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CATALYTIC ADDITION OF SECONDARY AMINES TO ETHYLENE
(Contribution No. 1720)

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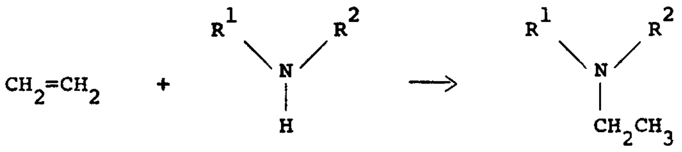
Although the catalytic addition of amines to olefins has been the subject of numerous investigations,[1] no additions homogeneously catalyzed by transition metal compounds have been reported. We now wish to report that various compounds of rhodium or iridium effectively catalyze the addition of secondary aliphatic amines to ethylene (eq. 1).



R^1, R^2 = alkyl

For example, a mixture of piperidine (17 g., 200 mmole), ethylene (9 g., 300 mmole), rhodium trichloride trihydrate (0.51 g., 2 mmole), and tetrahydrofuran (25 ml.) when heated to 180°C. for 3 hr. in an 80-cc autoclave afforded 14.6 g. (65% yield) of N-ethylpiperidine. The results obtained with other amines under similar conditions are described in Table I.

In all cases, the liquid phase remained homogeneous. The initial valence state of the rhodium complex appeared to be immaterial, since equally good results were obtained using the Rh(I) complex, μ-dichlorotetraethylene-dirhodium(I). Other complexes such as $RhI_3 \cdot 3H_2O$, $Rh(NO_3)_3$, and $IrCl_3 \cdot 3H_2O$ also proved to be effective. No reaction was noted in the absence of the metal complexes.

The reaction is apparently very sensitive to the nature of the amine. The first three amines in Table I gave a wide range of yields although they are of similar basicity. Possibly steric effects are operating here, since yields tend to decrease with increasing steric bulk around the nitrogen. However, basicity (or nucleophilicity) does appear to be a factor, since morpholine is much less reactive than piperidine.

Table I[a]

Amine	% Yield of N-Ethylamine	pK_a[c]
Dimethylamine	54	10.73
Diethylamine	4	10.49
n-Butylethylamine	3	ca. 10.5
Pyrrolidine	36[b]	11.27
Morpholine	<2	8.33
Piperidine	70	11.12

[a] Mole ratios; Amine:Ethylene:$RhCl_3 \cdot 3H_2O$ = 350:100:1; Temp. = 200°; Time = 3 hr.; Solvent = tetrahydrofuran.

[b] Appreciable side reactions noted.

[c] Handbook of Chemistry & Physics, 49th edition, p. D-87, The Chemical Rubber Co.

In preliminary studies of the kinetic order of the reaction of ethylene with piperidine catalyzed by rhodium trichloride, the reaction rate was found to be independent of the piperidine concentration and first order with respect to rhodium trichloride. The order in ethylene was not established because of difficulties in accurately measuring the amount of ethylene consumed. The reaction was also shown to be irreversible under the reaction conditions (limit of detection = 0.1% reaction).

In a remarkable display of specificity, homologs of ethylene were shown to be essentially unreactive. Also, primary amines or ammonia were unreactive. In the case of ammonia and, possibly, certain primary amines, thermodynamic considerations[1a] suggest that detectable quantities of adducts may not be formed under our reaction conditions.

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