Selective Synthesis of N-(Cyclohexylmethyl)-N-alkylamines from Primary Amines and Pimelaldehyde using Tetracarbonylhydridoferrate, $HFe(CO)_4^-$, as a Reducing Agent

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Ethanolic tetra carbonylhydridoferrate solution combined with dialdehyde (no of carbon; 4,5,6) is very efficient for the selective transformation of amino group into N-heterocyclic compound. However, a large variety of both aliphatic and aromatic amines react with the ferrate-pimelaldehyde at room temperature under an atmospheric pressure of carbon monoxide to give the corresponding N-(cyclohexylmethyl)-N-alkylamine derivatives in moderate yields instead of the corresponding N-substituted perhydroazocine derivatives.

Introduction

Recently, tetracarbonylhydridoferrate prepared from pentacarbonyliron and alkali metal hydroxide has been shown to be a convenient selective reagent for carbonylation and/or reduction of a variety of organic functional groups such as a nitro group,[2,3] and acetylenic bond,[4] olefinic bonds of conjugated diene,[5] enamine,[6] and α,β-unsaturated carbonyl compound,[7,8] alkyl halides,[9-11] olefinic oxides,[12,13] organic sulfurs,[14,15] schiff's base[16-19] and organic azides.[20]

Several workers have demonstrated that the ferrate is effective for reductive N-alkylation[21,22] of amines and aldehydes or ketones. More recently, S.C. Shim, *et al.*, reported that the ethanolic ferrate has been shown to be selective reducing reagent in the preparation of N-heterocycles with 5-, 6-, and 7-membered rings by the reductive amination of dicarbonyl compounds. For example, a large variety of both aliphatic and aromatic primary amines react with dialdehydes such as succinaldehyde, glutaraldehyde, and adipaldehyde in the presence of an atmospheric pressure of carbon monoxide to give the corresponding N-substituted pyrrolidine,[23] piperidine,[24] and perhydroazepine derivatives[25] in good to excellent yields.

Thus, we have had much interest in the synthesis of N-substituted 8-membered ring such as a perhydroazocine from pimelaldehyde and primary amine. In this reaction, however, the primary amines could react with pimelaldehyde under an atmospheric pressure of carbon monoxide to give the corresponding N-(cyclohexylmethyl)-N-alkylamine derivatives in moderate yields instead of the corresponding N-substituted perhydroazocine derivatives. A preliminary report of our work was published elsewhere.[26] To our knowledge, the only reported synthesis of N-(cyclohexylmethyl)-N-cyclohexylamine is from benzylaniline by catalytic hydrogenation.[27]

Accordingly, we wish to report a simple and convenient synthesis of N-(cyclohexylmethyl)-N-alkylamine derivatives from primary amines and pimelaldehyde using the ferrate as a selective reducing agent.

Results and Discussion

Table 1. Reaction Primary Amines Pimelaldehyde Using $HFe(CO)_4^-$[a]

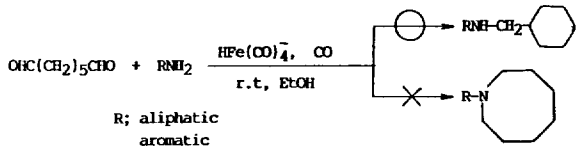
Exp. No.	Amine	Product	Yield (%)[b]
1	$C_6H_{11}NH_2$	$C_6H_{11}NHCH_2$-C_6H_{11}	47
2	$C_6H_5CH_2CH_2NH_2$	$C_6H_5CH_2CH_2NHCH_2$-C_6H_{11}	51
3	$C_6H_5CH_2NH_2$	$C_6H_5CH_2NHCH_2$-C_6H_{11}	63
4	$C_6H_5NH_2$	$C_6H_5NHCH_2$-C_6H_{11}	52
5	*p*-$CH_3C_6H_4NH_2$	*p*-$CH_3C_6H_4NHCH_2$-C_6H_{11}	49
6	*m*-$CH_3C_6H_4NH_2$	*m*-$CH_3C_6H_4NHCH_2$-C_6H_{11}	38
7	*o*-$CH_3C_6H_4NH_2$	*o*-$CH_2C_6H_4NHCH_2$-C_6H_{11}	22
8	*p*-$CH_3OC_6H_4NH_2$	*p*-$CH_3OC_6H_4NHCH_2$-C_6H_{11}	56
9	*m*-$CH_3OC_6H_4NH_2$	*m*-$CH_3OC_2H_4NHCH_2$-C_6H_{11}	46
10	*o*-$CH_3OC_6H_4NH_2$	*o*-$CH_3OC_6H_4NHCH_2$-C_6H_{11}	42
11	*p*-$ClC_6H_4NH_2$	*p*-$ClC_6H_4NHCH_2$-C_6H_{11}	45
12	*m*-$ClC_6H_4NH_2$	*m*-$ClC_6H_4NHCH_2$-C_6H_{11}	37
13	*o*-$ClC_6CH_4NH_2$	*o*-$ClC_6H_4NHCH_2$-C_6H_{11}	22
14	$HOCH_2CH_2NH_2$	$HOCH_2CH_2NHCH_2$-C_6H_{11}	37
15	$HOCH_2CH_2CH_2NH_2$	$HOCH_2CH_2CH_2NHCH_2$-C_6H_{11}	33
16[c]	$C_6H_5(CH_3)NH$	$C_6H_5(CH_2)NCH_2$-C_6H_{11}	25

[a] Amine(11 mmol), pimelaldehyde (11 mmol), KOH(33 mmol), $Fe(CO)_5$ (11 mmol), EtOH (17 m*l*), at r.t for 24 hr. [b] Based on the amount of the amine used; Isolated yield. [c] Using secondary amine.

A large variety of primary amines were converted into the corresponding N-(cyclohexylmethyl)-N-alkylamine derivatives in moderate yields with tetracarbonylhydridoferrate-pimelaldehyde at room temperature under carbon monoxide. The results are listed in Table 1. The reaction conditions were not optimized for each compound.

Ethanolic tetracarbonylhydridoferrate combined with dialdehyde is very efficient for the selective transformation of amino group into N-heterocyclic compound. In this reaction, however, primary amines react with pimelaldehyde to give the corresponding N-(cyclohexylmethyl)-N-alkylamine derivatives instead of the corresponding N-substituted perhydroazocine derivatives.

The reaction proceeds smoothly with an absorption of carbon monoxide and with a color change from pale yellow to

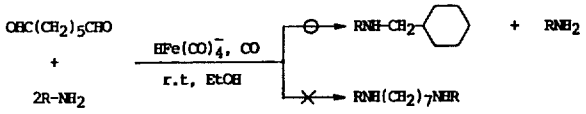


Scheme 1

Table 2. Base Effects on the Synthesis of N-(Cyclohexylmethyl)-N-phenylamine from Pimelaldehyde and Aniline[a]

Base	$MHFe(CO)_4$	Product	Yield (%)[b]
KOH	$KHFe(CO)_4$	$C_6H_5NHCH_2$-C_6H_{11}	52
NaOH	$NaHFe(CO)_4$	$C_6H_5NHCH_2$-C_6H_{11}	49
$Ca(OH)_2$	$Ca[HFe(CO)_4]_2$	N.R.	—

[a] Aniline (11 mmol), pimelaldehyde (11 mmol), base (33 mmol), $Fe(CO)_5$ (11 mmol), EtOH(17 m*l*), at r.t for 24 hr. [b] Isolated yield.



Scheme 2

Table 3. Iron Carbonyl Effects of the Synthesis of N-(Cyclohexylmethyl)-N-phenylamine from Pimelaldehyde and Aniline[a]

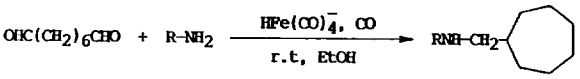
$Fe_m(CO)_n$	$KHFe_m(CO)_{n-1}$	Product	Yield (%)[b]
$Fe(CO)_5$	$KHFe(CO)_4$	$C_6H_5NHCH_2$-C_6H_{11}	52
$Fe_2(CO)_9$	$KHFe_2(CO)_8$	$C_6H_5NHCH_2$-C_6H_{11}	30
$Fe_3(CO)_{12}$	$KHFe_3(CO)_{11}$	$C_6H_5NHCH_2$-C_6H_{11}	22

[a] Aniline(11 mmol), pimelaldehyde(11 mmol), KOH(33 mmol), $Fe(CO)_5$(11 mmol), EtOH(17 m*l*), at r.t for 24 hr. [b] Isolated yield.

red brown. The reaction mixture become viscous at a middle stage of the reaction. Therefore, sometimes, the magnetic stirring bar was stopped because of an increased viscosity of the reaction mixture. Additional ethanol was added for dilution. This viscosity seems to come from same reaction intermediates such as schiff's bases and immonium salts.[24]

This reaction has a great tendency to undergo intramolecular aldol condensation of the pimelaldehyde, even at the ferrate-pimelaldehyde-amine molar ratio of 1.0/1.0/2.0; at this ratio N,N-disubstituted heptanediamines are expected to be formed, but the N-(cyclohexylmethyl)-N-alkylamine and unconsumed primary amine are identified.

This method can be applied to both aromatic and aliphatic amines. Aromatic amines such as *p*-anisidine, *o*-anisidine, *p*-toluidine, and *p*-chloroaniline were reacted with pimelaldehyde in the ferrate solution to give the corresponding N-(cyclohexylmethyl)-N-(*p*-anisidly)-, N-(cyclohexylmethyl)-N-(*o*-anisidyl)-, N-(cyclohexylmethyl)-N-(*p*-tolyl)-, and N-(cyclohexylmethyl)-N-(*p*-chloropheny) amines in 42-56% yields, respectively. The methyl, methoxy, and chloro groups at the benzene ring have almost no effects on the reaction. In general, we found that alkylamines such as benzylamine, β-phenylethylamine, and cyclohexylamine which are stronger bases than aromatic ones gave better yields.



Scheme 3

Table 4. The Reaction of Primary Amines with Suberaldehyde Using $HFe(CO)_4^-$[a]

Amine	Product	Yield (%)[b]
$C_6H_5NH_2$	$C_6H_5NHCH_2$-C_7H_{13}	43
p-$ClC_6H_4NH_2$	*p*-$ClC_6H_4NHCH_2$-C_7H_{13}	37
p-$CH_3C_6H_4NH_2$	*p*-$CH_3C_6H_4NHCH_2$-C_7H_{13}	38

[a] Amine (11 mmol), suberaldehyde(11 mmol), KOH(33 mmol), $Fe(CO)_5$(11 mmol), EtOH(17 m*l*), at r.t for 24 hr. [b] Isolated yield.

As a base, sodium hydroxide can be used instead of potassium hydroxide, but calcium hydroxide was not applied (Table 2). And also, instead of iron pentacarbonyl, the use of diiron nonacarbonyl or triiron dodecacarbonyl as a iron carbonyl complex resulted in lowering the product yields (Table 3).

Interestingly, in the case of suberaldehyde, the reaction gave N-(cycloheptylmethyl)-N-alkylamine in a reasonable yield as a similar route (Scheme 3, Table 4).

This cyclization reaction seems to proceed via intramolecular aldol condensation[28] of pimelaldehyde and Schiff's base formation and then reduction of Carbon-Carbon and carbon-nitrogen double bonds.

In conclusion, ethanolic tetracarbonylhydridoferrate solution combined with dialdehyde is very efficient for the selective transformation of amino group into N-heterocyclic compound. However, in this reaction, a large variety of both aromatic and aliphatic amines react with the ferrate-pimelaldehyde at room temperature under an atmospheric pressure of carbon monoxide to give the corresponding N-(cyclohexylmethyl)-N-alkylamine derivatives in moderate yields instead of the corresponding N-substituted perhydroazocine derivatives. These results show that the reaction of primary amines with pimelaldehyde in the presence of the ferrate is suitable for the synthesis of N-(cyclohexylmethyl)-N-alkylamines selectively, but not suitable for that of N-substituted perhydroazocines.

Experimental

Reagents and Instruments. Infrared spectra were recorded on Perkin-Elmer IR 843 and JASCO A-202 IR spectrophotometers. NMR spectra were run on Varian EM-360A and Bruker AM-300 spectrometers operating at 60 MHz or 300 MHz. Shimadzu QP-1000 spectrometer was used for Mass spectral determinations. Iron pentacarbonyl, DL-trans-1,2-cycloheptanediol, trans-1,2-cyclooctanediol, and amberlyst A26 resin were purchased from Aldrich Chemical Various primary amines were purchased from Junsei, Wako, Nakarai, Fluka, and Tokyo Chemicals, and were used without futher purification.

Preparation of Potassium Tetracarbonylhydridoferrate.[29] A 100 m*l* three necked flask fitted with three way cock, a stirrer, argon or carbon monoxide. Potassium hydroxide solution in ethyl alcohol (1M, 33 m*l*) and 17 m*l* ethyl

alcohol and 1.5 m*l* (11 mmol) of pentacarbonyliron were placed in the flask and then stirred vigorously for 1–1.5 hours at room temperature to give a pale yellow solution with a white precipitate.

Preparation of Pimelaldehyde.[30]DL- *trans*-1,2-cycloheptanediol (1.3g 10 mmol) in 50 m*l* of dichloromethane was stirred with the periodate form of amberlyst A26 resin (6.4 g, 10 mmol) for 2 hours at 20 °C. The resin was filtered off and washed on the filter which dichloromethane (2×25 m*l*). Evaporation of the combined filtrate gave pimelaldehyde (1.2g, 90%) as a colorless liquid.

Reaction of Pimelaldehyde and Primary Amines Using Potassium Tetracarbonylhydridoferrate. To the solution of potassium tetracarbonylhydridoferrate described above, 11 mmol of primary amines and then 11 mmol of pimelaldehyde were added dropwise for 10 minutes. The mixture was stirred under an atmospheric pressure of carbon monoxide at room temperature for 24 hours and absorption of carbon monoxide normally ceased in about 10 hours or longer times. The mixture was exposed to air, filtered, and the solvent was then evaporated. The residual oily material was extracted with diethyl ether. The etherial extract was dried, concentrated, and eluted on preparative TLC(SiO_2) to give the corresponding N-(cyclohexylmethyl)-N-alkylamines. Analytical data of these results are as follows:

N-(Cyclohexylmethyl)-N-Cyclohexylamine. ^{1}H nmr(CCl_4): δ 0.8–1.8(m, 22H, $2C_6H_{11}$), 1.9(b, 1H, NH), 2.5(d, 2H, CH_2); ^{13}C nmr($CDCl_3$): δ24(t, $2CH_2$), 26(t, $2CH_2$), 27(t, CH_2), 31(t, $2CH_2$), 34(t, $2CH_2$), 38(d, CH), 56(t, CH_2); ms: m/e 195 (M^+).

N-(Cyclohyxylmethyl)-N-(β-phenylethyl)amine. ^{1}H nmr(CCl_4): δ 0.9–1.9(m, 11H, C_6H_{11}), 2.7(d, 2H, CH_2), 3.0–3.3(m, 4H, $2CH_2$), 7.1–7.4(m, 5H, C_6H_5); ^{13}C nmr($CDCl_3$): 24(t, $2CH_2$), 25(t, CH_2), 30(t, $2CH_2$), 31(t, CH_2), 35(d, CH), 49(t, CH_2), 53(t, CH_2), 125(d, CH), 128(d, 2CH), 129(d, 2CH), 136(s, C); ms: m/e 217(M^+).

N-(cyclohexylmethyl)-N-benzylamine. ^{1}H nmr(CCl_4): δ0.8–1.9(m, 11H, C_6H_{11}), 2.0(br, 1H, NH), 2.5(d, 2H, CH_2), 3.8(s, 2H, CH_2), 7.1–7.4(m, 5H, C_6H_5); ^{13}C nmr($CDCl_3$): 26(t, $2CH_2$), 27(t, CH_2), 31(t, $2CH_2$), 38(d, CH), 54(t, CH_2), 56(t, CH_2) 126(d, CH), 128(d, 2CH), 129(d, 2CH), 140(s, C); ms: m/e 203(M^+).

N-(cyclohexylmethyl)-N-phenylamine. ^{1}H nmr (CCl_4): δ0.9–1.9(m, 11H, C_6H_{11}), 2.9(d, 2H, CH_2), 3.6(b, 1H, NH), 6.5–7.2(m, 5H, C_6H_5); ^{13}C nmr($CDCl_3$): δ25(t, $2CH_2$), 26(t, CH_2), 32(t, $2CH_2$), 37(d, CH), 50(t, CH_2), 112(d, 2CH), 117(d, CH), 129(d, 2CH), 149(s, C); ms: m/e 189(M^+).

N-(cyclohexylmethyl)-N-(*p*-tolyl)amine. ^{1}H nmr (CCl_4): δ1.0–2.0(m, 11H, C_6H_1), 2.3(s, 3H, CH_3), 3.0(d, 2H, CH_2), 3.6(b, 1H, NH), 6.6–7.1(m, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ20(q, CH_3), 26(t, $2CH_2$), 27(t, CH_2), 31(t, $2CH_2$), 38(d, CH), 50(t, CH_2), 112(d, 2CH), 126(s, C), 130(d, 2CH), 146(s, C); ms: m/e 203(M^+).

N-(cyclohexylmethyl)-N-(*m*-tolyl)amine. ^{1}H nmr (CCl_4): δ0.9–1.9(m, 11H, C_6H_{11}), 2.2(s, 3H, CH_3), 2.9(d, 2H, CH_2), 3.6(b, 1H, NH), 6.4–7.2(m, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ21(q, CH_3), 26(t, $2CH_2$), 27(t, CH_2), 31(t, $2CH_2$), 38(d, CH), 50(t, CH_2), 110(d, CH), 113(d, CH), 118(d, CH), 129(d, CH), 138(s, C), 149(s, C); ms: m/e 203(m^+).

N-(cyclohexylmethyl)-N-(*o*-tolyl)amine. ^{1}H nmr (CCl_4): δ0.9–1.9(m, 11H, C_6H_1), 2.4(s, 3H, CH_3), 3.0(d, 2H, CH_2), 3.6(b, 1H NH), 6.5–7.3(M, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ21(q, CH_3), 26(t, $2CH_2$), 27(t, CH_2), 31(5, $2CH_2$), 38(d, CH), 50(t, CH_2), 113(d, CH), 117(d, CH), 121(s, C), 127(d, CH), 130(d, CH), 152(s, C); ms: m/e 203(M^+).

N-(cyclohexylmethyl)-N-(*p*-anisidyl)amine. ^{1}H nmr (CCl_4): δ0.9–1.8(m, 11H, C_6H_{11}), 2.8(d, 2H, CH_2), 3.4(b, 1H, NH), 3.7(s, 3H, OCH_3), 6.5–6.8(m, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ26(t, $2CH_2$), 27(t, CH_2, 31(t, $2CH_2$), 38(d, CH), 51(5, CH_2), 55(q, OCH_3), 113(d, 2CH), 115(d, 2CH), 143(s, C), 152(s, C); ms: m/e 219 (M^+).

N-(cyclohexylmethyl)-N-(m-anisidyl)amine. ^{1}H nmr(CCl_4): δ0.9–1.8(m, 11H, C_6H_{11}), 2.9(d, 2H, CH_2), 3.6(b, 1H, NH), 3.7(s, 3H, CH_3), 6.2–7.0(m, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ25(t, $2CH_2$), 26(t, CH_2), 30(t, $2CH_2$), 38(d, CH), 50(t, CH_2), 55(q, OCH_3), 99(d, CH), 102(d, CH), 106(d, CH), 129(d, CH), 150(s, C), 161(s, C); ms: m/e 219(M^+).

N-(cyclohexylmethyl)-N-(*o*-anisidyl)amine. ^{1}H nmr (CCl_4): δ0.9–1.9(m, 11H, C_6H_{11}), 2.9(d, 2H, CH_2), 3.8(s, 3H, OCH_3), 4.2(b, 1H, NH), 6.5–6.9(m, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ25(t, $2CH_2$), 26(t, CH_2), 31(t, $2CH_2$), 38(d, CH), 50(t, CH_2), 55(q, OCH_3), 110(d, CH), 115(d, CH), 117(d, CH), 121(d, CH), 139(s, C), 147(s, C); ms: m/e 219(M^+).

N-(cyclohexylmethyl)-N-(*p*-chlorophenyl)amine. ^{1}H nmr(CCl_4): δ0.9–1.9(m, 11H, C_6H_{11}), 2.9(d, 2H, CH_2), 3.5(b, 1H, NH), 6.5–7.1(m, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ25(t, $2CH_2$), 26(t, CH_2), 31(t, $2CH_2$), 38(d, CH), 50(t, CH_2), 113(d, 2CH), 121(s, C), 129(d, 2CH), 147(s, C); ms: m/e 225 ($M^+ + 2$).

N-(cyclohexylmethyl)-N-(m-chlorophenyl)amine. ^{1}H nmr(CCl_4): δ0.8–1.8(m, 11H, C_6H_{11}), 2.9(d, 2H, CH_2), 3.6(b, 1H, NH), 6.4–7.1(m, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ26(t, $2CH_2$), 27(t, CH_2), 31(t, $2CH_2$), 38(d, CH), 50(t, CH_2), 111(d, CH), 112(d, CH), 116(d, CH), 130(d, CH), 135(s, CO), 149(s, C); ms: m/e 225($M^+ + 2$).

N-(cyclohexylmethyl)-N-(*o*-chlorophenyl)amine. ^{1}H nmr(CCl_4): δ0.8–1.9(m, 11H, C_6H_{11}), 3.0(d, 2H, CH_2), 4.3(b, 1H, NH), 6.5–7.3(m, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ26 (t, $2CH_2$), 27(t, CH_2), 31(t, $2CH_2$), 38(d, CH), 50(t, CH_2), 111(d, CH), 117(d, CH), 119(s, C), 128(d, CH), 129(d, CH), 145(s, C); ms: m/e 225($M^+ + 2$).

N-(cyclohexylmethyl)-N-ethanolamine. ^{1}H nmr (CCl_4): δ 0.9–1.9(m, 11H, C_6H_{11}), 2.0(s, 1H, OH), 2.5(d, 2H, CH_2), 2.5–2.8(t, 2H, CH_2), 3.3–3.6(t, 2H, CH_2); ms: m/e 157(M^+).

N-(cyclohexylmethyl)-N-propanolamine. ^{1}H nmr (CCl_4): δ 0.8–1.9(m, 11H, C_6H_{11}), 1.5–1.7(q, 2H, CH_2), 2.0(s, 1H, OH), 2.3–2.5(t, 2H, CH_2), 3.5–4.2(m, 4H, $2CH_2$); ms: m/e 171(M^+).

N-(cyclohexylmethyl)-N-methyl-N-phenylamine. ^{1}H nmr(CCl_4): δ 0.8–1.7(m, 11H, C_6H_{11}), 2.8(s, 3H, CH_3), 3.0(d, 2H, CH_2), 6.5–7.1(m, 5H, C_6H_5); ^{13}C nmr($CDCl_3$): 25(t, $2CH_2$), 26(t, CH_2), 31(t, $2CH_2$), 38(d, CH), 40(q, CH_3), 60(t, CH_2), 112(d, 2CH), 115(d, CH), 129(d, 2CH), 150(s, C); ms: m/e 203(M^+).

N-(cycloheptylmethyl)-N-phenylamine. ^{1}H nmr (CCl_4): δ 0.9–1.8(m, 13H C_7H_{13}), 2.9(d, 2H, CH_2), 3.4(b, 1H, NH), 6.4–7.2(m, 5H, C_6H_5); ms: m/e 203(M^+).

N-(cycloheptylmethyl)-N-(*p*-chlorophenyl)amine. ^{1}H nmr(CCl_4): δ0.9–1.8(m, 13H, C_7H_{13}), 29(d, 2H, CH_2), 3.5(b, 1H, NH), 7.0–7.5(m, 4H, C_6H_4); ^{13}C nmr($CDCl_3$): δ27 (t, $2CH_2$), 29(t, $2CH_2$), 30(t, $2CH_2$), 40(d, CH), 50(t, CH_2), 114(d, 2CH), 121(s, C), 129(d, 2CH), 147(s, C); ms: m/e

239($M^+ + 2$).

N-(cycloheptylmethyl)-N-(*p*-tolyl)amine. ^1H nmr (CCl_4): δ 0.9-1.9(m, 13H, C_7H_{13}), 2.3(s, 3H, CH_3), 3.3(b, 1H, NH), 6.3-7.1(m, 4H, C_6H_4); ms: m/e 217(M^+).

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