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SULFINATE AS COCATALYST 3[1]: PALLADIUM CATALYZED DIMERIZATION OF BUTADIENE WITH ACYLAMINO KETONES

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Abstract A catalyst generated in situ from $PdCl_2$ (1 mole) and $p\text{-}CH_3C_6H_4SO_2\text{-}Na\cdot 4H_2O$ (5 mole) promotes the dimerization of butadiene with the incorporation of α-acylamino ketones (**1a**∿**1h**) to provide α-acylamino α-(2,7-octadienyl) ketones (**2a**∿**2h**) in good yields. This new type of C-C bond forming reaction is not effected by the catalyst of $Pd(PPh_3)_4$ except for one example (with **1e**).

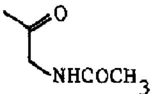
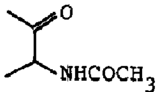
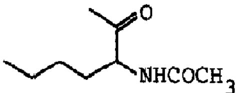
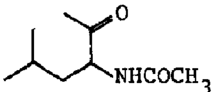
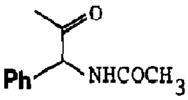
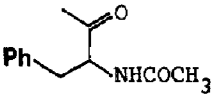
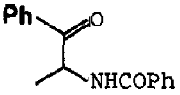
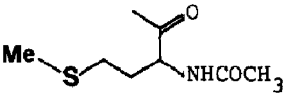
Palladium catalyzed allylation of active methylene compounds is one of the most extensively studied subjects on palladium chemistry and its synthetic utility has been fully proved by Trost, Tsuji and others.[3] Despite the ready availability of α-acylamino ketones (by Dakin-West reaction[4] from α-amino acids) and their usefullness as synthetic intermediate,[5] no report has appeared on the allylation of α-acylamino ketones making use of their characteristics as an active methylene compound.

In this paper, we wish to report the first example of the palladium catalyzed dimerization of butadiene with the incorporation of α-acylamino ketone, where the C-C bond formation product, α-acylamino α-(2,7-octadienyl)ketone **2**, was obtained selectively (Eq. 1). Unlike the dimerization of butadiene with α-hydroxy ketones, as described in the foregoing paper,[1] no C-N bond formation product was produced.

Reactions with seven kinds of α-acylamino ketones were undertaken uniformally at ambient temperature for 20h and no optimization of the conditions was made. Results are summarized in Table I, which reveals the efficiency of sodium toluenesulfinate[6] as a cocatalyst. For the most cases, tetrakis(triphenylphosphine)palladium proved to be ineffective as a catalyst and was recovered the starting material completely (entries 3 and 9). Only the successful case with $Pd(PPh_3)_4$ is the reaction with **1e**, which provided the expected butadiene dimer (77% isolated yield) together with a butadiene tetramer (**3**, 22% isolated yield), whose structure was assigned tentatively as depicted (entry 7, equation 2).

The reactivity of **1** seems to be well correlated to the acidity of the

Table 1. Palladium Catalyzed Dimerization of Butadiene with α-Acylamino Ketones[a]

Entry	α-Acylamino Ketone	Catalyst[b]	Conversion[c] (%)	Product[d] (Isolated Yield %)
1	 1a	$PdCl_2$-$TolSO_2Na$	34	2a (91)
2	 1b	$PdCl_2$-$TolSO_2Na$	84	2b (62)
3		$Pd(PPh_3)_4$	0	
4	 1c	$PdCl_2$-$TolSO_2Na$	45	2c (75)
5	 1d	$PdCl_2$-$TolSO_2Na$	56	2d (83)
6	 1e	$PdCl_2$-$TolSO_2Na$	100	2e (77)
7		$Pd(PPh_3)_4$	89	2e (77), 3 (22)
8	 1f	$PdCl_2$-$TolSO_2Na$	71	2f (71)
9		$Pd(PPh_3)_4$	0	
10	 1g	$PdCl_2$-$TolSO_2Na$	86	2g (84)
11	 1h	$PdCl_2$-$TolSO_2Na$	20	2h (62)

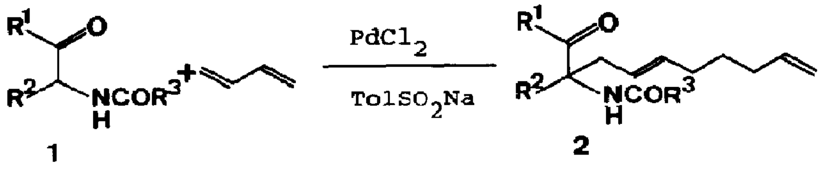
a) Molar ratio of reactants is as follows: Palladium complex (0.5 mmol), acylamino ketone (25 mmol), butadiene (70∿90 mmol) in 7.5 g of dimethylformamide (DMF).

b) For the formation of palladium complex $PdCl_2$-$TolSO_2Na$, see Experimental.

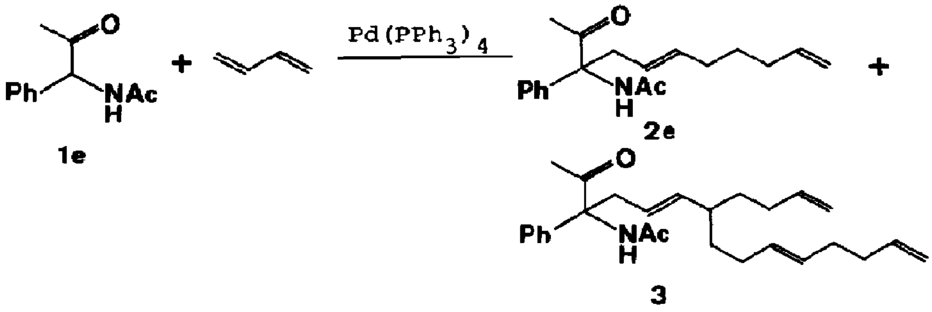
c) A conversion is determined on the basis of acylamino ketone, recovered.

d) For the structure of products, see equations 1 and 2.

e) For the structure of 3, see equation 2.



(1)

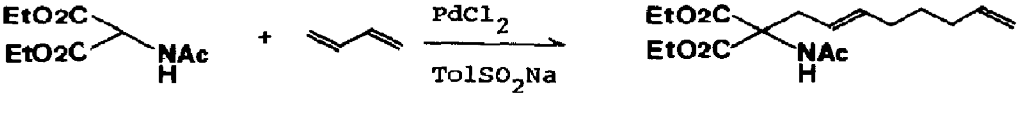


(2)

proton α to the carbonyl group: The higher the acidity, the higher the reactivity.

It is worth mentioning, among the α-acylamino ketones examined, 3-acetamido-4-methylpentan-2-one (1, R^1=CH_3, R^2=$CH(CH_3)_2$, R^3=CH_3), N-methyl-3-acetamidopropan-2-one (1a, with CH_3 in place of H), and 3-acetimidopropan-2-one (1a, with CH_3CO in place of H) were unreactive and recovered completely under the usual reaction conditions using $PdCl_2$-$TolSO_2Na$ catalyst. The first example suggests that the present reaction is sensitive to the steric bulk around the reaction site and the latter two examples seem to indicate that a hydrogen atom on nitrogen is required for the present reaction to proceed.[7]

The efficiency of the present catalytic system may be demonstrated by an application to the palladium catalyzed reaction of α-amino acid synthesis, recently developed by Chauvin et al.,[8] where they obtained diethyl 2-(octa-2',7'-dienyl)-2-acetamidomalonate in 91% crude yield by the reaction of butadiene with diethyl 2-acetamidomalonate [$Pd(OAc)_2$-PPh_3, 110°C, 2h, in the presence of a small amount of sodium phenoxide]. Under our reaction conditions [$PdCl_2$-$TolSO_2Na$, r.t., 20h, without a base], the same product was isolated in 83.6% yield [165∿170°C/0.1 mmHg, Kugelrohr distillation].



(3)

Experimental

Reaction of butadiene with 3-acetamido-3-phenylpropan-2-one (1e, cf. entry 6, Table 1): The $PdCl_2$-$TolSO_2Na$ catalyst is prepared in situ as homogeneous yellow solution by magnetical stirring of $PdCl_2$ (0.5 mmol) and p-CH_3-$C_6H_4SO_2Na\cdot 4H_2O$[6] (2.5 mmol) in 7.5 g of DMF. To the thus obtained mixture were added 1e (25 mmol) and butadiene (89 mmol), during which no care was payed for moisture and air. The reaction mixture was stirred vigorously at an ambient temperature for 20 h, during which no apparent change was observed except for precipitation of a very small amount of palladium black. After a recovery of butadiene, the reaction mixture was poured into sat.NaCl and extracted with benzene twice (100 + 50 ml). Drying over $MgSO_4$, evaporation of the solvent and subsequent purification by means of column chromatography (silica gel, benzene-EtOAc gradient) provided 3-acetamido-3-phenyl-3-(Octa-2',7'-dienyl)-propan-2-one (2e) as a colorless solid [5.8 g, 77% yield]. 2e: Mp. 58∿59°C (from ligroin); ^{1}H NMR ($CDCl_3$, TMS, δ) 1.2∿1.7 (m, 2H), 1.93(s, 3H), 1.97(s, 3H), 1.7∿2.3(m, 4H), 2.98(d.d, 14 and 7Hz, 1H), 3.76(d.d, 14 and 7Hz, 1H), 4.8∿6.25(m, 5H), 7.25(s, 1H), and 7.39(s, 5H); IR (KBr disc, cm^{-1}) 3230m, 3030w, 1705s, 1635s, 990w, 970m, 960m, 920m, 760m, and 700s; Mass (m/e, relative int.) 256(40), 240(15), 214(98), 190(11), 148(100), 132(66), 77(39), and 43(99).

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References and Notes

1) Part 2: Y. Tamaru, R. Suzuki, M. Kagotani, and Z. Yoshida, Tetrahedron Lett., proceeding paper in this issue.

2) Research Fellow from Daicel Chemical Co. Ltd.

3) For example, see (a) B. M. Trost and T. P. Klum, J. Am. Chem. Soc., 101, 6756 (1979); (b) J. Tsuji, Y. Kobayashi, H. Kataoka, and T. Takahashi, Tetrahedron Lett., 1475 (1980).

4) Org. Syn. Coll. Vol., 4, 5 (1963).

5) For example, see (a) S. Götze, B. Kübel, and W. Steglich, Chem. Ber., 109, 2331 (1976); (b) B. Kübel, P. Gruber, R. Rudolf, and W. Steglich, ibid., 112, 128 (1979); (c) G. Schulz, P. Gruber, and W. Steglich, ibid., 112, 3221 (1979); (d) G. Schulz and W. Steglich, ibid., 113, 770 (1980).

6) Sodium p-toluenesulfinate was purchased from Nakarai Chemical Co. and used without purification.

7) The similar inhibition of reaction has been observed for the dimerization of butadiene with α-acetoxycyclohexanone and α-acetoxyacetophenone, while the corresponding α-hydroxyl ketones reacted smoothly with butadiene to provide the α-2,7-octadienylated products.[1]

8) J.-P. Haudegond, Y. Chauvin, and D. Commereuc, J. Org. Chem., 44, 3063 (1979).

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