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LIGAND EFFECTS IN THE RHODIUM CATALYSED REACTION OF BUTADIENE AND AMINES

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Nickel and palladium complexes have been reported to catalyse the reactions of active hydrogen compounds with 1,3 butadiene. The reactions of butadiene with alcohols,[1] amines,[2] carboxylic acids[2,3] and active methylene and methyne compounds[4] have been shown to be catalytic in the presence of palladium (0) complexes. Alkylation of amines[5] and active methylene compounds[6] by butadiene has been shown to be catalysed by a nickel (0) complex prepared from a dialkoxy phosphine.[7] Rhodium complexes have been shown to catalyse the dimerisation of butadiene,[8] co-dimerisation of butadiene and other olefins[8,9,10] and reaction of butadiene with ethanol.[11] We now report that secondary amines and a number of primary aromatic amines may be alkylated with butadiene catalysed by rhodium(I) complexes.

To an ethanolic solution (10 ml.) of rhodium trichloride trihydrate (100 mg.) was added morpholine (4.35 ml., 0.05 moles) and butadiene (11.5 ml., 0.15 moles). The mixture, after heating in a sealed tube at 75 °C for 15 hrs., gave an 85% conversion to a mixture of amines (1) (70%) and (2) (30%).[†] Inclusion of triphenylphosphine in the reaction mixture (1:1 with respect to rhodium trichloride trihydrate) gave an 83% conversion to a mixture containing not only (1) (26%) and (2) (11.5%) but also (3) (5%) and (4) (57.5%).

A similar effect was noted in reaction of di-n-propylamine with butadiene. Initially a 58% conversion into a mixture of products (5 - 7) analogous to (1), (2) and (4) in amounts (17.5%), (70%) and (12.5%) respectively was obtained. Inclusion of a corresponding amount of triphenylphosphine gave a 77% conversion to a mixture of (5) (23%), (6) (10%) and (7) (67%). In reaction of butadiene with aniline an initial 9% conversion to the butenyl adducts (8) (81%) and (9) (19%) was raised to a 44.5% conversion to a mixture of (8) (58%), (9) (8%), (10) (20%) and (11) (14%) by the inclusion of triphenylphosphine.

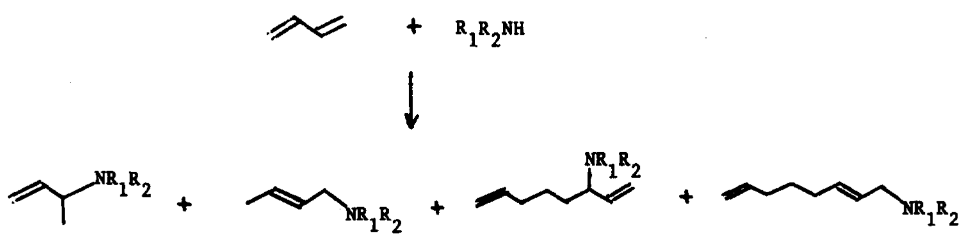
TABLE

Effect of Catalyst on Alkylation of Morpholine

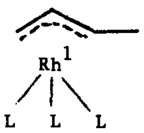
Catalyst*	Temp. °C	Time Hrs.	% RXN.	C_4 (1)	C_4 (2)	C_8 (3)	C_8 (4)
$RhCl_3.3H_2O$	75	15	85	70	30	-	-
$(Ph_3P)_3RhCl$	100	15	68	39.5	30	8.5	22
$(Ph_3P)_2Rh(CO)Cl$	100	17	43.5	13	2	7	78
$RhCl_3.3H_2O + PPh_3$ (1:1)	75	15	83	26	11.5	5	57.5
$RhCl_3.3H_2O + PPh_3$ (1:3)	75	18	33	21	29	5	45
$RhCl_3.3H_2O + PPh_3$ (1:9)	75	65	65	48	52	-	-
$RhCl_3.3H_2O + (PhO)_3P$ (1:1)	75	22	49	40	17	5	38
$RhCl_3.3H_2O + PhP(iOPr)_2$ (1:1)	75	22	94	59	23	5	13

* Morpholine (0.05 moles); Butadiene (0.15 moles); Rh complex (0.37 mmoles); EtOH(10 moles).

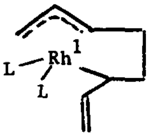
Inclusion of phosphine thus appears to encourage the formation of octadienyl adducts (Table) while increasing the efficiency of the process with respect of amine conversion in the cases of aniline and di-n-propylamine. Increasing the amount of free triphenylphosphine relative to rhodium trichloride trihydrate increased the amount of (1) formed, although octadienyl adduct formation decreased along with the amine conversion. Octadienyl adduct formation is less marked when triphenylphosphite or phenyldi-isopropoxy phosphine is employed as free ligand with rhodium trichloride trihydrate. Preformed rhodium(I) complexes such as $(Ph_3P)_3RhCl$ and $(Ph_3P)_2Rh(CO)Cl$ also favour octadienyl adduct formation (see Table).



(1)	(2)	(3)	(4)	R_1=R_2 = morpholine
(5)	(6)		(7)	R_1=R_2 = N-C_3H_7
(8)	(9)	(10)	(11)	R_1=H, R_2=Ph



(12)



(13)

The results can be very satisfactorily explained by a consideration of the intermediate present in the reaction mixture. A (π-allyl) rhodium complex is formed via a rhodium hydride intermediate by treatment of an ethanolic solution of rhodium trichloride trihydrate with butadiene.[10] Reaction with morpholine at either the 1- or 3-position yields (1) and (2). Alternatively, addition of a second molecule of butadiene could yield (13), which with morpholine would similarly lead to (3) and (4). Formation of (13) is enhanced by the presence of a stabilising ligand such as triphenylphosphine, with a consequential formation of octadienylated amine products. Formation of an analogous nickel complex in the presence of phosphine ligands is well established.[12] A large increase in amount of triphenylphosphine makes formation of (13) less likely due to competition between phosphine and butadiene for the available co-ordination sites. This explanation is further enhanced by use of preformed rhodium(I) complexes. Octadienyl adduct formation is favoured by use of both tris(triphenylphosphine)-rhodium(I) chloride and bis(triphenylphosphine)rhodium(I) carbonyl chloride; the latter containing the more strongly bound carbon monoxide ligand yielded 85% of the C_8-amine.

Morpholine also reacts with isoprene and piperylene but the extent of reaction under similar conditions decreases in the order butadiene > piperylene > isoprene. Furthermore, inclusion of triphenylphosphine serves only to reduce the extent of reaction without forming any octadienyl derivatives.

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† Products were identified on the basis of their mass and n.m.r. spectra, separation being achieved by fractional distillation and g.l.c. Vinyl cyclohexene is also formed in the reactions in varying amounts, probably by thermal dimerisation of butadiene.

References

1. E.J. Smutny, J. Amer. Chem. Soc., 89, 6793 (1967).
2. S. Takahashi, T. Shibano and N. Hagihara, Bull. Chem. Soc. Japan, 41, 454 (1968).
3. W.E. Walker, R.M. Manyik and K.E. Atkins, Tetrahedron Letters, 3817, (1970).
4. G. Hata, K. Takahashi and A. Miyake, J. Org. Chem., 36, 2116 (1971).
5. R. Baker, D.E. Halliday and T.N. Smith, Chem. Commun., 1583 (1971).
6. R. Baker, D.E. Halliday and T.N. Smith, J. Organometall. Chem., 35, C61 (1972).
7. A.A. Ario, B.B. Chastain and H.B. Gray, Inorg. Chim. Acta, 3, 8 (1969).
8. T. Alderson, E.L. Jenner, and R.V. Lindsey, Jr., J. Amer. Chem. Soc., 89, 6793 (1967).
9. R. Cramer, Accts. Chem. Res., 186 (1968).
10. R. Cramer, J. Amer. Chem. Res., 89, 1633 (1967).
11. K.C. Dewhirst, J. Org. Chem., 32, 1297 (1967).
12. B. Barnett, B. Büssemeier, P. Heimbach, P.W. Jolly, C. Krüger, T. Tkatchenko and G. Wilke, Tetrahedron Letters, 1972, 1457.