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# CATALYTIC REDUCTION OF OZONIDES. II. SYNTHESIS OF AMINES FROM OLEFINS

R. Winslow White[1], Stella W. King[2] and Joseph L. O'Brien

Rohm & Haas Company, Research Laboratories, 5000 Richmond Street
Philadelphia, Pennsylvania

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The reductive amination of aldehydes and ketones is an established reaction[3], but few reports of the direct reductive amination of olefin ozonides have been published. The ozonolysis products from cyclohexene in methanol or isopropanol were treated with ammonia and hydrogen in the presence of a nickel or cobalt hydrogenation catalyst to give ca. 30% yields of hexamethylenediamine.[4] The use of methylamine under similar conditions[5] gave a 38% yield of N,N' - dimethylhexamethylenediamine. The reductive amination of the ozonolysis products from ethyl 10-undecenoate with ethanolic ammonia at 100° and 1200-1400 psi in the presence of Raney nickel catalyst gave ethyl 10-aminodecanoate in 38-40% yield.[6] A series of olefin ozonides were reductively aminated at 150° and 2900 psi over Raney Ni to give amine mixtures in 14-59% yields.[7] The relatively low yields of amine products in these preparations may be attributed to the thermal decomposition of the peroxidic intermediates, yielding esters and amides. In contrast to the mediocre results from the direct reductive amination of ozonolysis products are the higher overall yields reported in the preparation of nonylamine and methyl 9-aminononanoate from methyl oleate.[8] However, this procedure required the isolation of the aldehydic intermediates, nonanal and methyl azelaaldehydate.

We now wish to report that olefins may be directly converted in good to excellent yields to primary, secondary, or tertiary amines by a three-stage sequence of ozonolysis, partial reduction, and reductive amination <u>without</u> isolation of the intermediate carbonyl derivations. (Equation 1)

$$R_1CH = CHR_2 + \begin{array}{r} a) \\ b) \\ c) \end{array} \left[\begin{array}{l} O_3,\ ROH \\ H_2,\ cat. \\ H_2,\ R'R''NH,\ cat. \end{array}\right] \longrightarrow R_1CH_2NR'R'' + R_2CH_2NR'R'' \qquad (1)$$

The ozonolysis and the partial reduction stage are carried out as previously described.[9] Ammonia (or the appropriate primary or secondary amine) is then added and the reductive amination is carried out at 50 - 60° (200-400 psi) with a rhodium catalyst or at 80 - 100° (600-1000 psi) with a Raney nickel catalyst. The results of some typical preparations of amines by this method are shown in Table 1.

TABLE I

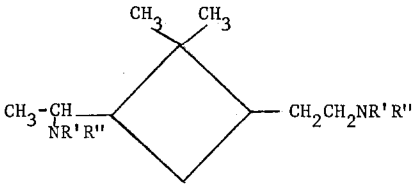
SYNTHESIS OF AMINES FROM OLEFINS

| Olefin | Reagent | Catalyst | Products[a] | Overall Yield, % |
|---|---|---|---|---|
| cyclohexene | $NH_3$ | Ni | $H_2N(CH_2)_6NH_2$ | 50 |
| | $CH_3NH_2$ | Rh | $CH_3NH(CH_2)_6NHCH_3$ | 70 |
| | i-$BuNH_2$ | Ni | i-$BuNH(CH_2)_6NHBu$-i | 30[b] |
| | $(CH_3)_2NH$ | Ni | $(CH_3)_2N(CH_2)_6N(CH_3)_2$ | 60 |
| | | Rh | | 57 |
| cyclooctene | $NH_3$ | Ni | $H_2N(CH_2)_8NH_2$ | 55 |
| | $CH_3NH_2$ | Ni | $CH_3NH(CH_2)_8NHCH_3$ | 73 |
| | | Rh | | 72 |
| | $(CH_3)_2NH$ | Rh | $(CH_3)_2N(CH_2)_8N(CH_3)_2$ | 80 |
| α-pinene | $NH_3$ | Ni | I(R',R" = H) | 80 |
| | $CH_3NH_2$ | Ni | I(R' = H,R" = $CH_3$) | 66 |
| | | Rh | | 75 |
| | i-$BuNH_2$ | Ni | I(R' = H,R" = i-Bu) | 70 |
| | $(CH_3)_2NH$ | Ni | I(R',R" = $CH_3$) | 65 |
| hexadecene-1 | $(CH_3)_2NH$ | Ni | n-$C_{15}H_{31}N(CH_3)_2$ | 65 |
| oleonitrile | $NH_3$ | Ni | n-$C_9H_{19}NH_2$ | 65 |
| | | | $H_2N(CH_2)_9NH_2$ | 70 |

[a] Physical constants of known compounds agreed with literature values; satisfactory elemental analyses were obtained for all new compounds.

[b] A 50% yield of N-isobutylhexamethyleneimine was also isolated from this reaction.

The yields of primary diamines from ammonia and cyclic olefins such as cyclohexene and cyclooctene are moderate (50-55%), but significantly higher than those reported by others employing a direct reductive amination method.[4] The N,N'-dimethyl diamines from methylamine and cyclic olefins were obtained in much better yield (70-73%), and α-pinene gave good yields of the novel cyclobutane diamines (I) with ammonia and all of the amine reagents tried.



I

Finally, the preparation of nonamethylenediamine in 70% yield from oleonitrile is especially noteworthy. In general, the present three-stage sequence offers a convenient method for the conversion of a wide variety of olefins to the corresponding amines at moderate temperatures and pressures in readily available equipment.

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