol) | Metal salt        | PhOAc (mmol) |
|-------------------|--------------|-------------------|--------------|
| PtCl <sub>2</sub> | 0.098        | OsCl <sub>3</sub> | 0.072        |
| RhCl <sub>3</sub> | 0.010        | IrCl <sub>3</sub> | <0.005       |
| RuCl <sub>3</sub> | 0.11         | AgOAc             | 0.026        |

<sup>a</sup> All reaction mixtures contain 15 mmol of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 25 mmol of PhHgOAc, 25 mmol of LiOAc, and 25 ml of HOAc. Most reaction mixtures contained some biphenyl product.

stitution. The reason for this could be that CuCl<sub>2</sub> is not a vigorous enough oxidizing agent to convert Pd(II) to Pd(IV). Thus the oxidation potential of PdCl<sub>6</sub><sup>2-</sup> in aqueous solution has been estimated to be about 1.20 V<sup>17</sup> while that for CuCl<sub>2</sub> is only about 0.54 V.<sup>18</sup> On the other hand, the successful oxidants in Table II have potentials in aqueous systems which are close to those of PdCl<sub>6</sub><sup>2-</sup>. Of course there is considerable uncertainty as to the actual potentials in the reaction systems.

The second mechanism is (2) formation of a Pd(II) aryl by direct substitution or exchange with a Hg(II) aryl. The Pd(II) aryl is decomposed by the oxidant to give substitution products (eq 5). The role of the



oxidant in this mechanism is uncertain but it must somehow participate in the decomposition step since control experiments demonstrate that X<sup>-</sup> will not attack the Pd(II) aryl in the absence of oxidant. Rather the Pd(II) aryl decomposes to biphenyl. The oxidant most likely causes decomposition by removal of electrons from the Pd(II) simultaneous with attack of X<sup>-</sup> on the Pd(II)-carbon bond. As discussed in the introduction, this mechanism is consistent with that previously proposed for decomposition of Pd(II) alkyls for which there is evidence that Pd(IV) species are not involved.<sup>9</sup>

The fact that CuCl<sub>2</sub> does not give the aromatic substitution reaction does not rule out mechanism 2 since it is quite reasonable that Pd(II) aryls are more stable than Pd(II) alkyls and require stronger oxidants to decompose them. The almost complete elimination of biphenyl as a product (compare expt 1 and 4 in Table I) would not be predicted by the first mechanism unless all the Pd(II) had been converted to Pd(IV). This result is expected, however; the Pd(II) aryl is intercepted by the oxidant before it can decompose to biphenyl.

### Experimental Section

**Reagents.**—Palladium(II) chloride was purchased from Engelhardt Industries, Inc. The thallic acetate was prepared as described earlier.<sup>19</sup> Hydroquinone diacetate was prepared by

(17) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1952 p 203.

(18) Reference 17, p 186.

(19) P. M. Henry, *J. Amer. Chem. Soc.*, **88**, 1597 (1966).

acetylating hydroquinone. The tetraacetate was purchased from K & K Laboratories, Inc.

**Analyses.**—All analyses were by vapor phase chromatography (vpc). Before analysis, all runs using acetic acid as solvent were diluted with  $\text{CH}_2\text{Cl}_2$ , and the organic phase was washed several times with water, dried, and concentrated to a known volume. Runs using other solvents were usually injected directly. Most reaction mixtures were analyzed using a 6-ft column packed with 20% Carbowax 20M on an 70–80 mesh ABS support. The temperature was programmed from 80 to 200° at a rate of 7.5°/min. The helium flow rate was 60 ml/min. Biphenyl analyses were carried out using a 6-ft Apiezon N on ABS, 15% 90–100 mesh. The temperature was 210° and the flow rate was 60 ml/min. Bitolyl analyses were carried out on the same column at 230°. Cresol acetate analyses were carried out using a 12 ft  $\times$   $3/16$  in diisodecyl phthalate, tri-*p*-tolyl phosphate trimer acid on G as Chrom 2, 5 g/95 g at 140°. The flow rate was 60 ml/min. The benzyl acetate and *m*-cresol acetate were not resolved on this column and the capacity was too low to allow this peak to be collected for nmr. However, the per cent of benzyl acetate compared to total acetate product was determined by the nmr of the reaction mixture. In the phenyl acetate oxidation both the phenyl acetate and diacetoxybenzenes were analyzed using the

6-ft Apiezon N programmed from 150 to 250° at 7.5°/min; the flow rate was 60 ml/min. These same conditions were used for phenyl isothiocyanate and benzonitrile analyses.

**Identification of Products.**—The phenyl acetate, phenyl azide, nitrobenzene were identified by vpc retention time as well as by collection from the vpc eluent followed by infrared in a microcell. The chlorobenzene was identified by vpc retention time and mass spectrometer analysis. The infrared spectrum of the phenyl isothiocyanate reaction mixture indicated this product was present. This was further confirmed by vpc retention time. Benzonitrile was identified by vpc retention time alone since there was not enough material for collection. The absence of phenyl isocyanate was demonstrated by adding ethanol to the reaction mixture followed by analysis for phenylurethane using the 6-ft Apiezon N at 230°. Fortification with an authentic sample demonstrated that none was present.

**Registry No.**—Benzene, 71-43-2; phenylmercuric acetate, 62-38-4; toluene, 108-88-3;  $\text{Pd}(\text{OAc})_2$ , 3375-31-3;  $\text{K}_2\text{Cr}_2\text{O}_7$ , 7778-50-9.

**Acknowledgment.**—The author gratefully acknowledges the excellent technical assistance of Mr. F. Kriss.

## Oxidation of Organic Compounds with Cerium(IV). XII. Oxidative Cleavage and Ketone Formation of Alkylphenylcarbinols<sup>1</sup>

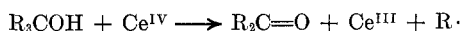
WALTER S. TRAHANOVSKY\*<sup>1c</sup> AND JÜRGEN CRAMER

*Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010*

*Received January 7, 1971*

Products from the oxidation of methyl-, ethyl-, isopropyl-, and *tert*-butylphenylcarbinols by 2 equiv of ceric ammonium nitrate in 50% aqueous acetonitrile at 90° are reported. The relative rates of oxidative cleavage to formation of the corresponding carbonyl compound are given by the ratios of benzaldehyde to alkyl phenyl ketone that were obtained from the alkylphenylcarbinols. These ratios are 0.04, 3.30, 184, and 195 for the methyl-, ethyl-, isopropyl-, and *tert*-butylphenylcarbinols, respectively. Previously reported results indicate that the cerium(IV) oxidative cleavage of alcohols is a one-electron oxidation, and the present results suggest that oxidative cleavage of an alcohol by cerium(IV) will occur if a radical as stable as a secondary carbon radical is produced by cleavage. The corresponding alkyl nitrates are the main products obtained from the ethyl and isopropyl radicals, but no *tert*-butyl nitrate from the *tert*-butyl radical is reported. It is proposed that the *tert*-butyl radical is oxidized to isobutylene.

Oxidations of alcohols by cerium(IV) tend to be oxidative cleavages, not reactions that form the corresponding carbonyl compounds.<sup>1a,2</sup> For example, none of the corresponding ketones were obtained from the cerium(IV) oxidation of 1,2-diarylethanol,<sup>1a,3</sup> *exo*- and *endo*-bicyclo[2.2.1]heptan-2-ol,<sup>2</sup> or bicyclo[2.2.2]octan-2-ol.<sup>2</sup> These oxidative cleavages have been shown to be one-electron oxidations which involve the formation of an intermediate radical.<sup>1a,2,3</sup> Moreover,



it has been shown that the rate of cleavage is dependent on the stability of the radical, and, in the transition state that leads to cleavage, a fair amount of positive charge develops on the fragment which becomes the radical.<sup>1a,3</sup>

(1) (a) Part XI: P. M. Nave and W. S. Trahanovsky, *J. Amer. Chem. Soc.*, in press. (b) This work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences and Grant GP-18031 from the National Science Foundation. We thank these organizations for their support. (c) Alfred P. Sloan Research Fellow, 1970–1972. (d) Preliminary communication: Abstracts of the Joint Chemical Institute of Canada–American Chemical Society Conference, Toronto, May 1970, PHYS 31.

(2) W. S. Trahanovsky, P. J. Flash, and L. M. Smith, *J. Amer. Chem. Soc.*, **91**, 5068 (1969).

(3) P. M. Nave and W. S. Trahanovsky, *ibid.*, **90**, 4755 (1968).

In two cases, benzyl alcohols<sup>4</sup> and cyclopropanemethanol,<sup>5</sup> the alcohol is oxidized to the corresponding aldehyde by cerium(IV). In both of these cases, the carbon radicals which would have to be formed during the cleavage reaction, substituted phenyl and cyclopropyl radicals, are relatively unstable. Evidently, when the radical which must be formed is unstable enough, another process takes over which leads to the corresponding carbonyl compound. In order to better define the stability of the radical needed for cleavage to occur, we studied a series of alkylphenylcarbinols in which the alkyl groups were methyl, ethyl, isopropyl, and *tert*-butyl with particular attention being paid to the relative rates of cleavage to ketone formation. This paper reports the results of this study.

### Results

Methyl-, ethyl-, isopropyl-, and *tert*-butylphenylcarbinols were oxidized by 2 equiv of ceric ammonium nitrate (CAN) in 50% aqueous acetonitrile at 90°. The oxidations took 1.5–6 min. The absolute yields of the recovered starting material and products were

(4) (a) W. S. Trahanovsky and L. B. Young, *J. Chem. Soc.*, 5777 (1965); (b) W. S. Trahanovsky, L. R. Young, and G. L. Brown, *J. Org. Chem.*, **32**, 3865 (1967).

(5) L. B. Young and W. S. Trahanovsky, *ibid.*, **32**, 2349 (1967).