those for 2-epizizaene<sup>9</sup> (e.g., in 2-epizizaene the C-2 methyl group is at  $\delta$  0.87;  $M_r$  calcd for  $C_{15}H_{24}$  204.1878, found 204.1874.

**Mesylate 6.** 3-Epizizanol (1) (95 mg, 0.43 mmol) was treated with mesyl chloride (0.4 mL, 5.17 mmol) in pyridine (8 mL) as described for the preparation of mesylate **5**. Separation of the crude product on HPLC yielded 102 mg of mesylate **6** (79%): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.06 (s, 3), 1.06 (d, 3, J = 7 Hz), 1.10 (s, 3), 1.25–2.55 (m, 10), 2.88 (mt, 1, J = 9 Hz), 3.01 (s, 3), 4.60 (br s, 1), 4.82 (br s, 1), 5.17 (dt, 1, J = 3.5 and 9 Hz); IR (CHCl<sub>3</sub>) 3085, 1630, 1350, 1325, 1170 cm<sup>-1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  155.25, 105.58, 83.95, 53.87, 48.70, 45.35, 45.09, 40.45, 38.16, 36.15, 32.49, 32.41, 28.44, 26.06, 25.84, 12.08; mass spectrum, m/e (relative intensity) 298 (weak, M<sup>+</sup>), 202 (16), 187 (23), 159 (29), 145 (19), 131 (37), 119 (16), 105 (22), 91 (30), 79 (23);  $M_r$  calcd for C<sub>16</sub>H<sub>26</sub>O<sub>3</sub>S 298.1603; found 298.1613.

Phenylselenyl Compound 7 and Diene 9. Sodium borohydride (35 mg, 0.9 mmol) was stirred with diphenvl diselenide (140 mg, 0.45 mmol) in 15 mL of ethanol to generate the colorless phenylselenide anion. Mesylate 5 (270 mg, 0.91 mmol) was added to the phenylselenide anion and then heated at reflux for 12 h. After 0.5 mL of water was added to the mixture, the ethanol was evaporated in vacuo. The residue was passed through silica gel and separated by HPLC (SKB/EtOAc = 30/1) to yield 38 mg of starting material 5 and the phenylselenyl compound 7 which was a little contaminated with PhSeX (presumably, X = H). Without further purification, the phenylselenyl compound 7 was heated at reflux with sodium periodate (2.00 g, 9.35 mmol) and sodium bicarbonate (400 mg, 4.76 mmol) in 20 mL of THF and 2 mL of water for 13 h. Normal workup and separation of the crude product on HPLC (SKB/EtOAc = 30/1) yielded 118 mg of a colorless oil, diene 9 (64%). Compound 7: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.06 (s, 6), 1.08 (d, 3, J = 6 Hz), 1.2–2.6 (m, 10), 2.86 (mt, 1, J= 9 Hz), 3.88 (td, 1, J = 6.5 and 9 Hz), 4.60 (m, 1), 4.79 (m, 1), 7.1-7.4 (m, 3), 7.4-7.8 (m, 2); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 156.15, 132.60, 131.59, 129.15, 128.93, 127.70, 126.47, 105.41, 55.27, 49.00, 45.63 (3 carbons), 40.49, 36.42, 33.40, 31.99, 28.66, 26.27, 26.05, 15.88; mass spectrum, m/e (relative intensity) 360 (weak, M<sup>+</sup>), 289 (1), 202 (2), 187 (1), 159 (2), 131 (3), 91 (2), 73 (2); M<sub>r</sub> calcd for C<sub>21</sub>H<sub>28</sub>Se 360.1356; found 360.1354. Compound 9: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.94 (d, 3, J = 6.5 Hz), 1.07 (s, 3), 1.11 (s, 3), 1.2–2.7 (m, 8), 3.47 (br s, 1), 4.73 (m, 2), 5.6–6.0 (m, 2); IR (CHCl<sub>3</sub>) 3080, 1635, 885 cm<sup>-1</sup>; <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 154.36, 137.82, 128.77, 103.67, 55.27, 53.20, 49.64, 47.49, 40.62, 35.13, 33.76, 27.78, 25.96, 25.62, 14.89; mass spectrum, m/e (relative intensity) 202 (26, M<sup>+</sup>) 187 (33), 159 (74), 145 (34), 131 (100), 119 (55), 105 (66), 91 (98), 77 (52).

Phenylselenyl Compound 8 and Dienes 9 and 10. Mesylate 6 (250 mg, 0.84 mmol) was treated with sodium borohydride (45 mg, 1.16 mmol) and diphenyl diselenide (150 mg, 0.48 mmol) in 15 mL of ethanol as described for the preparation of the phenylselenyl compound 7. The resulting phenylselenyl compound 8 was subjected to the same treatment as in oxidative elimination reaction of the phenylselenyl compound 7. Separation of the crude product on HPLC gave 129 mg of an unseparable mixture of dienes 9 and 10 (76%), of which GC-mass spectroscopic analysis showed the ratio of 9:10 = 3.5:1. The major product 9 of the mixture was identical with the product derived from mesylate 5 as judged by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectrum. Compound 8: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.95-1.10 (d, 3), 1.04 (s, 6), 1.2-2.9 (m, 11), 3.10 (m, 1), 4.53 (m, 1), 4.71 (m, 1), 7.2-7.5 (m, 3), 7.5-7.8 (m, 2); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 155.48, 134.19, 131.57, 129.14, 128.81, 127.69, 127.07, 105.47, 54.37, 48.86, 48.70, 48.43, 47.78, 40.21, 36.36, 35.38, 33.50, 28.33, 25.90 (2 carbons), 18.99; mass spectrum, m/e(relative intensity) 360 (2, M<sup>+</sup>), 289 (3), 234 (7), 202 (16), 159 (14), 131 (27), 91 (18), 77 (20); Mr calcd for C21H28Se 360.1356; found 360.1364. Compound 10 (as the minor isomer of the mixture): <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.36 (m); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 123.37, 104.79; GC-mass spectrum, m/e (relative intensity) 202 (20, M<sup>+</sup>), 187 (5), 159 (22), 147 (17), 131 (100), 119 (25), 105 (45), 91 (63), 77 (38).

**Registry No.** 1, 28624-26-2; 2, 28102-79-6; 3, 28051-97-0; 4, 18444-94-5; 5, 91466-52-3; 6, 91548-24-2; 7, 91466-53-4; 8, 91548-25-3; 9, 91466-54-5; 10, 91466-55-6.

## Friedel-Crafts Reactions of Tetramethylphenyl Ketones with Tetramethylbenzenes

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In a previous article we reported a novel reaction of the hindered ketones acetomesitylene and propiomesitylene with mesitylene which results in the formation of 1,1-dimesitylethene and 1,1-dimesitylpropene, respectively.<sup>1</sup> In this paper we extend our study to the reaction of the tetramethylbenzenes with the corresponding tetramethylphenyl ketones in order to see the effect of increasing the nucleophilicity of the aromatic hydrocarbon and the steric hindrance of the ketone upon the course of the reaction leading to 1,1-diarylalkenes.

We describe here the reactions of durene (1,2,4,5)tetramethylbenzene, 1), isodurene (1,2,3,5)-tetramethylbenzene, 2), and prehnitene (1,2,3,4)-tetramethylbenzene) with acetyl and propionyl chloride and also the reactions of the acetyl and propionyl derivatives of each of these tetramethylbenzenes with the parent hydrocarbons.

**Durene.** Heating a mixture of durene, acetyl chloride, and AlCl<sub>3</sub> at 100 °C for 6 h in a molar ratio of 2:1:0.25, respectively, gave acetyldurene (3a, 18%) and 1,1didurylethene (7a, 25%).<sup>2</sup> Similarly, the reaction of durene with propionyl chloride gave propiodurene (3b, 12%) and 1,1-didurylpropene (7b, 40%).

**Isodurene.** Heating a mixture of isodurene, acetyl chloride, and  $AlCl_3$  in a molar ratio of 2:1:0.25, respectively, at 100 °C for 6 h gave acetoisodurene (4a) and 1,1-diisodurylethene (8a) in 13% and 50% yields, respectively. Similarly, the use of propionyl chloride in place of acetyl chloride led to the formation of propioisodurene (4b) and 1,1-diisodurylpropene (8b) in 12% and 78% yields, respectively.

The intermediacy of the ketones 3a, 3b, 4a, and 4b was confirmed by preparing them by acylation at low temperature and then heating them with durene or isodurene and AlCl<sub>3</sub> at 150–160 °C to yield the diarylalkenes 7a, 7b, 8a, and 8b.

**Prehnitene.** Unlike the reactions of durene and isodurene, the reaction of prehnitene with acetyl chloride and propionyl chloride gave only the acyl prehnitenes. No 1,1-diprehnitylalkenes could be isolated from these reactions, nor could they be obtained by reaction of the acylprehnitenes with prehnitene.

It is clear from these results that the three tetramethylbenzenes are acylated normally by acetyl and propionyl chlorides to give the corresponding tetramethylphenyl ketones, but whereas the acyldurenes and acylisodurenes react further with another hydrocarbon molecule to give the corresponding 1,1-diarylalkenes, as in the case of the trimethylbenzenes,<sup>1</sup> the acylprehnitenes fail to react further to give the 1,1-diarylalkenes.

This different behavior of the acylprehnitenes can be explained in terms of combined steric and electronic effects. As in the case of acylmesitylenes,<sup>1</sup> the two ortho methyl groups in acyldurene and acylisodurene prevent coplanarity of the carbonyl group with the aromatic ring. A positive charge on the carbonyl carbon cannot be dissipated into the ring as it can be in an acylprehnitene, which has only one ortho methyl group. This leads to the

<sup>(9)</sup> Hanayama, N.; Kido, F.; Sakuma, R.; Uda, H.; Yishikoshi, A. Tetrahedron Lett. 1968, 6099.

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**2.4.6.8:**  $R_1 = R_2 = R_3 = R_5 = CH_3$ ,  $R_4 = H_5$ 

following order of electrophilicity: acyldurene  $\approx$  acylisodurene  $\gg$  acylprehnitene. On the other hand, the order of nucleophilicity of the tetramethylbenzenes at an unsubstituted carbon atom is directly related to the number of methyl groups ortho and para to this carbon atom. On this basis, the order of nucleophilicity of the arenes is isodurene > durene  $\approx$  prehnitene. Consideration of these orders of reactivity of the tetramethylbenzenes and their acyl derivatives suggests an explanation for the failure of an acylprehnitene to react with prehnitene to give a 1,1diarylalkene: the combined effect of low electrophilicity of the ketone and the low nucleophilicity of the arene.

#### **Experimental Section**

<sup>1</sup>H NMR spectra were obtained on an NT-200 spectrometer. GC/MS analyses were performed on a Finnigan MAT 4023 instrument with an Incos data system, using a J & W Scientific, Inc. 50-m DBI bonded phase capillary column (0.25- $\mu$ m film thickness). The tetramethylbenzenes were commercially available (Aldrich Chem. Co.); they were purified before use by distillation (isodurene and prehnitene) or by crystallization (durene). The tetramethylacetophenones were prepared according to a literature procedure.<sup>3</sup> The tetramethylpropiophenones were synthesized by a modification of a procedure described for the synthesis of propiodurene.<sup>4</sup>

Reaction of Durene with Acetyl Chloride at 100 °C. A mixture of 24.5 g (0.184 mol) of durene, 50 mL of 1.2.4-trichlorobenzene, 7.2 g (0.092 mol) of acetyl chloride, and 3.1 g (0.023 mol) of AlCl<sub>3</sub> was stirred at 100 °C for 6 h, allowed to cool to room temperature, poured into 50 mL of ice-water, and extracted with ether. The ether extract was washed with 10% NaHCO<sub>3</sub> solution and water and dried over anhydrous MgSO<sub>4</sub>. Ether was removed by rotary evaporation and the residue was distilled under reduced pressure. A 5.0-g fraction, bp 90 °C (1.0 torr), and a 4.5-g fraction, bp 160 °C (1.0 torr), were collected. The lower boiling fraction solidified in the receiver and was recrystallized from methanol to give 4.9 g (18%) of acetodurene as white platelets; mp 72-73 °C; mass spectrum, m/e 176 (M<sup>+</sup>), 161, 133, 115, 105, 91, 77, 65; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.09 (s, 3- and 5-CH<sub>3</sub>), 2.28 (s, 2- and 6-CH<sub>3</sub>), 2.47 (s, COCH<sub>3</sub>), 6.86 (s, 4-H, Ar H). The higher boiling fraction also solidified in the receiver and was recrystallized from methanol to produce 6.7 g (25%) of 1,1-didurylethene as rhombic crystals: mp 134–135 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.09 (s, 12 H, 4 o-Me), 2.20 (s, 12 H, 4 m-Me), 5.16 (s, 2 H, CH<sub>2</sub>=), 6.91 (s, 2 H, Ar H); mass spectrum, calcd for  $C_{22}H_{28}$  [M<sup>+</sup>], m/e 292.21909, found 292.21877.

**Reaction of Acetodurene and Durene at 150–160 °C.** Durene (20.1 g, 0.15 mol) and acetodurene (8.8 g, 0.05 mol) were dissolved in 50 mL of 1,2,4-trichlorobenzene, and 1.33 g (0.01 mol) of AlCl<sub>3</sub> was added. The reaction mixture was heated while stirring for 3-4 h and then cooled to room temperature, decomposed with water, and extracted with ether. The ether extract was worked up as before to yield 6.6 g (45%) of 1,1-didurylethene, bp 160 °C (1.0 torr). It solidified in the receiver and was recrystallized from methanol, giving colorless rhombic crystals, mp 134-135 °C.

Reaction of Durene with Propionyl Chloride at 100 °C. The reaction was carried out under the conditions described for durene and acetyl chloride with the exception that 8.48 g (0.092 mol) of propionyl chloride was used. The products were isolated in the same way. Two fractions, bp 120-125 °C (4 torr) and 160-170 °C (4 torr), were collected and both solidified in the receiver. The lower boiling fraction was recrystallized from pentane to give 3.10 g (18%) of propiodurene: mp 79 °C; mass spectrum, m/e 190 (M<sup>+</sup>), 161, 133, 117, 109, 91, 77; calcd for  $C_{13}H_{18}O[M^+] m/e$  190.13511, found 190.13504; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.2 (t, 3 H, CH<sub>3</sub>CH<sub>2</sub>-), 2.05 (s, 6 H, 2 o-Me), 2.20 (s, 6 H, 2 m-Me), 2.71 (q. 2 H, CH<sub>2</sub>), 6.93 (s. 1 H, Ar H). The higher boiling fraction was recrystallized from ethanol to give 11.20 g (40%) of 1,1didurylpropene as white needles: mp 115-116 °C; mass spectrum, m/e 306 (M<sup>+</sup>), 291, 277, 262, 171, 157, 119; calcd for C<sub>23</sub>H<sub>30</sub>[M<sup>+</sup>] m/e 306.23474, found 306.23376; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.62 (d, 3 H), 2.02 (s, 6 H, 2 o-Me), 2.07 (s, 6 H, 2 o-Me), 2.20 (s, 12 H, 4 m-Me), 5.73 (q, 1 H, CH<sub>3</sub>CH=), 6.88 (s, 2 H, Ar H).

**Reaction of Propiodurene and Durene at 150–160** °C. Reaction of 12.0 g (0.09 mol) of durene and 6.68 g (0.03 mol) of propiodurene in 50 mL of trichlorobenzene with 0.80 g (0.006 mol) of AlCl<sub>3</sub> at 160 °C for 3 h gave 5.3 g of a viscous yellow oil (50% yield as 1,1-didurylpropene). It solidified in the receiver and was recrystallized from absolute ethanol, yielding white needles of 1,1-didurylpropene, mp 116–117 °C.

**Reaction of Isodurene with Acetyl Chloride at 100** °C. A mixture of 24.5 g (0.184 mol) of isodurene, 7.2 g (0.092 mol) of acetyl chloride, and 3.1 g (0.023 mol) of AlCl<sub>3</sub> was heated at 100 °C for 6 h. The reaction mixture was worked up as before to give 2.1 g (12.5%) of acetoisodurene, bp 120 °C (0.6 torr), and a 6.0-g fraction, bp 180–230 °C (10.0 torr), which crystallized in the receiver. The higher boiling fraction was recrystallized from methanol and gave 5.8 g of 1,1-diisodurylethene (50%) as white rhombic crystals: mp 87–88 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.03 (s, 6 H, 2 o-Me), 2.14 (s, 6 H, 2 m-Me), 2.20 (s, 6 H, 2 o-Me), 2.23 (s, 6 H, 2 p-Me), 5.48 (s, 2 H, CH<sub>2</sub>=), 6.8 (s, 2 H, Ar H); mass spectrum, calcd for C<sub>22</sub>H<sub>28</sub>[M<sup>+</sup>] m/e 292.21909, found 292.21881.

**Reaction of Acetoisodurene and Isodurene at 150–160 °C.** A mixture of 8.8 g (0.05 mol) of acetoisodurene, 20.1 g (0.15 mol) of isodurene, and 1.33 g (0.01 mol) of AlCl<sub>3</sub> was heated at 150–160

<sup>(1)</sup> Roberts, R. M.; El-Khawaga, A. M.; Roengsumran, S. J. Org. Chem., in press.

<sup>(2)</sup> Snyder and Roeske (Snyder, H. R.; Roeske, R. W. J. Am. Chem. Soc. 1952, 74, 5820) reported 1,1-didurylethene as a product of the reaction of durene and propionic acid in polyphosphoric acid. The crude product (10% yield) after "repeated recrystallizations" had mp 109–111 °C, "with a small portion melting up to 118°". The product we obtained by repeating the procedure of Snyder and Roeske was shown by GC/MS analysis to be a mixture of propiodurene and 1,1-didurylpropene in a 9:1 ratio.

<sup>(3)</sup> Schlosberg, R. H.; Woodbury, R. P. J. Org. Chem. 1972, 37, 2627.
(4) Baum, F.; Meyer, V. Ber. 1895, 28, 3213.

°C for 3 h. The reaction mixture was worked up as before to yield 10.2 g (70%) of material, bp 180-230 °C (10.0 torr). It solidified in the receiver and was recrystallized from methanol, giving white rhombic crystals of 1,1-diisodurylethene, mp 87-88 °C.

Reaction of Isodurene with Propionyl Chloride at 100 °C. The procedure was the same as that for reaction of acetyl chloride with isodurene at 100 °C except that 8.5 g (0.092 mol) of propionyl chloride was used. Vacuum distillation gave two fractions. The first fraction, 2.3 g (12%), bp 95 °C (1.2 torr), was identified by GC/MS as propioisodurene: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.3 (t, 3 H), 2.05-2.28 (t, 12 H), 2.7 (q, 2 H), 6.85 (s, 1 H); mass spectrum, calcd for  $C_{13}H_{18}O[M^+] m/e$  190.13511, found 190.13494. The second fraction, 2.23 g (78%), bp 195 °C (1.0 torr), became a hard glass upon cooling: GC/MS showed it to be a pure compound; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.6 (d, 3 H), 1.9–2.3 (t, 24 H), 5.72 (q, 1 H), 6.78 (s, 2 H, Ar H); mass spectrum, calcd for  $C_{23}H_{30}$  [M<sup>+</sup>] m/e 306.23474, found 306.23462.

Reaction of Propioisodurene with Isodurene at 150-160 °C. A mixture of 20 g (0.15 mol) of isodurene, 9.5 g (0.05 mol) of propioisodurene, and 1.33 g (0.01 mol) of AlCl<sub>3</sub> was heated at 160 °C for 3 h. The reaction mixture was worked up in the usual way to give 1.0 g (10%) of propioisodurene, bp 95 °C (1.2 torr), and 12.2 g (80%) of 1,1-diisodurylpropene, bp 195 °C (1.0 torr), as a viscous yellow oil, which solidified into a hard glass upon cooling.

Reaction of Prehnitene with Acetyl Chloride and Pro**pionyl Chloride.** When prehnitene was treated with acetyl chloride or propionyl chloride and AlCl<sub>3</sub> under the conditions used with durene and isodurene, the products were recovered prehnitene, acetoprehnitene or propioprehnitene, and smaller amounts of other products. Although these other products were not identified, it was established by GC/MS analysis that no more than traces (1%) of 1,1-diprehnitylethene and 1,1-diprehnitylpropene were present in the product mixtures.

**Reaction of Acetoprehnitene and Propioprehnitene with Prehnitene.** When acetoprehnitene or propioprehnitene was treated with prehnitene and AlCl<sub>3</sub> under the conditions used with acetodurene or propiodurene and the corresponding arenes, mainly the starting materials were recovered, along with small amounts of other compounds. Although these other compounds were not identified, it was established by GC/MS analysis that no more than traces (1%) of 1,1-diprehnitylethene and 1,1-diprehnitylpropene were present in the product mixtures.

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Registry No. 1, 95-93-2; 2, 527-53-7; 3a, 2142-79-2; 3b, 2040-16-6; 4a, 2142-78-1; 4b, 91390-77-1; 7a, 91390-74-8; 7b, 91390-75-9; 8a, 91390-76-0; 8b, 91390-78-2; acetyl chloride, 75-36-5; propionyl chloride, 79-03-8; prehnitene, 488-23-3; acetoprehnitene, 34764-71-1; propioprehnitene, 91390-79-3.

## **Reduction Process in the Photostimulated Reaction of Benzeneselenate Ion with Haloarenes**

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Benzeneselenate (PhSe<sup>-</sup>) and benzenetellurate (PhTe<sup>-</sup>) ions react under photostimulation with haloarenes by the  $S_{RN}$ 1 mechanism of nucleophilic substitution.<sup>1-3</sup>

The frangibility of the radical anion 1 formed in the coupling reaction between the anions and the aromatic

Table I. Photostimulated Reactions of Benzeneselenate Ions with Different Substrates in Liquid Ammonia<sup>a</sup>

			PhSe⁻.	yield, %	
expt	substrate	$M \times 10^3$	$M \times 10^3$	$\overline{Ph_2Se}$	PhH
16	PhI	22.4	22.6	55	3.5
2°	PhI	4.2	16.2	44	31
3°	PhI	2.1	16.0	13	91
$4^d$	PhI	2.1	16.1	28	17
5			30.4	0	2
6	$Ph_2Se$	1.7	16.3	18	51
7	2-ClQ <sup>e</sup>	1.8	16.0	$95^{f}$	1
8	2-ClQ <sup>e</sup>	3.4	16.5	98 <sup>f</sup>	1
9	$Ph_2S$	1.6	14.5	0	1

<sup>a</sup>140 min of irradiation with four 250-W lamps. <sup>b</sup>PhI recovered 38.5%. "No PhI recovered unreacted. d Irradiation with two 250-W lamps; PhI recovered was no quantified. e2-ClQ = 2chloroquinoline. <sup>†</sup>2-Quinolyl phenyl selenide.

radical depends on both the nature of the radical and the nucleophile involved. This fact will determine the product distribution and the relative reactivities of the nucleophiles toward radicals.<sup>4</sup>

When the reaction takes place under irreversible conditions,  $k_{\rm t}({\rm ArX}) \gg k_{\rm f} \approx k_{\rm f'}$ , the product observed is the expected substitution one, ArZPh (Z = Se, Te), while three compounds, ArZPh, Ar<sub>2</sub>Z, and Ph<sub>2</sub>Z, are obtained when the reversible conditions prevail. In this case,  $k_f \approx k_{f'} \approx$  $k_{\rm t}({\rm ArX}) \ ({\rm eq} \ 1).$ 

$$Ar^{*} + PhZ^{-} \xrightarrow{k_{c}} (ArZPh)^{-} \cdot \xrightarrow{k_{c}} ArZ^{-} + Ph \cdot (1)$$

$$\downarrow k_{t}(ArX)$$

$$ArZPh$$

$$Z = Se, Te$$

In the reaction of benzeneselenate ion with phenyl radicals we have found a decrease in the percentage of the substitution product together with an increase in the percentage of the reduction one (hydrogen substitution) as a function of the concentration of the nucleophile.<sup>4</sup> In this paper we report the study of this reduction process.

# **Results and Discussion**

The photostimulated reaction of iodobenzene with PhSe<sup>-</sup> and PhTe<sup>-</sup> ion with a ratio of concentration (1:2:2) gave  $Ph_2Te$  (97%) and  $Ph_2Se$  (3%). In order to increase the yield of Ph<sub>2</sub>Se in the competition experiments we increased the concentration of PhSe<sup>-</sup> ion. In the reaction carried out with a ratio of PhI:PhTe<sup>-</sup>:PhSe<sup>-</sup> of 1:2:8, we found  $Ph_2Te$  (14%) and  $Ph_2Se$  (5% yield) while the percentage of halide liberated was 92%.

This decrease in the overall yield of substitution product must result from the excess of PhSe<sup>-</sup> ion. In the photostimulated reaction of PhSe<sup>-</sup> with PhI (1:1) the ratio of Ph<sub>2</sub>Se:PhH was approximately 16. The ratio Ph<sub>2</sub>Se:PhH was  $\sim 1.5$  with a ratio PhSe<sup>-</sup>:PhI of 4, and it was 0.15 with a ratio PhSe<sup>-</sup>:PhI of 8 (Table I). In the reaction carried out with the latter ratio of nucleophile to substrate but with half the number of irradiation lamps, the ratio  $Ph_2Se:PhH$  was ~1.6.

These results clearly show that the concentration of benzene, the reduction product, depends on the concentration of nucleophile and on the light intensity.

A mechanism that accounts for the formation of benzene could be the electron transfer from the nucleophile to phenyl radical (eq 2). This reaction is in competition with

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