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Carbon Dioxide-Promoted Telomerization of 1,2- and 1,3-Dienes with Benzenesulfinate Catalyzed by Palladium(0)[*]

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Synopsis. The telomerization of 1,2- and 1,3-dienes with benzenesulfinate dihydrate catalyzed by palladium(0) has been promoted by the presence of carbon dioxide.

Palladium complexes catalyze the dimerization of 1,3-butadiene with incorporation of nucleophiles such as alcohols, phenols, carboxylic acids, amines, enamines and active methylene compounds to form 1-substituted 2,7-octadiene and 3-substituted 1,7-octadiene.[1)]

$$2CH_2{=}CHCH{=}CH_2 + YH \xrightarrow{Pd} CH_2{=}CH(CH_2)_3CH{=}CHCH_2Y + CH_2{=}CH(CH_2)_3CH(Y)CH{=}CH_2$$

Allene reacts similarly to afford 2,3-dialkyl-1,3-butadiene derivatives.[1)]

$$2CH_2{=}C{=}CH_2 + YH \xrightarrow{Pd} CH_2{=}C(CH_3)C(CH_2Y){=}CH_2$$

In certain cases, introduction of carbon dioxide profoundly alters the properties of the catalyst. For example, formation of 2,7-octadien-1-ol has been accomplished from the reaction of water with two moles of 1,3-butadiene in the presence of a considerable amount of carbon dioxide.[2)] In the absence of carbon dioxide, the formation of the alcohol is very sluggish. The telomerization of 1,3-dienes with arenesulfinic acids or sodium arenesulfinates in acetic acid has been carried out in the presence of palladium catalysts to afford high yields of allylic sulfones.[3)]

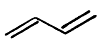
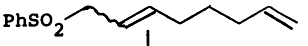
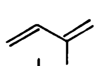
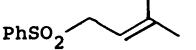
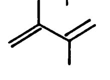
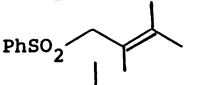
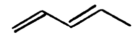
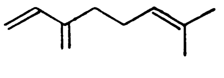
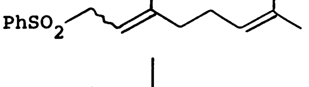
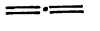
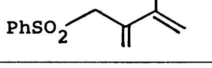
In the course of the study on the CO_2-promoted reactions,[4)] we have discovered that 1,2- and 1,3-dienes react with sodium benzenesulfinate dihydrate in the presence of a palladium(0) catalyst to give allylic sulfones under CO_2 atmosphere.

The results are shown in Table 1. The reaction of sodium benzenesulfinate dihydrate with 3.8 equiv of 1,3-butadiene (**1a**) in *N*,*N*-dimethylformamide (DMF) at 80 °C for 2 h under the pressure of CO_2 in the presence of $[Pd(PPh_3)_3]$ gave the 1:1 addition product, 2-butenyl pheny sulfone (**2a**), in 20% yield (*E*:*Z*=2:1) together with the 1:2 addition product, (*E*)-2,7-octadienyl phenyl sulfone, in 78% yield. The effect of CO_2 was remarkable because the addition reaction did not take place at all in the absence of CO_2.

Isoprene (**1b**) afforded exclusively the 1:1 addition product 3-methyl-2-butenyl pheny sulfone (**2b**).

$$CH_2{=}CHC(CH_3){=}CH_2 + PhSO_2Na\cdot 2H_2O \xrightarrow[CO_2]{Pd} PhSO_2CH_2CH{=}C(CH_3)_2$$

Table 1. Reaction of Dienes with Sodium Benzenesulfinate Dihydrate[a)]

Diene	Reaction temp/time °C/h	Product	Yield %
 1a	80/2	 2a	20 (*E*:*Z*=2:1)
			78 (*E*:*Z*=6:1)
 1b	80/2	 2b	94
 1c	100/4	 2c	67
 1d	110/4	 2d	31[b)] (*E*:*Z*=19:1)
 1e	80/2	 2e	48 (*E*:*Z*=3:1)
 3	80/2	 4	44

a) $PhSO_2Na\cdot 2H_2O$ 9.1 mmol, 1,3-diene 10—34 mmol, $[Pd(PPh_3)_3]$ 0.2 mmol, DMF 10 cm³, CO_2 15 kg/cm². For the 1,2-diene **3**, see the experimental part. b) 2-Pentenyl phenyl sulfone was also formed in 11% yield.

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[*] The term "telomerizartion" is meant here to imply formation of adducts between one or more dienes and a second substance.

These results contrasted sharply with those reported earier,[3] where the reaction of dienes with arenesulfinic acid or sodium arenesulfinate in acetic acid gave allylic sulfones containing large proportion of the more substituted isomer. 2,3-Dimethyl-1,3-butadiene (**1c**) gave predominantly 2,3-dimethyl-2-butenyl phenyl sulfone (**2c**) in a moderate yield at the reaction temperature of 100 °C. The reaction of (*E*)-1,3-pentadiene (**1d**) with the sulfinate was sluggish at the reaction temperature of 80 °C. Under forced conditions (110 °C, 4 h), the diene afforded 1-methyl-2-butenyl phenyl sulfone (**2d**) in 31% yield. Myrcene (**1e**) underwent the addition reaction at 80 °C to give mainly geranyl phenyl sulfone. 1,4-Disubstituted 1,3-dienes such as 1,3-cyclooctadiene and methyl sorbate did not take part in this reaction.

Allene (**3**) underwent smoothly the 2:1 addition reaction to afford 3-methyl-2-methylene-3-butenyl phenyl sulfone (**4**) selectively under the pressure of CO_2 in the presence of the palladium catalyst.

$$2CH_2{=}C{=}CH_2 + PhSO_2Na\cdot 2H_2O \xrightarrow[CO_2]{Pd} PhSO_2CH_2C({=}CH_2)C({=}CH_2)CH_3$$

We point out here one of possible roles of CO_2 in the telomerization reaction. Benzenesulfinic acid may be formed from its sodium salt as follows.

$$PhSO_2Na\cdot 2H_2O + CO_2 \rightleftharpoons PhSO_2H\cdot H_2O + NaHCO_3$$

Although the equilibrium is declined to the left due to the strong acidity of the free sulfinic acid (pK_a ca. 2), the sulfinic acid thus formed may, in turn, begin to undergo telomerization with dienes in the presence of a palladium catalyst.[3]

The intermediate has been supposed to be a π-allylpalladium species, which is attacked by benzenesulfinate to afford allylic sulfones.[3] There are several preceedings concerning the attack of sulfinate on an in situ-generated π-allyl palladium complex.[5] Usually thermodynamically-controlled products were reported to be predominated. The observations coincide well with our results.

As free sulfinic acid is unstable having a tendency to undergo disproportionation into thiosulfonic *S*-ester and sulfonic acid,[6] the employment of CO_2 and a sulfinic acid salt, that is stable, instead of free sulfinic acid may be a choice in the diene telomerization reaction.

Experimental

Materials. The dienes (1,2- and 1,3-) were used as received except myrcene. Myrcene was distilled under reduced pressure before use. $[Pd(PPh_3)_3]$ was prepared according to the reported method.[7]

General Procedure for the Telomerization of Dienes with Benzenesulfinate Dihydrate. A mixture of sodium benzenesulfinate dihydrate (1.82 g, 9.1 mmol), a diene, and $[Pd(PPh_3)_3]$ (179 mg, 0.2 mmol) in 10 cm^3 of DMF was stirred in an autoclave under CO_2 pressure (15 kg cm^{-2}) under the conditions described in Table 1. After the teaction was completed, the whole content was poured into water. The products were extracted with diethyl ether and the organic layer was dried on $MgSO_4$. After the solvent was evaporated, the residue was subjected to column chromatography on silica gel eluting with hexane–ethyl acetate.

Reaction of 1,3-Butadiene (1a) with Benzenesulfinate. Reaction of **1a** (1.86 g, 34.4 mmol) in the usual way as above gave an oil after column chromatography (hexane/ethyl acetate=2/1). Yield 2.13 g. GLC analysis (OV-1, 3 m, 3%, 194 °C) showed the formation of 2-butenyl phenyl sulfone (**2a**) and 2,7-octadienyl phenyl sulfone in a 1:4 ratio. The products were isolated by GLC and characterized spectroscopically (IR,^{1}H NMR, Mass).[3] The *E*/*Z* ratios of **2a** and 2,7-octadienyl phenyl sulfone were determined by ^{1}H NMR spectroscopy to be 2:1 and 6:1, respectively.

Reaction of Isoprene (1b) with Benzenesulfinate. Reaction of **1b** (1.36 g, 20 mmol) in the usual way gave 3-methyl-2-butenyl phenyl sulfone (**2b**) as a pale yellow oil after column chromatography (hexane/ethyl acetate=2/1). Yield 1.79 g (8.52 mmol, 94%). Spectroscopic (IR, ^{1}H and ^{13}C NMR, Mass) and elemental analysis supported the structure.

Reaction of 2,3-Dimethyl-1,3-butadiene (1c) with Benzenesulfinate. Reaction of **1c** (0.8 g, 10 mmol) at 100 °C for 4 h in the usual way gave 2,3-dimethyl-2-butenyl phenyl sulfone (**2c**)[8] after column chromatography (hexane/ethyl acetate=3/1). Yield 1.36 g (6.1 mmol, 67%). Recrystallization from toluene/hexane (1/3) afforded pure material as white needles: mp 98—99 °C. IR (KBr) 1285, 1135, 750, 580 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.24 (s, 3H), 1.60 (s, 3H), 1.74 (s, 3H), 3.80 (s, 2H), 7.40—7.92 (m, 5H). Found: C, 64.27; H, 7.31. Calcd. for $C_{12}H_{16}O_2S$: C, 64.29; H, 7.14.

Reaction of (*E*)-1,3-Pentadiene (1d) with Benzenesulfinate. Reaction of **1d** (0.77 g, 10.3 mmol) at 110 °C for 4 h in the usual way gave an oil after kugelrohr distillation at 140 °C (4 mmHg) (1 mmHg=133.322 Pa). Yield 796 mg (42%). Found: C, 63.10; H, 7.01. Calcd. for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71. IR (neat) 1300, 1140, 965, 720, 680 cm^{-1}. GLC analysis (OV-1, 2 m, 3%, 150 °C) of the product showed two peaks in the ratio of 77:23. The major portion, which was isolated by GLC, was composed of (*E*)- and (*Z*)-1-methyl-2-butenyl phenyl sulfone (**2d**). (*E*)-Isomer: ^{1}H NMR ($CDCl_3$) δ=1.36 (d, *J*=7 Hz, 3H), 1.58 (d, *J*=5 Hz, 3H), 3.40—3.90 (m, 1H), 5.24—5.60 (m, 2H), 7.30—7.96 (m, 5H). The absorption of the (*Z*)-isomer occurred differently at δ=1.40 (d, *J*=7 Hz) instead of δ=1.36 in the (*E*)-isomer. The *E*/*Z* ratio was determined by ^{1}H NMR to be 19:1. The minor portion, which was also isolated by GLC, was composed of (*E*)- and (*Z*)-2-pentenyl phenyl sulfone. (*E*)-Isomer: ^{1}H NMR ($CDCl_3$) δ=0.84 (t, *J*=8 Hz, 3H), 1.60—2.00 (m, 2H), 3.68 (d, *J*=6 Hz, 2H), 5.24—5.65 (m, 2H), 7.35—7.90 (m, 5H). The absorption of the (*Z*)-isomer occurred at δ=3.78 (d, *J*=9 Hz) instead of δ=3.68 in the (*E*)-isomer. The *E*/*Z* ratio was determined by ^{1}H NMR to be 9:1.

Reaction of Myrcene (1e) with Benzenesulfinate. Reaction of **1e** (1.36 g, 10 mmol) in the usual way gave 3,7-dimethyl-2,6-octadienyl phenyl sulfone[5] as an oil on chromatography (hexane/ethyl acetate=2/1) followed by kugelrohr distillation at 165 °C (3 mmHg). Found: C, 69.08; H, 7.72. Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.97. The *E*/*Z* ratio was determined by GLC (OV-1, 2 m, 3%, 200 °C) to be 3:1. IR (neat) 1445, 1310, 1150 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.28 (s, 3H), 1.56 (s, 3H), 1.64 (s, 3H), 1.80—2.24 (m, 4H), 3.78 (d, *J*=8 Hz, 2H), 4.80—5.40 (m, 2H), 7.20—8.00 (m, 5H).

Reaction of Allene (3) with Benzenesulfinate. $PhSO_2Na\cdot 2H_2O$ (3.64 g, 20 mmol) and **3** (0.70 g, 17.5 mmol) were reacted in an autoclave at 80 °C for 2 h in the presence of $[Pd(PPh_3)_3]$ (179 mg, 0.2 mmol) in DMF (20 cm^3) under CO_2 pressure (15 kg cm^{-2}). Isolation as above by column chromatography on silica gel (hexane/ethyl acetate=3/2) gave 3-methyl-2-methylene-3-butenyl phenyl sulfone as a pale yellow oil. Yield 860 mg (3.87 mmol, 44%). An analytical sample was obtained by kugelrohr distillation at 150 °C (4 mmHg). This compound polymerized partially during the distillation. ^{1}H NMR ($CDCl_3$) δ=1.83 (s, 3H), 4.08 (s, 2H), 4.96 (s, 1H), 5.02 (s, 1H), 5.06 (s, 1H), 5.36 (s, 1H), 7.20—7.96 (m, 5H). ^{13}C NMR ($CDCl_3$) δ=140.585 (s), 138.730 (s), 136.102 (s), 133.467 (d), 128.789 (d), 128.399 (d), 120.949 (t), 115.003 (t), 60.133 (t), 20.710 (q). IR (neat) 1722, 1300, 1145, 895, 775 cm^{-1}. Mass (70 eV) m/z 222 (M^+), 143, 81, 79, 77, 53. Found: C, 64.71; H, 6.24. Calcd. for $C_{12}H_{14}O_2S$: C, 64.84, H, 6.35.

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