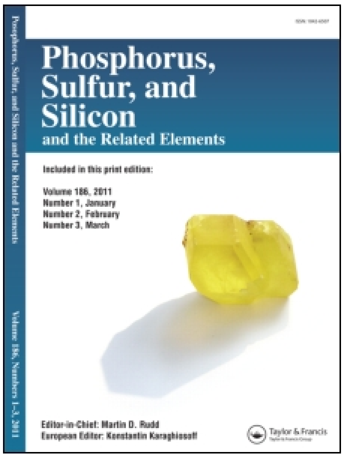

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A NEW SYNTHESIS OF HETEROCYCLES VIA CARBONYLATION OF AMINES WITH CARBON MONOXIDE IN THE PRESENCE OF SELENIUM

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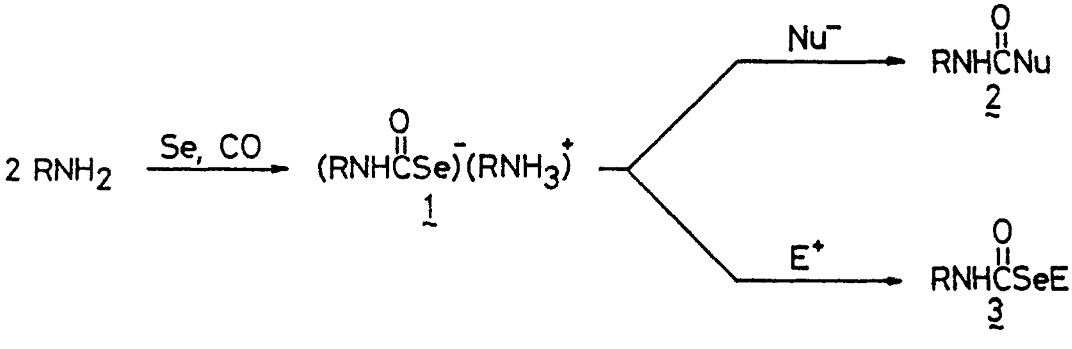
Abstract Amines which contain a second functional group in the appropriate position react with carbon monoxide in the presence of selenium to form heterocyclic derivatives in which carbon monoxide is incoporated. For instance, diamines, aminoalcohols, and their related compounds undergo carbonylation to give cyclic ureas, urethanes and the corresponding carbonylated compounds. For diamines and amino alcohols with more than two carbon atoms between the functional groups, intermolecular carbonylative coupling takes place competing with the intramolecular reaction. High selectivity has been attained under specified reaction conditions. Anilines having cyano or acetyl groups on the ortho position afford new classes of selenium-containing heterocycles. In these reactions, carbamoselenoate has been suggested as the common key intermediate.

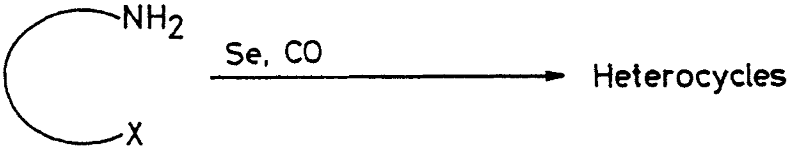
INTRODUCTION

The carbonylation of amines is one of the fundamental reactions in organic synthesis. Phosgene or phosgene-based reagents are widely used in organic synthesis as N-carbonylating reagents.[1a-d] An attractive alternative is the use of carbon monoxide in the presence of transition metal catalysts. These reaction often gave a mixture of ureas, formamides, and/or oxamides, in which the selectivity depends largely upon the ligands as well as metals used.[2a-b]

We have reported that selenium, a non-transition element, displays a unique catalytic activity in the carbonylation of amines with carbon monoxide.[3a-1] This reaction has been postulated to proceed via ammonium carbamoselenoate 1 as a key intermediate which then reacts with another nucleophile Nu^- or electrophile E^+ to give 2 or 3, respectively.[3a,g]



Hence, it is expected that when amines having nucleophilic or electrophilic functional groups in the same molecule are employed, the corresponding heterocycles will form through an intramolecular reaction.

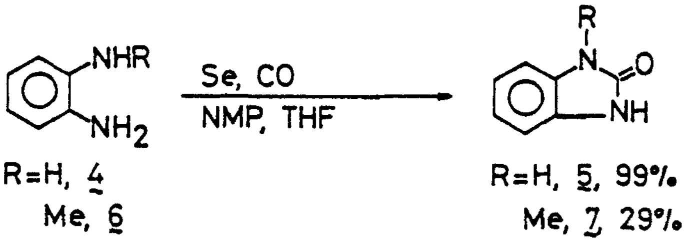


In this paper are described the results of the study of selenium-assisted carbonylation of amines with carbon monoxide directed towards the syntheses of heterocycles.

Hereafter, the carbonylation in which one molecule of amine reacts with one molecule of carbon monoxide to give a cyclic compound as the product will be called as intramolecular carbonylation. The term intermolecular carbonylation will mean the reaction of two molecules of amine and one molecule of carbon monoxide to produce an open-chain product.

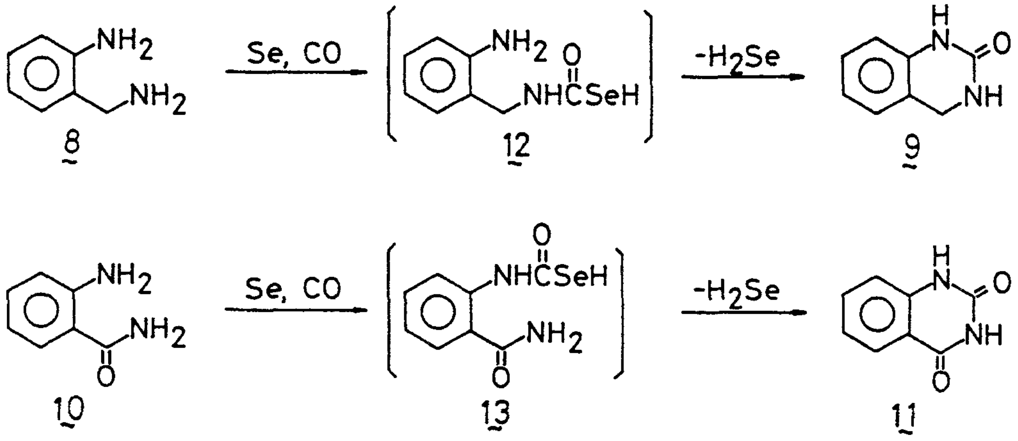
INTRAMOLECULAR CARBONYLATION OF AROMATIC AMINES WITH CARBON MONOXIDE USING A STOICHIOMETRIC AMOUNT OF SELENIUM[3i,k]

o-Phenylenediamine 4 was allowed to react at 100°C with carbon monoxide (31 Kg/cm^2) and a stoichiometric amount of selenium in the presence of N-methylpyrrolidine (NMP) in THF for 20h. After stirring the resulting mixture in air at 25°C for 1 h, 2H-benzimidazol-2(3H)one 5 was obtained in 89% yield. When the reaction was carried out at 25°C the starting material was recovered. In the absence of NMP, 4 gave 5 in 67% yield under similar conditions. The reaction period could be shortened when excess amounts of selenium were used. The reaction seems to be susceptible to steric effects. For example, 7 was obtained in only 29% yield from N-methylphenylenediamine 6 under the same conditions.

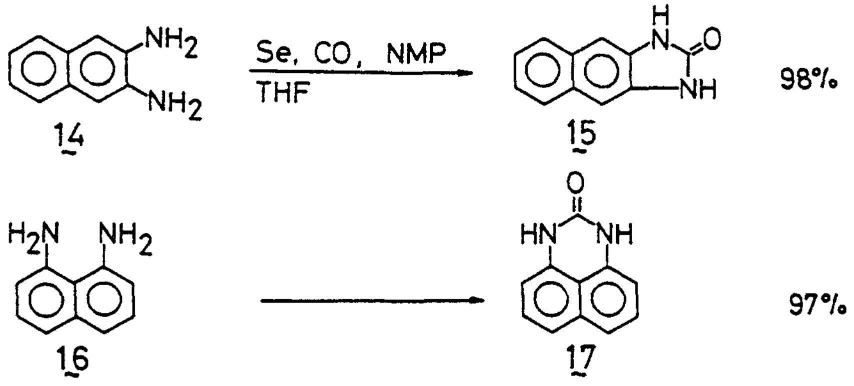


Aniline derivatives such as 8, having an aminoalkyl substituent in the ortho position, underwent similar carbonylation in THF to yield the corresponding cyclic urea, 9, in good yields. It is interesting to note that 2-carbamoylaniline 10 was also carbonylated to give 11 in 23% yield in DMF.

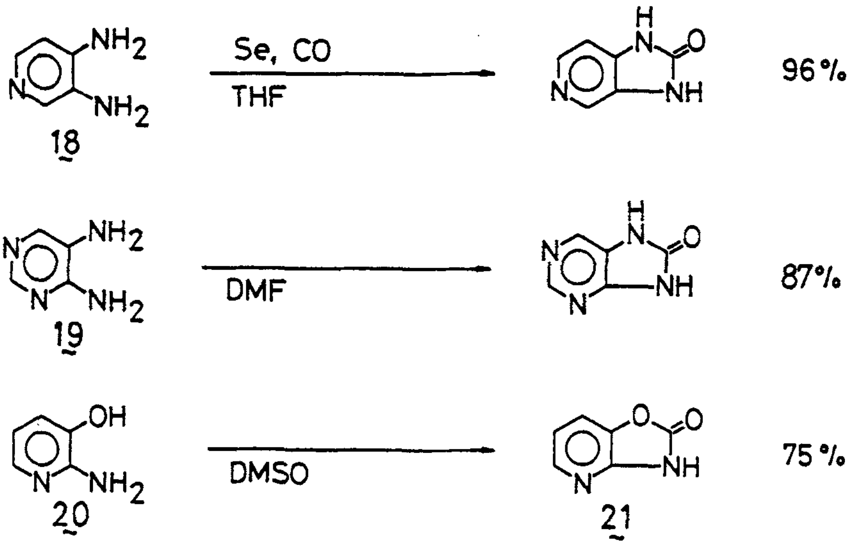
A possible reaction path is as follows. In the case of 2-(aminomethyl)aniline, 8, the aliphatic amino group would be more reactive than the aromatic one and may react faster with carbon monoxide and selenium, leading to carbamoselenolate 12. In case of 2-carbamoylaniline, 10, the carbamoselenoate 13 may be formed through the reaction at the site of the aromatic amino group, due to the low reactivity of the carbamoyl nitrogen. The attempted isolation and trapping of the intermediate 12 failed and resulted in the formation of 9. The intermediates 12 and 13 then undergo aminolysis by the intramolecular nucleophilic attack of the remaining NH_2 group to give the corresponding cyclic ureas 9 and 11, respectively, together with the formation of hydrogen selenide.



The reaction of 2,3- and 1,8-naphthalenediamines, 14 and 16, under similar conditions afforded 15 and 17, respectively in good yields.



Pyridine- and pyrimidinediamines, 18 and 19, undergo similar carbonylation. In case of 2-amino-3-pyridinol 20, the carbonylation also proceeded without NMP to afford the corresponding cyclic urethane 21 in 87% yield.

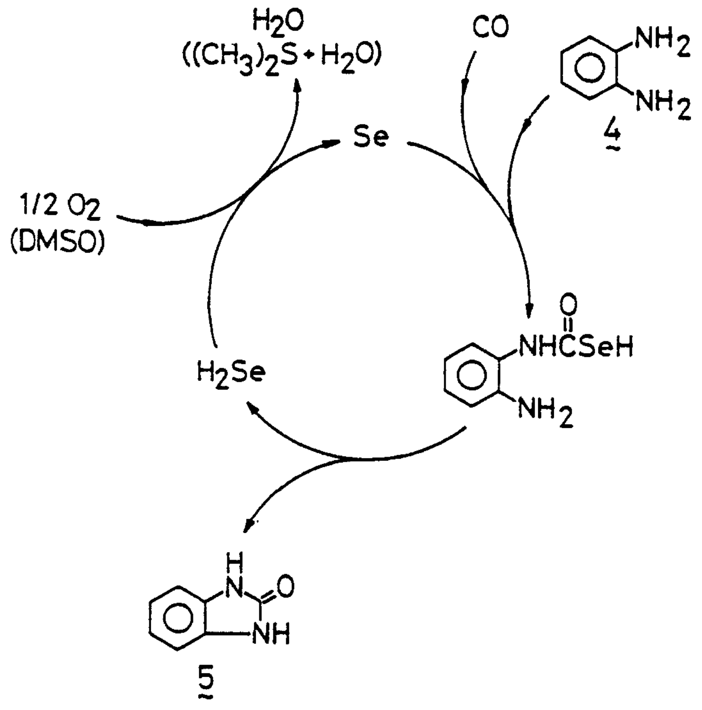


SELENIUM CATALYZED CARBONYLATION WITH CARBON MONOXIDE IN THE PRESENCE OF AN OXIDIZING AGENT

The carbonylation has been found to proceed using a catalytic amount of selenium in the presence of an oxidizing agent.[3a,e,k] For instance, when the reaction *o*-phenylenediamine 4 was carried out at 100°C using 0.05 equivalent of selenium with 3 equivalents of NMP under a gas mixture of carbon monoxide (29 Kg/cm^2) and oxygen (2 Kg/cm^2), the cyclic urea 5 was obtained in 99% yield.

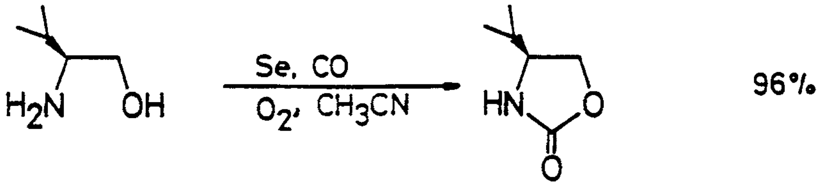
A plausible catalytic reaction course in which the resulting hydrogen selenide is oxidized to regenerate selenium is shown below. Dimethyl sulfoxide was also functional effectively as an oxidizing agent.

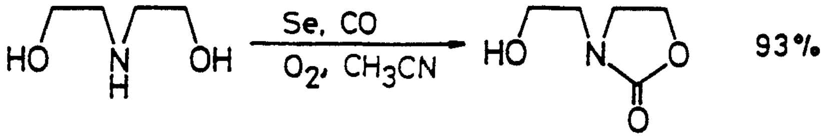
What should be emphasized is that this catalytic reaction proceeds under much milder conditions than the stoichiometric reaction. At room temperature 4 gave 5 in 77% yield, while the reaction of 4 at room temperature under stoichiometric conditions results in the recovery of the starting materials as mentioned

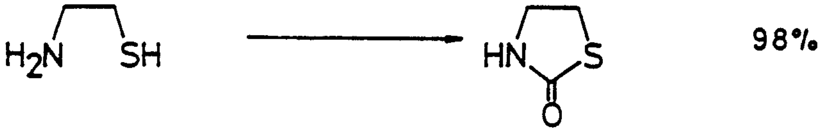


before. This fact suggests that an alternative path may exist in the catalytic carbonylation. A possible alternative path involves the intramolecular amminolysis of biscarbamoyldiselenide which is formed in situ by the oxidation of the corresponding carbamoselenolate. Attempts to isolate the diselenide from the reaction mixture failed.

This catalytic reaction could also be applicable to carbonylation of a variety of aminoalcohols and aminothiol under mild conditions as shown below.[3e,4]

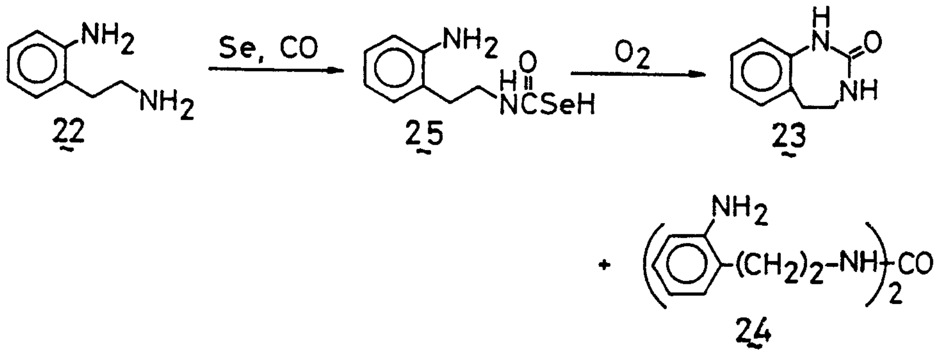






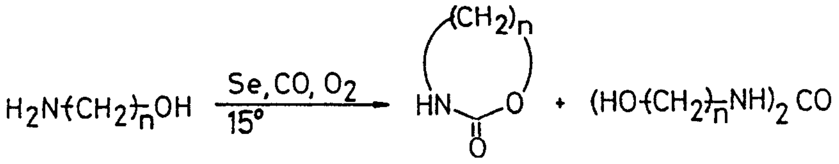
Selectivity Between Intra- and Intermolecular Carbonylation

Under catalytic conditions, intra- and intermolecular carbonylation sometimes compete with each other resulting in the formation of a mixture of cyclic and acyclic products. Reaction of 2-(2-aminoethyl)aniline 22 gave acyclic urea 24 (95%) together with a trace amount of cyclic urea 23 (ca. 1%), although in the stoichiometric reaction 23 was obtained as the sole product. Hence the effects of temperature, concentration, carbon monoxide and oxygen pressures, and amount of selenium used on the selectivity were examined. As might be expected, the cyclic urea 23 was preferentially formed under more dilute conditions and at higher temperatures. The acyclic urea 24 was obtained selectively when the reaction was carried out at room temperature. Selective formation of the cyclic urea 23 was attained only when a stoichiometric or excess amount of selenium was used.[3k]



These results may be interpreted as follows. The aliphatic amino group is more nucleophilic than the aromatic amino group and may react faster with selenium and carbon monoxide to form carbamoselenolate 25. Therefore in the stoichiometric reaction all of the aliphatic amino group might be converted rapidly to carbamoselenolate moieties which then undergo intramolecular cyclization by the attack of the aromatic amino group. On the other hand, in the catalytic reaction, most of the starting material retains an aliphatic amino group which can attack the carbamoyl carbon of the carbamoselenolate 25 intermolecularly to form the acyclic urea 24. Thus, both reactions via intra- and intermolecular carbonylation may compete under catalytic conditions.

We have also succeeded in the selective preparation of aliphatic cyclic urethanes and acyclic ureas from the corresponding aminoalcohols as shown below.



n	Equiv. of Se	Yield, %	
3	1.0	97	-
3	0.5	68	24
3	0.05	-	91
4	1.1	92	-
4	1.0	89	2
4	0.05	-	96
5*	3.0	87	2
5**	0.05	-	93

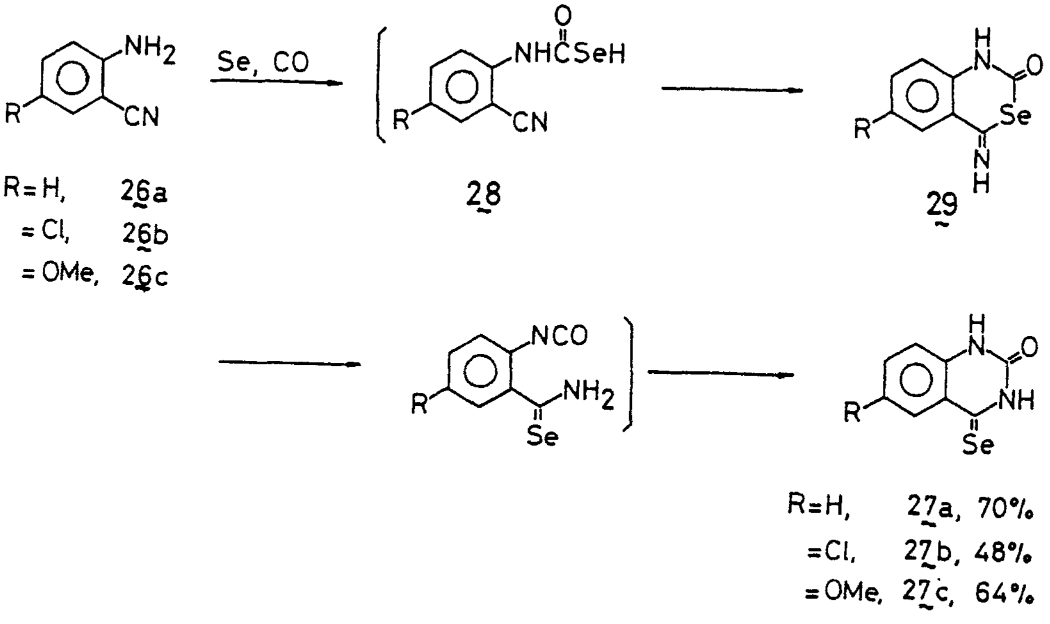
Conditions: substrate (5 mmol), Et_3N (5 mmol), CO (40 mL/min), O_2 (0.7 mL/min), CH_3CN (20 mL).
*substrate (1 mmol), CH_3CN (40 mL). **substrate (1 mmol).

SYNTHESIS OF NEW CLASSES OF SELENIUM-CONTAINING HETEROCYCLES

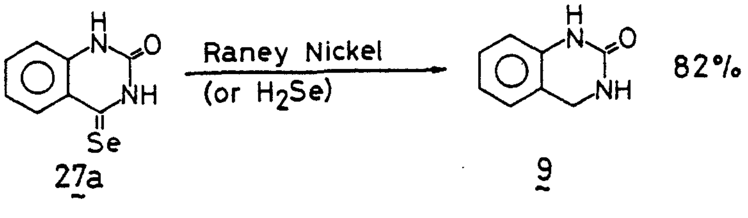
Since carbamoselenolate group ($-NCOSe^-$) has a nucleophilic site at selenium, it can be expected that a nucleophilic reaction of the carbamoselenolate may proceed intramolecularly to give a new class of selenium-containing heterocycles when anilines which carry a substituent having an electrophilic center at the ortho position are employed in this reaction system.[3j]

o-Aminobenzonitriles 26a-c were treated with excess amounts of selenium and carbon monoxide (30 Kg/cm^2) in the presence of N-methylpyrrolidine (NMP) at 100°C for 20h to give selenoxoquinazolinone derivatives 27a-c in good yields.

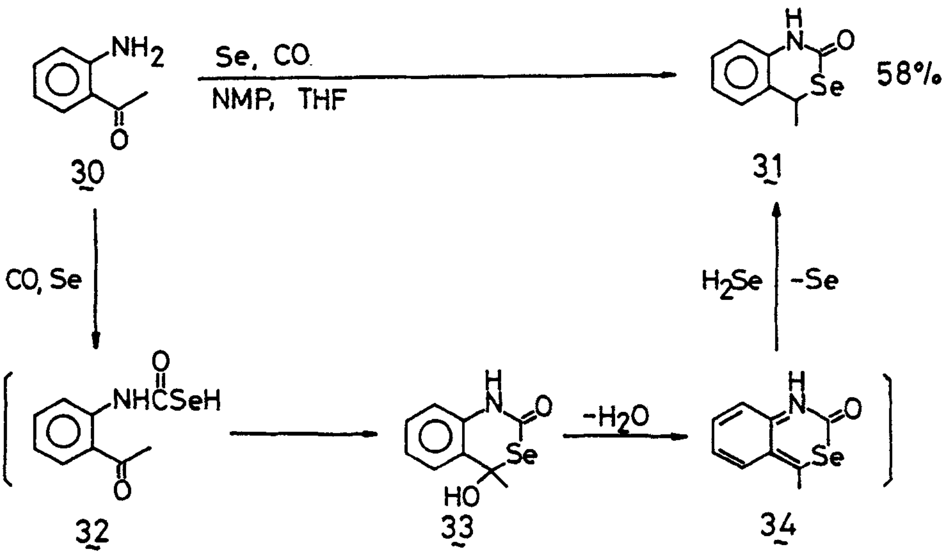
This reaction may involve the initial formation of carbamoselenolate 28 by the reaction of the aromatic amino group with selenium and carbon monoxide. Intramolecular addition of the -SeH moiety of 28 to the cyano group might occur to form cyclic intermediate 29, followed by a ring-opening, ring-closure sequence to yield 27a-c.



The C=Se bond of 27a was easily reduced with Raney nickel to give 9 in 82% yield. Hydrogen selenide could also be used as the reducing agent.



o-Aminoacetophenone 30 also reacted with carbon monoxide and selenium under similar reaction conditions to afford benzoselenazinone 31 in moderate yield. This reaction may also proceed via carbamoselenolate intermediate 32. Subsequent cyclization gives rise to 33, followed by reduction via 34 may afford 31.



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