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PALLADIUM CATALYZED REACTION OF BUTADIENE WITH ALCOHOLS USING ALKYL- AND ARYLSULFINATES AS COCATALYSTS

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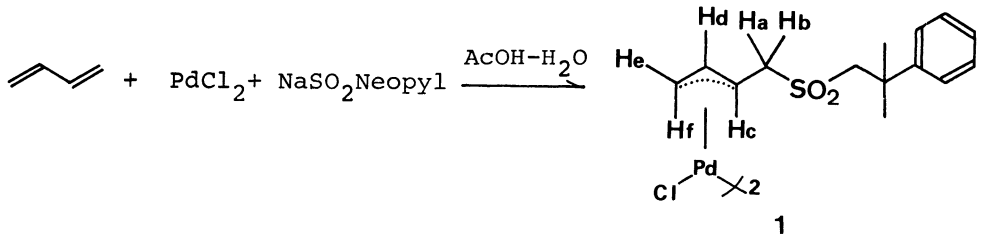
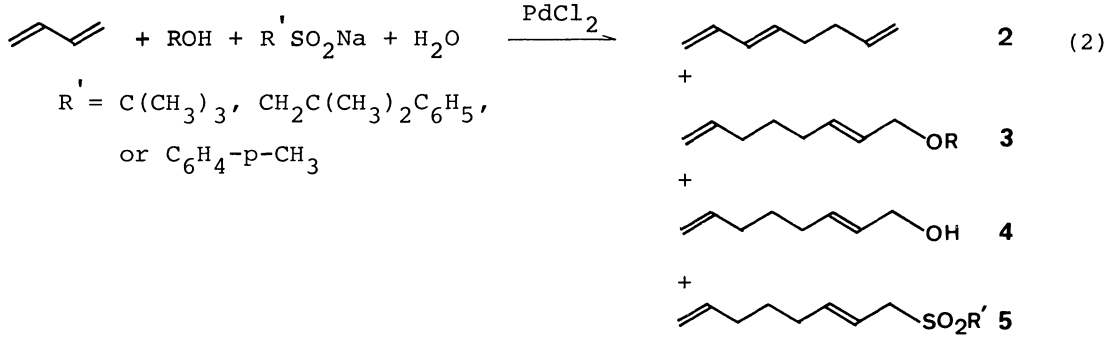
Sodium alkyl- and arylsulfinates serve as excellent cocatalysts for the palladium catalyzed dimerization of butadiene in alcohols to give 2,7-octadienyl alkyl (Me, Et, Pr, and i-Pr) ethers selectively together with small amounts of 2,7-octadienyl sulfones. 1,3,7-Octatriene is formed in less than 4% yield.

Recently, we have reported that sodium alkylsulfinates react with substituted 1,3-dienes in the presence of an equimolar amount of palladium chloride to give di-μ-chloro-bis-(1-syn-alkylsulfonylmethyl-π-allyl)dipalladium(II).[1] With substituted 1,3-dienes this reaction is performed successfully in glacial acetic acid, while with butadiene it requires a small amount of water in order to isolate complex 1 in a satisfactory yield (eq 1); an argon purged homogeneous orange solution of $PdCl_2$ (1.13 mmol) and $NaSO_2CH_2(CH_3)_2C_6H_5$ (1.13 mmol)[2] in 2 ml of water and 20 ml of acetic acid was frozen in a dry-ice-acetone bath and onto this was added butadiene (14 mmol). The reaction mixture was heated at 70°C for 7 h. Extraction with EtOAc, neutralization with $NaHCO_3$, drying over Na_2SO_4, evaporation of the solvent (at room temperature or below), and purification by column chromatography (silica gel, benzene-ethyl acetate gradient)[3] gave a yellow crystalline solid 1[4] in 53% yield.[5]

During our attempts for the optimization of the reaction conditions of the above reaction, we have found that the course of the reaction changes dramatically depending on the nature of solvents and equivalency of sulfinates to palladium salt; under similar conditions, using alcohol instead of acetic acid and using 5-6 equivalents of sulfinates to palladium chloride, the reaction gave 2,7-octadienyl ether 3 selectively together with a small amount of 2,7-octadienyl sulfone 5 (eq 2).[6,7] Results of the present catalytic reaction with variations of alcohols and sulfinates are summarized in Table I. The efficiency of sodium sulfinate as a cocatalyst is evident; without this, no reaciton took place (entry 8). Addition of tert-butyl-



1 (1)



(2)

sulfinate into this reaction mixture initiated the reaction and the same result as entry 1 was obtained. Neophylsulfinate is much more effective and selective cocatalyst than tert-butylsulfinate for the ether formation. It is worthwhile to note that p-toluenesulfinate[8] serves as an efficient cocatalyst similarly to alkylsulfinates; alkyl- and arylsulfinates are known to react with 1,3-dienes in a completely different manner.[9] For the reaction in methanol, octadienyl methyl ether was obtained in a satisfactory yield (entry 2), but for the reactions in the bulkier and less nucleophillic alcohols (i.e., 1-propanol and 2-propanol), the yields of ethers 3 decreased; only a small amount (<5%) of ether 3 (R = ^{t}Bu) was isolated in the reaction with 2-methyl-2-propanol. The most important characteristic of the present reaction is the diminished formation of octatriene 2, even for the reaction with 2-propanol. The selectivity (2 vs. 3) in the reaction using triphenylphosphine as a cocatalyst largely depends on solvents; in methanol, 2,7-octadienyl methyl ether 3 (R = Me) is obtained in 90% yield based on butadiene consumed, while in 2-propanol octatriene 2 is the only isolable product (72%).[10]

General procedure is as follows (entry 2): in a 50 ml heavy-walled Pyrex bottle were charged $PdCl_2$ (0.5 mmol), sodium neophylsulfinate (2.6 mmol), and 3 ml of water and stirred for 10 min at ambient temperature. Then 15 ml of methanol was added and the mixture was stirred for an additional hour. Homogeneous orange solution formed was cooled to -78°C and then 60 mmol of butadiene was introduced under argon. After allowing to warm to ambient temperature, the reaction mixture was stirred for 20 h

Table I. Palladium Catalyzed Reaction of Butadiene with Alcohols Using Alkyl- and Arylsulfinates as Cocatalysts[a]

Entry	Alcohol	Sulfinate[b]	Products (Isolated Yields)[c]			
			2	3	4	5
1	MeOH	t-Butyl	-	56	-	3
2	MeOH	Neophyl[d]	-	94	-	1
3	EtOH	t-Butyl	-	42	-	4
4	PrOH	t-Butyl	-	43	-	5
5	i-PrOH	Neophyl	(2.6)	55	5[e]	2
6	i-PrOH	p-Tolyl	(3.5)	(51.6)	(9.9)[f]	(2.4)
7	i-PrOH	t-Butyl	(1)	21	(2)	5
8	MeOH	g	-	-	-	-

a. Usual scale is as follows: butadiene (60-65 mmol), $PdCl_2$ (0.5 mmol), sodium alkylsulfinate (2.5-2.8 mmol) in alcohol (15 ml) and H_2O (3 ml). b. Sodium tert-butyl-, neophyl-, or p-tolylsulfinate. c. Yields refer to isolated, spectrally and gas chromatographically homogemeous material; reported yields are not based on recovered butadiene. Values in parentheses refer to VPC yields, taking bibenzyl as an internal standard. d. The same results were obtained with 120 mmol of butadiene. e. In addition to 4, 15% of di-2,7-octadienyl ether was isolated. f. In addition to 4, 18% of di-2,7-octadienyl ether was isolated. g. Without sulfinate.

at ambient temperature. After recovery of butadiene (dry-ice-acetone trap, no recovery in this run), the reaction mixture was diluted with ether (50 ml) and passed through a cellulose column 2 cm long to remove palladium black and inorganics. The filtrate was washed with water, dried over $MgSO_4$, and then condensed through a Vigreux column. Distillation of the residue under reduced pressure gave 3[11] (R = CH_3, 78°C/37 mmHg) and 5[12] (R' = neophyl, 180-190°C/0.3 mmHg, Kugel rohr) in 94 and 1% yields, respectively. For all runs, almost complete material balance was realized based on butadiene consumed.

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References and Notes

1. Y. Tamaru, M. Kagotani, and Z. Yoshida, J. Chem. Soc., Chem. Commun., 367 (1978).
2. Sodium neophylsulfinate was prepared according to the method reported by Allen [P. Allen, Jr., J. Org. Chem., 7, 23 (1942)] and kept in a refrigerator. Sodium tert-butylsulfinate was prepared similarly, using care not to introduce any excess of SO_2 into an etheral solution of tert-butyl magnesium chloride [Org. Syn., coll. vol. 1, 524] and avoiding contact with air during workup, otherwise

it decompeses to sulfonate appreciably.

3. Complex 1 decomposes gradually during column purification.
4. 1: mp 163°C (dec., from $CHCl_3$- EtOAc); NMR ($CDCl_3$, 100 MHz) δ 1.64 (s, 3H), 1.67 (s, 3H), 2.54 (d.d, J = 14.0 and 10.5 Hz, H_a, 1H), 2.92 (d.d, J = 14.0 and 4.0 Hz, H_b, 1H), 3.03 (d, J = 11.5 Hz, H_f, 1H), 3.33 (s, 2H), 3.50 (t.d, J = 10.5 and 4.0 Hz, H_c, 1H), 4.06 (d, J = 7.0 Hz, H_e, 1H), 5.32 (d.d.d, J = 11.5, 10.5, and 7.0 Hz, H_d, 1H), and 7.4 (m, 5H); IR (KBr disc) 1310s, 1295m, 1123s, 773m, 765s, 516m, and 438m cm^{-1}.
5. All new compounds reported in this paper gave satisfactory analytical data.
6. For a review on the telomerization of butadiene catalyzed by palladium complex, see (a) J. Tsuji, Acc. Chem. Res., 6, 8 (1973); (b) B. M. Trost, Tetrahedron, 33, 2615 (1977). See also (c) M. Green, G. Scholes, and F. G. A. Stone, J. Chem. Soc., Dalton, 309 (1978).
7. Isoprene dimers were obtained under similar conditions. Detail will be reported in due course.
8. Sodium p-toluenesulfinate (commercially available) was used without any purification.
9. Sodium alkylsulfinates react with 1,3-dienes as a S-nucleophile in the presence of an equimolar amount of palladium chloride to give di-μ-chloro-bis-(1-syn-alkylsulfonylmethyl-π-allyl)dipalladium(II), while sodium arylsulfinates react with 1,3-dienes, accompanying the SO_2 extrusion, to give di-μ-chloro-bis-(1-syn-arylmethyl-π-allyl)dipalladium(II). See text, ref. 1, and the following articles: (a) J. P. Collman and W. R. Roper, J. Am. Chem. Soc., 88, 180 (1966); (b) C. D. Cook and G. S. Jauhal, Canad. J. Chem., 45, 301 (1967); (c) K. Garves, J. Org. Chem., 35, 3273 (1970).
10. (a) S. Takahashi, T. Shibano, and N. Hagihara, Tetrahedron Lett., 2451 (1967); (b) S. Takahashi, H. Yamazaki, and N. Hagihara, Bull. Chem. Soc. Jpn., 41, 254 (1968); (c) E. J. Smutny, J. Am. Chem. Soc., 89, 6793 (1967).
11. 3 [R = $CH(CH_3)_2$]: bp 92-93°C/18 mmHg; NMR (CCl_4) δ 1.12 (d, J = 6 Hz, 6H), 1.55 (m, 2H), 2.09 (br. q, J = 6 Hz, 4H), 3.53 (hept, J = 6 Hz, 1H), 3.84 (d, J = 3.5 Hz, 2H), 4.8-5.6 (m, 2H), and 5.45-6.10 (m, 3H); IR (neat film) 3095w, 1645m, 1385 s, 1375s, 1340m, 1150s, 1130s, 1060s, 975s, and 915s cm^{-1}; Mass (m/e, rel. intensity) 126 (P^+- CH_2=$CHCH_3$, 30), 109 (63), 93 (60), 82 (86), and 67 (100).
12. 5 [R' = $CH_2C(CH_3)_2C_6H_5$]: NMR (CCl_4) δ 1.5 (m, 2H), 1.60 (s, 6H), 2.05 (m, 4H), 2.95 (d, J = 6 Hz, 2H), 3.10 (s, 2H), 4.73-5.20 (m, 2H), 5.25-6.0 (m, 3H), and 7.3 (m, 5H); IR (neat film) 1640m, 1310s, 1130s, 1115s, 970m, 910m, 765s, and 700s cm^{-1}.

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