J. Org. Chem. **1984**, 49, 2875–2880

showed no trace of benzhydrol after the reaction.

Thermal Decomposition of Benzhydrol. A solution of benzhydrol (75.6 mg, 0.413 mmol) and naphthalene (28.3 mg, 0.221 mmol) was prepared in benzene (2 mL). A glass capillary (10 cm, 9 mm OD, 2.5 mm ID) was filled with 25 μL of this solution, degassed and sealed under argon, and heated for 20 min in the sandbath at 400 °C. Upon cooling to room temperature, the capillary was cooled under liquid nitrogen and opened and the contents were extracted into chloroform. Gas chromatography revealed that 60% of the benzhydrol had been converted to products: diphenylmethane (42%), benzophenone (44%), triphenylmethane (<1%), 1,1,2,2-tetraphenylethane (1%), tetraphenylethylene (<1%), and bis(diphenylmethyl) ether. The properties of all products were recorded by GC–MS and NMR spectroscopy and were identical to authentic samples.

Experiments with naphthalene in the presence of these materials showed that naphthalene was unreactive under these conditions.

Benzene-d_6 was substituted for benzene as the co-solvent in a replicate experiment and the biphenyl produced in the reaction was examined by GC–MS techniques. The MS data were in close agreement with previous reports of the spectrum of biphenyl-d_{10}.[26] Signals corresponding to biphenyl or biphenyl-d_5 were absent.

Thermal Decomposition of Bis(diphenylmethyl) Ether. A solution of bis(diphenylmethyl) ether (87.8 mg, 0.251 mmol) and naphthalene (16.4 mg, 0.128 mmol) was prepared in benzene (1 mL). A glass capillary was filled with 25 μL of this solution, sealed under argon, and reacted for 20 min at 400 °C. Gas chromatography revealed that 46% of the ether had been converted to products: diphenylmethane (46%), benzophenone (54%), triphenylmethane (<1%), and tetraphenylethane (<1%).

Reaction of Benzhydrol with Phenol. Benzhydrol (0.712 g, 3.91 mmol), phenol (1.81 g, 19.2 mmol), and benzene (200 μL) were placed in a stainless steel reactor and heated at 400 °C for 30 min. The reaction mixture was washed several times with 0.5 N sodium hydroxide and water and extracted into diethyl ether. The ether was dried over magnesium sulfate and the volatile solvents were removed under vacuum. The reaction products were chromatographed on a silica gel column and eluted with mixtures ranging from 1% to 50% diethyl ether in hexane. Fifteen fractions were collected and examined by gas chromatography, mass spectrometry, and nuclear magnetic resonance techniques. Diphenylmethane (28%), dibenzofuran (0.6%), fluorene (trace), benzophenone (15%), triphenylmethane (0.5%), diphenylmethyl phenyl ether (0.5%), 2-(diphenylmethyl)phenol (5%), 4-(diphenylmethyl)phenol (20%), 9-phenylxanthene (29%), and tetraphenylethylene (0.3%) were shown to be present by comparison with the properties of authentic materials.

Reaction of Benzhydrol in Nonacidic Aqueous Solution. (A) In Neutral Solution. Benzhydrol (10 mg, 0.05 mmol) dissolved in benzene (25 μL) and distilled water (50 μL) were sealed in a glass capillary. The capillary was heated at 400 °C for 60 min. The products were dissolved in ether and dried over magnesium sulfate and the volatile solvents were removed under vacuum. Analysis by NMR spectroscopy established that 5% of benzhydrol was converted to diphenylmethane.

(B) In Basic Solution. Benzhydrol (10 mg, 0.05 mmol) dissolved in benzene (25 μL) and aqueous sodium hydroxide (1 N, 50 μL) were reacted in a glass capillary at 400 °C for 60 min. The contents of the capillary were acidified with dilute hydrochloric acid and extracted into ether. The solution was dried over magnesium sulfate and the ether was removed under vacuum. Only 1% of benzhydrol was converted to diphenylmethane.

Exchange Reactions. In a typical experiment, bis(diphenylmethyl) ether (81 mg, 0.23 mmol), tetralin-d_{12} (22 μL, 0.23 mmol), and benzene (50 μL) were sealed in a glass capillary under an argon atmosphere. The capillary was heated at 350 °C for 120 min. After cooling, the contents of the vessel were extracted into methylene chloride and separated by preparative GC. The deuterium contents of the recovered tetralin and diphenylmethane were examined by NMR spectroscopy and gas chromatography with mesitylene as an internal standard.

Acknowledgment. We thank the United States Department of Energy for support of this work.

Registry No. Ph_2CO, 119-61-9; Ph_2CHOH, 91-01-0; $(Ph_2CH)_2O$, 574-42-5; Ph_2CHOD, 90718-39-1; Ph_2CDOH, 17498-07-6; $PhSCH_2Ph$, 831-91-4; Ph_2CH_2, 101-81-5; tetralin, 119-64-2; dihydroanthracene, 613-31-0; 1,1,2,2-tetraphenylethane, 632-50-8; diphenylmethyl phenyl ether, 4733-41-9; 2-(diphenylmethyl)phenol, 4970-23-4; 4-(diphenylmethyl)phenol, 791-92-4; diphenylmethane-1,1-d_2, 3947-98-6; fluorenone, 486-25-9; naphthalene, 91-20-3; phenol, 108-95-2; 1,2,3,4-tetrahydroquinoline, 635-46-1; 5,12-dihydrotetracene, 959-02-4; 1,2,3,4,5,6,7,8-octahydroanthracene, 1079-71-6; 9,10-dihydrophenanthrene, 776-35-2; Decalin, 91-17-8; 9-phenylxanthene, 3246-80-8.

Selective Cleavage of Carbon–Nitrogen Bonds with Platinum

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The selective hydrogenolysis of carbon–nitrogen bonds relative to carbon–carbon bonds with a heterogeneous platinum catalyst is studied on a wide variety of nitrogen-containing organic molecules. Nitriles, secondary and primary amines, nitro compounds, heterocycles, and aromatic amides are cleanly converted to the parent hydrocarbon and ammonia in the gas phase with a platinum on silica catalyst and hydrogen. Aliphatic amides pass the catalyst unchanged. Unusual is the high platinum content of the catalyst (40%) which proved to be essential for the catalytic activity reported.

Introduction

The cleavage of carbon–nitrogen bonds is a desirable but rarely addressed problem in organic synthesis. Hydrodenitrogenation (HDN) has received increasing attention during the past decade, as the high nitrogen content of synthetic oils derived from shale oil, oil sands, and coal makes hydrodenitrogenation imperative if the liquids are to be refined to replace products presently obtained from petroleum. The major research activity in hydrodenitrogenation has been the investigation of HDN properties of hydrodesulfurization catalysts which are composed of various combinations of Ni, Mo, W, and Co on different supports.[2] Numerous investigations have consistantly shown that these catalysts are not selective

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0022-3263/84/1949-2875$01.50/0

Table I. Calculated Free Energy of Reaction for C–N Hydrogenolysis Reactions

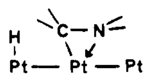
reactn	Gr_{298}[a]	Gr per bond[a]
$C_4H_9NH_2 + H_2 \rightarrow C_4H_{10} + NH_3$	−19.7	−19.7
$C_5H_{12} + H_2 \rightarrow C_4H_{10} + CH_4$	−14.3	−14.3
$C_6H_5NH_2 + H_2 \rightarrow C_6H_6 + NH_3$	−12.7	−12.7
$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$	−10.3	−10.3
$C_3H_7CN + 3H_2 \rightarrow C_4H_{10} + NH_3$	−33.9	−11.3
$C_3H_7C{\equiv}CH + 3H_2 \rightarrow C_4H_{10} + CH_4$	−66.5	−22.2
$C_5H_5N + 3H_2 \rightarrow H_2C{=}CHCH{=}CHCH_3 + NH_3$	−14.5	−4.5
$C_6H_6 + 3H_2 \rightarrow H_2C{=}CHCH{=}CHCH_3 + CH_4$	−8.3	−2.8

[a] Values in kcal/mol.

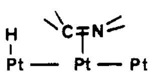
and require very high hydrogen consumptions to achieve HDN. Katzer has pointed out that these catalysts which have been optimized for petroleum desulfurization are not suitable for HDN and new catalysts need to be developed.[3]

We were especially interested in catalytic C–N hydrogenolysis as a possible synthetic tool for the selective cleavage of C–N bonds in organic synthesis. Inspection of thermochemical data[4] (see Table I) documents the energetic similarity of C–N and C–C bonds.

The hydrogenolysis of an aliphatic C–N bond is more exothermic than that of a C–C bond by 5 kcal/mol. This difference decreases for single bonds connected to an aromatic ring and is strongly reversed for double and triple bonds indicating that hydrogenolysis of C–N bonds relative to C–C bonds becomes less favorable with increasing multiple bond character. On catalyst surfaces hydrogenolysis usually occurs at higher temperatures than C–H activation.[5] Mechanistic studies indicate that C–N hydrogenolysis is initiated by insertion of the catalyst into the α-C–H bond to form a σ-complexed (A) or α,β-adsorbed intermediate.[6]



A



B

In hydrodenitrogenation reactions the most common side reaction is the unselective cleavage of C–C bonds.[7] Under hydrogenolysis conditions the metal surface seems to insert into C–H and N–H bonds, and even aliphatic compounds may exhibit considerable multiple bond character in the chemisorbed form. The most significant differences between carbon and nitrogen in noncatalytic organic chemistry, the nitrogen lone pair, may lose its significance on a metal surface, and chemisorbed carbon and nitrogen may behave similarly accounting for the unselectivity of bond cleavage reactions, especially at higher temperatures. In order to achieve selective C–N hydrogenolysis, a catalyst had to be found which differentiated between carbon and nitrogen. If the above considerations are valid than we should either find a catalyst which, due to its nature differentiates chemically between carbon and nitrogen, or the catalytic activity of common catalysts has to be increased to allow efficient reactions at lower temperatures. Since very little general information is available about the HDN properties of transition metals other than those used for hydrodesulfurization we have conducted a comparative investigation of HDN properties with catalysts prepared from numerous transition metals.[8] In this survey we have found platinum to be most reactive and also selective for C–N cleavage with our test compounds *n*-hexylamine and aniline.[8] To detect scope and limitations of this promising hydrodenitrogenation catalyst we have conducted the following study.

Results and Discussion

Throughout the investigation we have used the same reactivated platinum catalyst prepared from hydroplatinic acid and normal column chromatography silica. From the preparative procedure (see Experimental Section) and X-ray photoelectron spectroscopy (XPS) studies[8] we conclude that the catalyst consists of silica particles partly covered by platinum zero. The particular silica, which does not react with *n*-hexylamine and aniline under our reaction conditions at temperatures up to 400 °C, was chosen not only to mechanically stabilize the catalyst but also to minimize direct support interaction.[8] (Pure metal black catalysts tend to clog the flow tube.) The activated catalyst (surface area 280 m^2/g) was composed of 40% platinum and 60% silica. The large Pt content in the catalyst, although not optimized, proved to be essential for the reactions reported. When we studied the change in catalytic activity of Pt catalysts with decreasing Pt content with *n*-hexylamine, we noted that at a Pt content of less than 10% a sharp drop in catalytic activity is observed. This could be confirmed with a commercial 5% Pt/Kieselgur catalyst which did not produce significant amounts of *n*-hexane (<5%) at reaction temperatures ranging from 150 to 400 °C. All these exeriments were conducted under conditions (same and lower flow rate, 1 g of catalyst, 1 g of substrate) where our 40% Pt catalyst resulted in quantitative conversion to *n*-hexane. This suggests that the unusual activity of our Pt catalyst may be due to bulk metal properties of the Pt (low dispersion). Our results parallel a recent investigation by Vausudevan et al.,[9] who found that the catalytic hydrogenation activity of Pd catalysts decrease rapidly with increasing dispersion. Although not commercially practical, such bulk metal catalysts seem to exhibit a highly increased reactivity for certain catalytic reactions. The well appreciated Raney nickel, the Adams catalyst, and other metal "black" catalysts used in synthetic organic chemistry obviously belong to the same category of highly reactive "bulk metal" catalysts.

A more detailed study of the relationship between dispersion and hydrodenitrogenation activity of our Pt catalyst is indicated.

This investigation has been conducted with a gas phase flow system. No solvent interactions, no workup, and the inexpensive equipment make the flow method superior to normal liquid phase conditions. The major limiting factor is the volatility of the educts.

In the following we report the hydrodenitrogenation properties of the 40% Pt on silica catalyst. The above study with catalysts of different Pt content has also shown that the catalyst is reproducible and the catalytic activity reported only changes at concentrations below 20%. It

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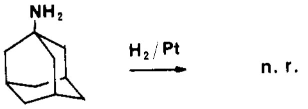
Table II. Platinum Catalyzed Hydrogenolysis of Amines

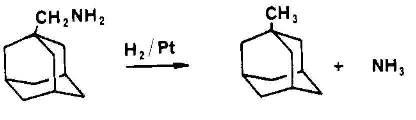
compd	substrate temp, °C	product	reactn temp, °C	yield, %
n-hexylamine	50	*n*-hexane	150	99
cyclohexylamine	45	cyclohexane	150	99
1-adamantane-amine	225	1-adamantane-amine	225	99
1-(methylamino)-adamantane	200	1-methyl-adamantane	200	99
piperidine	40	*n*-pentane	150	99
quinuclidine	88	3-ethylpentane	200	88
		ethylcyclopentane	200	12
aniline	150	cyclohexane	150	99
diphenylamine	150	cyclohexane	150	99

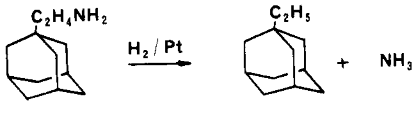
may be of interest to point out that most of the reported yields, especially in the cases of high conversion, are readily reproducible and quite insensitive to flow rate and reaction temperature. Precise experimental control is therefore not essential as can be concluded from the reaction temperatures listed in the tables which resulted from crude screening experiments in 50 °C steps.

Amines. One-step reduction of unactivated amines has never been reported as a practical procedure for amine defunctionalization. Several multistep methods for such a conversion are based on the transformation of the amino group to a better leaving group followed by hydride substitution. Primary amines are reacted with difluoroamine[10] or hydroxylamine-*o*-sulfonic acid[11] or converted to *N*,*N*-disulfonimides[12] and reduced. Primary aromatic amines can be diazotized and reduced.[13] Only activated benzylic or allylic amines can be reduced directly with (bulk) PtO_2.[14] Aromatic, allylic, or benzylic amines are also converted to the parent hydrocarbons by transformation to the pyridinium salts followed by reduction and pyrolysis.[15]

Aliphatic amines are easily hydrogenolized at 150 °C with our heterogeneous platinum catalyst (see Table II). Primary amino groups connected to primary (*n*-hexylamine) or secondary positions (cyclohexylamine) are quantitatively converted to the parent hydrocarbon. Contrary to previous results where nickel was shown to deaminate 1-aminoadamantane in high yield to adamantane,[16] no reaction is observed with our platinum catalyst.

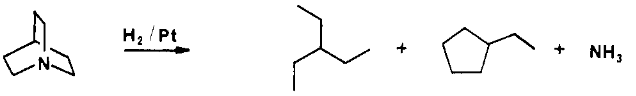






This lack of reactivity with aminoadamantane, where the amino group is connected to a tertiary position must be due to the lack of an α-hydrogen (no C–H insertion possible to allow the formation of α,β-adsorbed intermediates). The other possible reason, steric hindrance, is less likely since no steric effects were noted in the investigations with the heterogeneous nickel catalyst mentioned above (steric effects in surface reactions should be independent of the chemical nature of the catalyst). The quantitative deamination of 1-(aminomethyl)adamantane with the Pt supports the importance of α-hydrogen since now α,β-absorption is possible. The results furthermore indicate that α,β-adsorption is sufficient for C–N hydrogenolysis; no allylic interaction needs to be postulated It is not surprising that 2-adamantylethylamine also is selectively deaminated in high yields.

The secondary amine piperidine is readily converted to *n*-pentane and ammonia. The bicyclic quinuclidine is not only a tertiary amine but also strained and inflexible. According to molecular mechanics calculations bicyclo[2.2.2.]octane has a strain energy of about 10 kcal/mol.[17] Assuming a similar value for quinuclidine we expected less selective deamination since any C–C or C–N hydrogenolysis releases this strain energy. However, no C–C hydrogenolysis was observed and the high yield formation of 2-ethylpentane and ethylcyclopentane further demonstrates the unusual selectivity of platinum for C–N cleavage. It may also indicate that α,β-chemisorption is sufficient for the hydrogenolysis since for steric reasons no convenient allylic adsorption is possible with quinuclidine on a surface. Furthermore, due to the rigid cage structure of quinuclidine, a π-complexed surface intermediate as indicated in A becomes less likely since a douuble bond on nitrogen would be extremely twisted.



The result furthermore indicates that hydrogen atoms introduced in the molecule by the hydrogenolysis reaction must originate from surface hydrogen since approach of hydrogen from the gas phase to the backside of the chemisorbed C–N bond (Eley–Rideal mechanism[18]) seems impossible for steric reasons.

The stronger aromatic C–N bond (see Table I) in aniline and diphenylamine is hydrogenolyzed readily with cyclohexane being the only reaction product. Here in addition to hydrogenolysis complete hydrogenation of the aromatic ring is observed. The absence of any aromatic product may be due to the low reaction temperature. The formation of benzene from aniline and hydrogen becomes favorable above 280 °C (entropy effect)[19] whereas at lower temperatures cyclohexane formation dominates. The exclusive formation of cyclohexylamine at lower temperatures shows that hydrogenation of the aromatic ring is more facile than hydrogenolysis. Based on the above mechanistic considerations it is unlikely that hydrogenation is a prerequisite for hydrogenolysis, especially if hydrogenolysis occurs from an π-chemisorbed intermediate (dehydrogenated). α-Hydrogen atoms are not important in aromatic systems since π-interaction is facilitated by the aromatic π-system.

Nitriles. The stability and versatility of the nitrile group makes it a frequently used functional group in or-

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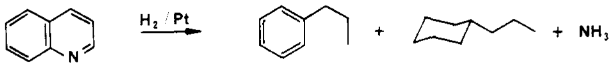
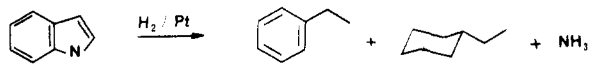
Table III. Platinum Catalyzed Hydrogenolysis of Nitriles

compd	substrate temp, °C	product	reactn temp, °C	yield, %
decanenitrile	75	decane	150	98
		octane		2
cyclohexane-carbonitrile	75	methylcyclohexane	150	99
1-cyano-adamantane	225	1-methyl-adamantane	225	99
1-adamantane-acetonitrile	200	1-ethyl-adamantane	200	94
		1-methyladamantane		6
benzonitrile	124	methylcyclohexane	150	75
		toluene		20
		benzene/cyclohexane		5

ganic synthesis, often used to mask carboxylic acids and their derivatives. We have shown that nickel on alumina is an effective catalyst for the conversion of cyano into methyl groups with aromatic nitriles and aliphatic cyano groups bound to a quarternary carbon. With cyano groups located at a secondary or primary center predominant defunctionalization (C–C hydrogenolysis) is observed with nickel.[20] Platinum, however, maintains its selectivity for C–N bond hydrogenolysis. Not only the tertiary cyanoadamantane and the aromatic benzonitrile but also the primary decanenitrile, adamantaneacetonitrile, and the secondary cyclohexanecarbonitrile are converted quantitatively to the associated methyl compounds with platinum (see Table III). At lower temperature we see formation of amines. Whether the amine formation is a prerequisite for the hydrogenolysis of the C–N triple bond cannot be decided. On the basis of the mechanistic considerations mentioned above we postulate that hydrogenation does only occur at lower temperatures because it is thermodynamically favorable and hydrogenolysis is a separated process which is facilitated by a chemisorbed C–N triple bond. This is also in agreement with defined surface studies, where it has been shown that hydrogenation, H/D-exchange, and hydrogenolysis reactions are catalyzed by different surface structures indicating their mechanistic separation.[21]

Heterocycles. Nitrogen-containing aromatic heterocycles like indole, quinoline, and pyridine not only contain the most stable C–N bonds but are also representative of the nitrogen-containing compounds in synthetic oils.[22]





Furthermore, these heterocycles have been found to be most difficult to denitrogenate since all remaining nitrogen compounds after incomplete HDN of synthetic oils are indole and quinoline derivatives.[2,3,23] Because of these problems associated with catalytic HDN of indol and quinoline and derivatives, they seem to be the ideal test molecules to detect limits of our unoptimized catalyst. The results are summarized in Table IV.

Table IV. Platinum Catalyzed Hydrogenolysis of Heterocycles

compd	substrate temp, °C	product	reactn temp, °C	yield, %
pyridine	40	piperidine	50	11
		pyridine		89
	45	piperidine	100	94
		n-pentylamine		5
		n-pentane		1
	45	piperidine	150	2
		n-pentylamine		6
		n-pentane		90
quinoline	124	propylcyclohexane	200	59
		propylbenzene		10
		o-propylaniline		12
1,2,3,4-tetrahydro-quinoline	120	propylcyclohexane	200	72
		propylbenzene		11
indole	124	ethylcyclohexane	200	46
		ethylbenzene		14
		o-ethylaniline		6
		aniline		28
indoline	124	ethylcyclohexane	200	28
		ethylbenzene		18
		o-ethylaniline		9
		aniline		39

The temperature study with pyridine reveals some mechanistic aspects of platinum-catalyzed HDN. At lower temperatures the first step, hydrogenation of the aromatic ring, dominates (exclusive formation of piperidine) and at higher temperatures formation of *n*-pentylamine, the product formed from hydrogenolysis of the first C–N bond, was detectable. Only at higher temperatures the desired compound, *n*-pentane, became the dominating product. This suggests a stepwise mechanism where the hydrogenolysis is rate determining.[24]

At 200 °C quinoline is converted to a mixture of 70% propylbenzene and propylcyclohexane (1:6), 12% *o*-ethylaniline, and 18% unidentified material. The partially hydrogenated tetrahydroquinoline under identical conditions gave 83% propylbenzene and propylcyclohexane. Even indole can be converted to a 3:1 mixture of pure HDN products ethylcyclohexane and ethylbenzene (60%). The relatively large amount of aniline formation observed with indole and indoline however is surprising since no aniline was observed with 6-membered quinolines suggesting a different mechanism with *n*-ethylaniline as intermediate. The higher yields with the quinolines relative to the indoles is also not in agreement with the results observed with HDS catalysts where indoles are consistently hydrodenitrogenated more effectively than the quinolines.[2,3,23]

Nitro Compounds. Several methods for the direct conversion of nitro compounds to the parent hydrocarbons have already been developed.[25] So far no catalytic process for the direct defunctionalization of nitro compounds has been reported; however the reduction of nitro to amino groups is a well established reaction.[26]

The platinum catalyst may be used for both processes. At a high flow rate aniline was the major reaction product from nitrobenzene whereas at lower rates and temperatures

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Table V. Platinum Catalyzed Hydrogenolysis of Various Functionalized Molecules

compd	substrate temp, °C	product	reactn temp, °C	yield, %
nitrohexane	100	*n*-hexane	150	91
nitrobenzene	124	cyclohexane	150	89
heptanamide	80	heptanamide	250	89
		high M_r compd		11
2-azacyclooctanone	250	heptanamide	250	3
		2-azacyclooctane		82
benzamide	140	m/t[a]	250	49
		b/c[b]		48
phthalamide	250	m/t	250	43
		b/c		57
phthalimide	250	*o*-xylene	250	54
		m/t		35
		b/c		11
phenylhydrazine	190	cyclohexane	200	99
DL-α-phenylglycine	250	m/t	250	99

[a] m/t = methylcyclohexane/toluene. [b] b/c = benzene/cyclohexane.

quantitative formation to cyclohexane is achieved. The aliphatic nitrohexane gives *n*-hexane in quantitative yields at lower rates and hexylamine at higher rates and temperatures indicating a similar mechanism for the conversion of aliphatic and aromatic nitrocompounds.

Amides. The amide group, which contains the energetically most stable C–N single bond in organic compounds, is ideal to test limits and scope of our Pt catalyst. The results, listed in Table V, show that we finally approached limits of the catalyst. The aliphatic heptanoic amide passed the catalyst unchanged even at 250 °C. The 7-membered caprolactam is recovered almost unchanged, only 3% hydrogenolysis to the heptanoic amide is observed indicating exclusive cleavage of the weaker aliphatic C–N bond. The amide group passed the catalyst unchanged. Quite on the contrary, the aromatic amides are readily converted to parent hydrocarbons, but the formation of benzene/cyclohexane in all cases indicates some undesired and unselective C–C hydrogenolysis. Most curious is the difference between the products formed from phthalamide and phthalimide. Under identical reaction conditions phthalamide is converted to benzene and toluene whereas phthalimide produced more than 50% of the desired *o*-xylene.

Others. Phenylglycine is defunctionalized completely to toluene/methylcyclohexane indicating C–C and C–N cleavage. Phenylhydrazine is reduced directly to cyclohexane; no intermediate aniline formation could be detected.

Conclusion

We have examined the potential of a heterogeneous platinum catalyst for the selective hydrogenolysis of carbon–nitrogen bonds. We have found platinum to be most successful for the defunctionalization of amines, nitriles, and nitro compounds. Aromatic heterocycles and amides in general require higher reaction temperatures for denitrogenation than amines, nitriles, or nitro compounds. Although neither method nor catalyst have been optimized, the method can already be recommended to the synthetic chemist for convenient defunctionalization of nitrogen-containing organic molecules to the parent hydrocarbon. However, we have not studied the tolerance of the catalyst toward other functional groups and an attempted selective defunctionalization may result in complete defunctionalization of polyfunctional molecules.

The preparative application of the method is mainly limited by the volatility of the educts. Exploratory experiments with decalin as solvent have already indicated that the reaction may also be carried out under liquid phase condition, but further optimization of the method is necessary.

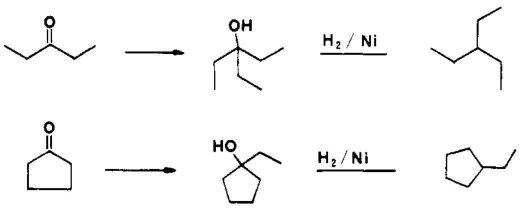
The inertness of aliphatic amides is an unexpected result and further exploration of this feature of platinum could lead to new applications of heterogeneous platinum catalysts.

In addition to the specific catalytic results this study demonstrates that even well investigated catalyst metals like platinum are far from being completely explored with respect to their chemical and catalytic properties. We recognize the fact that many questions are still open and this investigation is rather incomplete, but a lack of funding for this project did not allow us to study this interesting reaction in as much detail as we would have liked.

Experimental Section

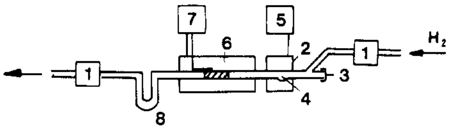
NMR spectra were recorded on a Varian EM 390. Gas chromatographic analysis were performed on a Perkin Elmer 3920 flame-ionization gas chromatograph equipped with a 6 × $^1/_8$ in. Apiezon L (20%), KOH (2%), on 80/100 Chromosorb W (used for nitrogen-containing compounds) and a SE-30 (3%) on 80/100 Supelcoport (used for hydrocarbons). A Hewlett Packard 3390 A integrator was used for the recording and integration of the GC signals. Products were identified by coinjection with authentical samples and NMR analysis. For product composition relative FID yields were used without correction as determined by the integrator.

Materials. All chemicals were used as received from commercial suppliers with the exception of diphenylamine which was recrystallized from water/ethanol. Heptanoic amide and 1-adamantaneacetonitrile were prepared from the acid chloride and 1-(hydroxymethyl)adamantane, respectively, by standard procedures. 2-Ethylpentane and ethylcyclopentane were prepared from the ketones by reaction with ethylmagnesium bromide followed by quantitative catalytic deoxygenation of the alcohol with nickel.[24] Both hydrocarbons were generated in pure form (GC, MS, NMR) by this procedure.



Catalyst Preparation. To a solution of 697 mg of $H_2PtCl_6{\cdot}H_2O$ (1.7 mmol) in 20 mL of water was added 500 mg of silica [Baker silica gel for column chromatography, 60–200 mesh, surface area 325 m^2/g (N_2 BET method)]. The water was removed on a rotary evaporator, and the orange solid was dried for 1 h at 120 °C. This raw catalyst was ground with a mortar and pestel, packed between glass wool plugs in the reaction tube, and reduced with H_2 (flow rate 20 mL/min). The temperature was increased stepwise: 3 h at 150 °C, 1.5 h at 200 °C, 1.5 h at 250 °C, 1 h at 300 °C, 0.5 h at 350 °C, 0.5 h at 400 °C. At 150 °C the catalyst turns black and an orange gas is evolved. The surface area of the reduced catalysts, determined by the N_2 BET method, was 281 m^2/g.

Apparatus and Experimental Procedure. The reactions were carried out in a flow apparatus shown below. A general method is described for *n*-hexylamine. Other experimental data are given in Tables II–V. The catalyst was reduced with H_2 for 30 min at 400 °C before each experiment. Liquid educt was injected via syringe into the substrate chamber after catalyst activation; solid samples were placed there before catalyst activation. After the reactor temperature had stabilized the sample oven was set to the sample temperature (see Tables II–V) which started the experiment. The products were analyzed by the NMR of the product and coinjection with an authentic sample by GC analysis.



1, flow controller; 2, preheater; 3, injector port; 4, substrate chamber; 5, temperature controller for preheater; 6, reactor oven; 7, temperature controller (omega, Model 49); 8, cooled U tube for product collection

General Procedure. *n*-Hexylamine (154 mg, 2 mmol) was placed in the reaction tube by injection. The sample temperature was set to 50 °C with the preheater and the reaction temperature was set to 150 °C with the temperature controller. The substrate was passed through the reactor containing all the reduced catalyst by a slow stream of hydrogen (40 mL/min). The product was collected in a U tube cooled by dry ice. The product (144 mg, 100% yield) was identified by NMR and GC to be pure *n*-hexane.

Acknowledgment. We thank the Department of Chemistry at Berkeley which has provided the entire support for this and all our related investigations.

Registry No. N_2, 7727-37-9; Pt, 7440-06-4; H_2PtCl_6, 16941-12-1; hexylamine, 111-26-2; cyclohexylamine, 108-91-8; 1-adamantaneamine, 768-94-5; 1-(aminomethyl)adamantane, 17768-41-1; piperidine, 110-89-4; quinuclidine, 100-76-5; aniline, 62-53-3; diphenylamine, 122-39-4; decanenitrile, 1975-78-6; cyclohexanecarbonitrile, 766-05-2; 1-cyanoadamantane, 23074-42-2; 1-adamantaneacetonitrile, 16269-13-9; benzonitrile, 100-47-0; pyridine, 110-86-1; quinoline, 91-22-5; 1,2,3,4-tetrahydroquinoline, 635-46-1; indole, 120-72-9; indoline, 496-15-1; nitrohexane, 25495-95-8; nitrobenzene, 98-95-3; heptanamide, 628-62-6; 2-azacyclooctanone, 673-66-5; benzamide, 55-21-0; phthalamide, 88-96-0; phthalimide, 85-41-6; phenylhydrazine, 100-63-0; DL-α-phenylglycine, 2835-06-5; hexane, 110-54-3; cyclohexane, 110-82-7; 1-methyladamantane, 768-91-2; pentane, 109-66-0; 3-ethylpentane, 617-78-7; ethylcyclopentane, 1640-89-7; decane, 124-18-5; octane, 111-65-9; methylcyclohexane, 108-87-2; 1-ethyladamantane, 770-69-4; toluene, 108-88-3; benzene, 71-43-2; phenylamine, 110-58-7; propylcyclohexane, 1678-92-8; propylbenzene, 103-65-1; *o*-propylaniline, 1821-39-2; ethylcyclohexane, 1678-91-7; ethylbenzene, 100-41-4; *o*-ethylaniline, 578-54-1; azacyclooctane, 1121-92-2; *o*-xylene, 95-47-6; 1-adamantylethylamine, 26482-53-1; 3-pentanone, 96-22-0; cyclopentanone, 120-92-3.

Small-Ring Cyclic Cumulenes: The Structure and Energetics of Cyclic Butatrienes and the Synthesis of 1,2,3-Cyclononatriene

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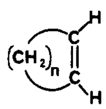
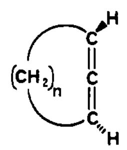
The possibility of incorporating a 1,2,3-butatriene moiety in various sized carbocyclic rings is explored through semiempirical (MNDO) and ab initio model calculations and through complete geometry optimization (MNDO) for five- through nine-membered rings. Strain in the butatriene is estimated to double with each decreasing carbon in the ring. 1,2,3-Cyclononatriene is synthesized for the first time. This is likely to be the smallest isolable cyclic butatriene.

Introduction

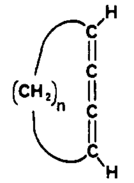
Experimentalists and theoreticians alike long have been fascinated by the incorporation of double and triple bonds in small carbocyclic rings.[1] Cyclic structures which contain noncumulated double bonds (1) are stable in any ring size.



1, $n \geqslant 1$



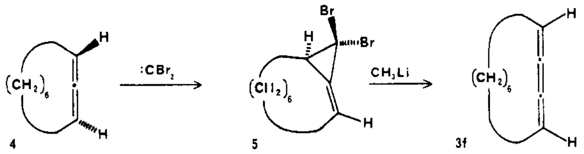
2
2a, $n = 3$



3a, $n = 1$
3b, $n = 2$
3c, $n = 3$
3d, $n = 4$
3e, $n = 5$
3f, $n = 6$

For allenes (2), small rings engender considerable deformation from a linear geometry in which π orthogonality is maintained. This results in increased kinetic reactivity with the result that the smallest kinetically stable cyclic allene is 1,2-cyclononadiene.[2] Ultimately, allene π bonding must yield to ring constraints. Through some very elegant experiments, Jones has trapped optically active 1,2-cyclohexadiene (**2a**)[3] and we have used ab initio MCSCF methods to calculate a barrier to racemization of 13 kcal/mol.[4] More recently, Wentrup has successfully trapped **2a** in a low temperature matrix.[5]

In contrast to the allenes, very little is known about the structure and chemistry of cyclic butatrienes (**3**).[1] The only stable example of simple cyclic butatrienes reported to date is 1,2,3-cyclodecatriene (**3f**), which was prepared (eq 1) by Moore and Ozretich in 1965.[6] This compound, generally



(1)

considered as the smallest stable cyclic butatriene,[1] was

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