Potassium–Graphite as a Metalation Reagent. Synthesis of Aldehydes and Ketones by Alkylation of Imines and Dihydro-1,3-oxazine

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The metalating properties of potassium–graphite (C_8K) toward imines **1** and 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine (**4**) are described. Alkylation of the potassium salts **2** and **5** with a variety of alkyl halides affords in good yields the corresponding carbonyl compounds **3** and **6**. The Wurtz coupling of alkyl halides is a side reaction in tetrahydrofuran; it can be suppressed using hexane as solvent, but in this case the yield of alkylated imine is lower. The alkylation reaction is regioselective. The formation of the enaminic anion **2** in this reaction is confirmed by filtering under argon the solution from the solid reagent before adding the alkyl halide. By the same procedure it is possible to perform the condensation between *N*-2-propylidenecyclohexylamine (**1d**) and nonanal to give, after acidic hydrolysis, the corresponding β-hydroxy and α,β-unsaturated carbonyl compounds **13** and **14**.

In recent years reactions under heterogeneous conditions have found interesting applications in the synthesis of organic molecules, since several advantages can be accomplished.[1] The facile separation of the insoluble reagents from products is one of the most convenient features of the solid phase synthesis. This method reduces possible losses of substances and simplifies the choice of the solvent. For example, polymer bound reagents have been prepared and utilized by several research groups.[2]

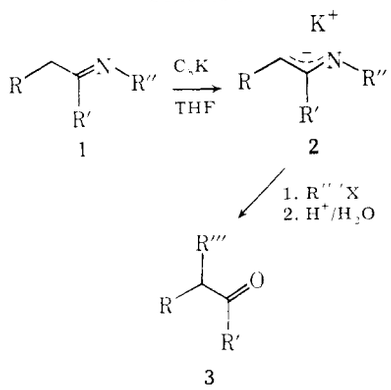
Recently graphite has found application for trapping reagents between the carbon layers, thus affording new compounds which possess definite stoichiometry and show modified reactivity with respect to the bulk reagent.[3] In fact a large number of inorganic substances such as mineral acids, metals, metal halides, and oxides can penetrate between the carbon layers.[3] Intercalation occurs spontaneously or by electrolysis. Mineral acids such as H_2SO_4, H_3PO_4, and HNO_3 can be intercalated after chemical or anodic oxidation of the graphite.

The catalytic properties of graphite–bisulfate $C_{24}^{+}HSO_4^{-}\cdot 2H_2SO_4$ in the esterification of carboxylic acids with alcohols[4] and of graphite–$AlCl_3$ in the Friedel–Crafts alkylation with alkyl halides[5] have been investigated.

The oxidizing capacity of graphite–CrO_3 toward primary alcohols has been reported.[6] More recently graphite–NbF_5 was found to be an effective catalyst for the reduction of 2-chloropropane and its reactions with alkanes.[7]

Alkali metals such as K, Rb, and Cs can be easily intercalated in graphite.[8] Depending on the amount of potassium used, compounds of different stoichiometry can be obtained, i.e., C_8K, $C_{24}K$, $C_{36}K$, and $C_{48}K$, to which correspond structures with one, two, three, or more carbon layers between each potassium layer.[8] When potassium is inserted, the distance between the carbon layers is increased from 3.35 to 5.40 Å.[8] Potassium–graphite (C_8K), a bronze-colored powder obtained by melting potassium over graphite under argon, has been found to act as a catalyst in polymerization reactions[9] and in the nuclear and side-chain alkylation of aromatic hydrocarbons with ethylene.[10] Furthermore it has found application as a reducing agent toward carbonyl compounds[6] and metal carbonyls.[11]

Scheme I



R = H, alkyl, aryl; R′ = H, alkyl; R″ = *tert*-butyl, cyclohexyl; R‴ = alkyl; X = Cl, Br, I

Recently we have extended the application of potassium–graphite for the reductive cleavage of the carbon–sulfur bond in α,β- and β,γ-unsaturated sulfones to give alkenes in good yields.[12] We also found that C_8K exhibits metalating properties toward weakly acidic substrates;[13] indeed, aliphatic nitriles and esters afforded the corresponding alkylated products after treatment with C_8K and alkyl halides at low temperature.[13]

The promising results obtained prompted us to extend the study of the metalating properties of C_8K,[14] examining other substrates such as the imines of aliphatic carbonyl compounds and 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine, in order to realize, by a sequence of reactions shown in Schemes I and II, a convenient method for the preparation of carbonyl compounds.

It is known that aliphatic imines, bearing a bulky *N*-alkyl group, are metalated at the α position by means of lithium dialkylamides,[15] or from lithium and dialkylamines in benzene–hexamethylphosphoric triamide.[16] The resulting metalated imines are known to be excellent nucleophiles.[15]

We have now found that imines **1** are easily metalated with a heterogeneous suspension of C_8K in tetrahydrofuran at room temperature to give the ion pairs **2** which are alkylated with alkyl halides affording, after hydrolysis, the corresponding carbonyl compounds **3** (Scheme I).

Similarly aldehydes **6** are obtained when 2,4,4,6-tetramethyl-5,6-dihydro-1,3-oxazine (**4**) is used as starting material, following a reaction sequence which includes metalation with C_8K in THF at room temperature, alkylation with alkyl halides, reduction with sodium borohydride in aqueous ethanol, and hydrolysis with aqueous oxalic acid[17] (Scheme II).

As shown in Table I our procedure is very efficient for the formation of aldehydes and ketones. The data in Table I in-

Scheme II

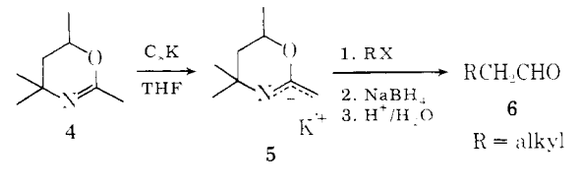
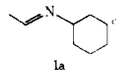
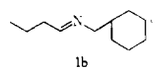
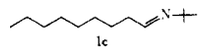
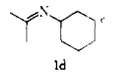
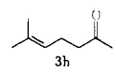
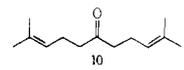
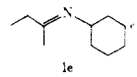
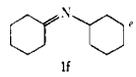
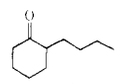
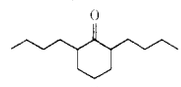
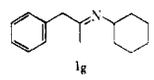
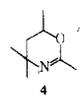


Table I. Carbonyl Compounds from Imines and 2,4,4,6-Tetramethyl-5,6-dihydro-1,3-oxazine[a]

Entry	Starting material	Registry no.	Alkyl halide	Registry no.	Carbonyl compd	Registry no.	Yield, %[b]
1	 1a	1193-93-7	1-$C_{13}H_{27}Br$	765-09-3	$C_{13}H_{27}CH_2CHO$ (**3a**) $(C_{13}H_{27})_2CHCHO$ (**7**)	2765-11-9 65899-12-9	64, 35[d] 8, 3[d]
2	**1a**		2-$C_8H_{17}Br$	557-35-7	$C_6H_{13}(CH_3)CHCH_2CHO$ (**3b**)	65899-13-0	63
3	 1b	1197-52-0	1-$C_7H_{15}Br$	629-04-9	$C_7H_{15}(C_2H_5)CHCHO$ (**3c**)	37596-40-0	70
4	**1b**		$C_6H_5CH_2CH_2$-Br	103-63-9	$C_6H_5CH_2CH_2(C_2H_5)CHCHO$ (**3d**)	33856-83-6	55
5	 1c	65956-94-7	1-C_4H_9Br	109-65-9	$C_7H_{15}(C_4H_9)CHCHO$ (**3e**)	65899-14-1	67
6	 1d	6407-36-9	1-$C_7H_{15}Br$		$C_8H_{17}COCH_3$ (**3f**) $(C_8H_{17})_2CO$ (**8**)	693-54-9 540-08-9	40, 35,[f] 48,[g] 25[h] 20, 5,[f] 40,[g] 8[h]
7	**1d**		$C_6H_5CH_2Cl$	100-44-7	$C_6H_5CH_2CH_2COCH_3$ (**3g**) $(C_6H_5CH_2CH_2)_2CO$ (**9**)	2550-26-7 5396-91-8	55 8
8	**1d**			870-63-3	 3h  10	110-93-0 2520-57-2	64 9
9	 1e	6125-75-3	1-$C_8H_{17}Br$	111-83-1	$C_9H_{19}COCH_2CH_3$ (**3i**)	1534-27-6	66
10	 1f	10468-40-3	1-C_4H_9Br		 3j  11	1126-18-7 65899-15-2	56 8
11	 1g	65899-11-8	1-C_4H_9Br		$C_6H_5(C_4H_9)CHCOCH_3$ (**3k**) $C_6H_5(C_4H_9)CHCOC_5H_{11}$ (**12**)	54929-04-3 65899-16-3	70 9
12	 4	26939-18-4	1-C_3H_7I	107-08-4	C_4H_9CHO (**6a**)	110-62-3	50
13			$C_6H_5CH_2Cl$		$C_6H_5CH_2CH_2CHO$ (**6b**)	104-53-0	58

[a] The general procedure is reported in the Experimental section. In all cases reported the molar ratio imine/C_8K/alkyl halide is 1:2:2. [b] Yields refer to pure isolated carbonyl compounds and are calculated on starting imines or oxazine. Analytical GLC yields of alkylated imines are always about 10% higher with respect to those of carbonyl compounds reported in the table. [c] See ref 15d. [d] The metalated imine is filtered under argon from the excess of C_8K and then allowed to react with 1 equiv of the alkyl halide. [e] See ref 20. [f] Molar ratio imine/C_8K/alkyl halide = 1:1:1. [g] Molar ratio imine/C_8K/alkyl halide = 1:4:4. [h] The reaction is performed at room temperature in hexane, instead of THF, with molar ratio imine/C_8K/alkyl halide (1:2:1). [i] See ref 17.

dicate that the optimum conditions for monoalkylation of imines are obtained with a molar ratio substrate/C_8K/alkyl halide 1:2:2 (entry 6).

The Wurtz coupling reaction of the alkyl halide in tetrahydrofuran with C_8K always accompanies the alkylation reaction, especially if C_8K is used in large excess; therefore a corresponding amount of alkyl halide is required. With hexane as solvent instead of THF, the Wurtz product disappears, thus no excess of alkyl halide is necessary. However, the yield of alkylated product is, in this case, lower (entry 6).

The reaction seems to have a wide applicability, giving good results with primary, secondary, allylic, and benzylic halides. In the same way both ketimines and aldimines can be employed in this reaction. As amine components of the Schiff's bases, cyclohexylamine and *tert*-butylamine were found to be suitable, since Schiff's bases having branched *N*-alkyl groups have less tendency toward self-addition than those with unbranched chains.

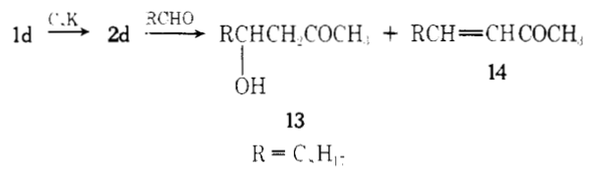
The alkylation reaction is regioselective.[18] In fact *N*-2-butylidenecyclohexylamine (**1e**) and *N*-1-phenyl-2-propylidenecyclohexylamine (**1g**) reacted with alkyl halides to give alkylated products at the methyl or methylene group, respectively[18] (entries 9 and 11).

Little of the α,α'-dialkylated ketimines were observed, while in the case of aldimines only *N*-ethylidenecyclohexylamine (**1a**) gave a partially dialkylated product.

Metalated imines **2** may be regarded as ambident anions. In fact partial alkylation at the nitrogen atom (about 5%) was observed treating the potassium salt of *N*-cyclohexylidenecyclohexylamine (**2f**) with bromobutane[19] (entry 10).

To ascertain that alkylation of imines occurs through the anion intermediate **2** as shown in Scheme I, experiments were performed where imines were treated with C_8K as previously described, then the solution was filtered by means of a bench-top apparatus under argon and allowed to react with an electrophile. Thus using *N*-ethylidenecyclohexylamine (**1a**) and 1-bromotridecane, pentadecanal (35%) was obtained. With the same procedure as described above, the reaction of

Scheme III



N-2-propylidenecyclohexylamine (**1d**) with nonanal as the electrophile afforded 4-hydroxydodecan-2-one (**13**) (30%) and dodeca-3-en-2-one **14** (5%) (Scheme III).

Finally, we wish to emphasize that the good yield obtained in this alkylation reaction, the inexpensiveness of the reagent, and the simplicity of workup may provide an attractive synthetic alternative to previously reported methods involving bases such as lithium alkylamides[15] or poisonous solvents such as hexamethylphosphoric triamide.[16]

Experimental Section

General. Infrared spectra (IR) were recorded on a Perkin-Elmer 710B spectrometer and are given in reciprocal centimeters. Nuclear magnetic resonance spectra (NMR) were determined in tetrachloromethane on a Perkin-Elmer R12B spectrometer. Chemical shifts are expressed as δ in ppm from internal tetramethylsilane. Mass spectra (MS) were taken on a Varian MAT 111 (70 eV). Vapor-phase chromatography was performed on a Hewlett Packard 5750 B instrument using 0.25 in. × 6 ft columns of 2% FFAP (nitroterephtalic acid) and 5% SF96 (silicon oil) on 80/100 mesh silanized Chromosorb G. TLC were performed on silica gel HF_{254} (Merck) and column chromatography on silica gel (Merck, 0.05–0.20 mesh) with hexane–ether as solvent. Tetrahydrofuran (THF) was obtained anhydrous and oxygen free by distillation over sodium benzophenone ketyl under argon. Graphite was supplied from Roth (impurities less than 500 ppm) and potassium from Carlo Erba (RPE, 99.5%). Melting points (mp) and boiling points (bp) are uncorrected.

General Procedure. Preparation of Aldimines and Ketimines. To a solution of cyclohexylamine (0.11 mol) in 30 mL of ether, 20 g of anhydrous sodium sulfate and the aldehyde or ketone (0.10 mol) were added at −20 °C with stirring. The mixture was allowed to stand at room temperature for 10 h, sodium sulfate was filtered off, the solvent was evaporated, and the residue was distilled under vacuum. Aldimines and ketimines **1** obtained in about 90 and 70% yield, respectively, were identified by the characteristic IR and NMR frequency values:[21] IR ν 1665–1670 cm^{-1} (C=N); NMR δ 7.6–7.8 (CH=N), 2.2 (CH_2C=N), 1.8–1.9 ppm (CH_3C=N).

Among the prepared imines **1** two were not reported in the literature. ***N*-Nonylidene-*tert*-butylamine (1c)** had bp 85 °C (0.1 mm): IR (neat) 1650 (C=N); NMR δ 7.65 (CH=N, t, 1 H), 2.2 (**CH_2**CH=N, m, 2 H), 1.1 (t-C_4H_9, s, 9 H); MS m/e 197 (M^+). ***N*-2-(1-Phenylpropylidene)cyclohexylamine (1g)** had bp 155–160 °C (15 mm): IR (neat) 1660 (C=N); NMR δ 7.3 (C_6H_5, s, 5 H), 3.5 (C_6H_5**CH_2**C=N, s, 2 H), 1.75 (CH_3C=N, s, 3 H); MS m/e 215 (M^+).

Preparation of Potassium–Graphite (C_8K). In a two-necked flask flushed with argon and equipped with a magnetic stirrer, 3.84 g (0.32 mg-atom) of graphite was stirred and heated with a bunsen flame under argon in order to desorb any oxygen and water. Then 1.6 g of potassium (0.04 mg-atom) was added in small pieces to the stirred graphite previously heated to about 200 °C. C_8K, a bronze-colored powder, was so obtained. It is easily prepared but must be handled in inert atmosphere since it is water sensitive and pyrophoric.

Alkylation and Hydrolysis of Imines. Synthesis of Aldehydes and Ketones. A solution of the imine (20 mmol) in 30 mL of THF was added over 10 min at room temperature to a heterogeneous mixture of C_8K (40 mmol) in 20 mL of THF. After 1 h a solution of the alkyl halide (40 mmol) in 20 mL of THF was dropped over 30 min. Stirring was continued for 2 h, then the excess of C_8K was quenched with 2 mL of water; the graphite was filtered and washed with ether. Solvent was evaporated and the residue was vigorously stirred with 100 mL of 4% oxalic acid aqueous solution at 0 °C for 3 h. After extraction with ether, the organic phase was evaporated and the residue was chromatographed on a silica gel column. The Wurtz coupling hydrocarbon was eluted with hexane, then the carbonyl compound was collected eluting with hexane/ether (98:2).

Pentadecanal (3a): mp 24 °C (hexane); IR (neat) 1720 (C=O); NMR 9.9 (t, 1 H, CHO), 2.3 (m, 2 H, **CH_2**CHO); MS m/e 226 (M^+).

2-Tridecylpentadecanal (7): mp 48–50 °C (hexane); IR (Nujol) 1720 (C=O); NMR 9.7 (d, 1 H, CHO), 2.3 (m, 1 H, **CH**CHO).

3-Methylnonanal (3b): bp 104 °C (18 mm); IR (neat) 1725 (C=O); NMR 9.9 (t, 1 H, CHO), 2.3 (dd, 2 H, **CH_2**CHO); MS m/e 156 (M^+).

2-Ethylnonanal (3c): bp 108 °C (18 mm); IR (neat) 1715 (C=O); NMR 9.45 (d, 1 H, CHO), 2.5 (m, 1 H, **CH**CHO); MS m/e 170 (M^+).

2-Ethyl-4-phenylbutanol (3d): bp 148 °C (22 mm); IR (neat) 1720 (C=O); NMR 9.7 (d, 1 H, CHO), 7.2 (s, 5 H, C_6H_5), 2.6 (t, 2 H, C_6H_5**CH_2**); MS m/e 176 (M^+).

2-Butylnonanal (3e): bp 115 °C (16 mm); IR (neat) 1715 (C=O); NMR 9.45 (d, 1 H, CHO), 2.35 (m, 1 H, **CH**CHO); MS m/e 198 (M^+).

Decan-2-one (3f): bp 96 °C (12 mm); IR (neat) 1715 (C=O); NMR 2.35 (t, 2 H, CH_2CO), 2.05 (s, 3 H, CH_3CO); MS m/e 156 (M^+).

Heptadecan-9-one (8): mp 53 (hexane); IR (Nujol) 1705 (C=O); NMR 2.3 (t, 4 H, CH_2COCH_2).

4-Phenylbutan-2-one (3g): bp 115 °C (13 mm); IR (neat) 1715 (C=O); NMR 7.2 (s, 5 H, C_6H_5), 2.7 (m, 4 H, CH_2CH_2), 1.95 (s, 3 H, CH_3CO); MS m/e 148 (M^+).

1,5-Diphenylpentan-3-one (9): bp 230 °C (18 mm); IR (neat) 1710 (C=O); NMR 7.2 (s, 10 H, $2C_6H_5$), 2.7 (m, 8 H, $2CH_2CH_2$); MS m/e 238 (M^+).

6-Methylhept-5-en-2-one (3h): bp 173 °C; IR (neat) 1710 (C=O); NMR 5.15 (m, 1 H, CH=C), 2.35 (t, 2 H, CH_2CO), 2.1 (m, 2 H, CH_2C=C), 2.0 (s, 3 H, CH_3CO), 1.7 and 1.6 (s, 6 H, $2CH_3C$=C); MS m/e 126 (M^+).

2,10-Dimethylhendeca-2,9-dien-6-one (10): bp 117 °C (15 mm); IR (neat) 1720 (C=O); NMR 5.15 (m, 2 H, CH=C), 2.3 (t, 4 H, $2CH_2CO$), 2.05 (m, 4 H, $2CH_2C$=C), 1.7 and 1.6 (s, 12 H, $4CH_3C$=C); MS m/e 194 (M^+).

Dodecan-3-one (3i): bp 134 °C (18 mm); IR (neat) 1710 (C=O); NMR 2.3 (m, 4 H, $2CH_2CO$); MS m/e 184 (M^+).

2-Butylcyclohexanone (3j): bp 70 °C (2 mm); IR (neat) 1715 (C=O); NMR 2.2 (m, 3 H, CH_2CO and CHCO); MS m/e 154 (M^+).

2,6-Dibutylcyclohexanone (11): bp 168 °C (18 mm); IR (neat) 1710 (C=O); NMR 2.3 (m, 2 H, 2CHCO); MS m/e 210 (M^+).

3-Phenylheptan-2-one (3k): bp 95 °C (2 mm); IR (neat) 1705 (C=O); NMR 7.3 (s, 5 H, C_6H_5), 3.5 (t, 1 H, CHCO), 2.0 (s, 3 H, CH_3CO); MS m/e 190 (M^+).

5-Phenylhendecan-6-one (12): bp 167–170 °C (18 mm); IR (neat) 1710 (C=O); NMR 7.2 (s, 5 H, C_6H_5), 3.5 (t, 1 H, CHCHO), 2.3 (t, 2 H, CH_2CO); MS m/e 246 (M^+).

Alkylation of 2,4,4,6-Tetramethyl-5,6-dihydro-1,3-oxazine. Synthesis of Aldehydes. The oxazine **4** (20 mmol) was metalated with C_8K (40 mmol) in dry THF and alkylated with alkyl halide (40 mmol) by a procedure identical to that reported for the imines. The crude alkylated oxazine was directly reduced to tetrahydrooxazine by means of $NaBH_4$ (20 mmol) in THF–EtOH (1:1) and successively hydrolyzed to aldehyde by 4% oxalic acid aqueous solution, as described by Meyers.[17]

Pentanal (6a): bp 103 °C; IR (neat) 1720 (C=O); NMR 9.8 (t, 1 H, CHO), 2.4 (dt, 2 H, **CH_2**CHO); MS m/e 86 (M^+).

3-Phenylpropanal (6b): bp 104 °C (13 mm); IR (neat) 1720 (C=O); NMR 9.7 (t, 1 H, CHO), 7.2 (s, 5 H, C_6H_5), 2.5 (m, 4 H, CH_2CH_2); MS m/e 134 (M^+).

Reaction of *N*-2-Propylidenecyclohexylamine (1d) with Nonanal. C_8K (40 mmol) was prepared in a two-necked flask connected by a fritted tube to a second flask equipped with an argon inlet. A solution of N-2-propylidenecyclohexylamine (**1d**) (2.8 g, 20 mmol) in dry THF (20 mL) was added to the suspension of C_8K in THF (40 mL) at room temperature under stirring. After 2 h the apparatus was overturned and a clear green solution of **2d** was vacuum filtered through the frit under argon and collected into the second flask. Nonanal (2.84 g, 20 mmol) in THF (20 mL) was added at −60 °C and the reaction was stirred for 1 h and then allowed to reach room temperature and quenched with water (10 mL).

After usual workup, the residue was chromatographed on silica gel to afford 1.11 g (30%) of 4-hydroxydodecan-2-one (**13**) and 0.17 g (5%) of dodeca-3-en-2-one (**14**).

4-Hydroxydodecan-2-one (13): bp 136 °C (12 mm); IR (neat) 3380 (OH), 1710 (C=O); NMR 4.0 (m, 1 H, CHOH), 2.8 (broad, 1 H, OH), 2.55 (d, 2 H, CH_2CO), 2.1 (s, 3 H, CH_3CO); MS of acetylated title compound, m/e 242 (M^+).

Dodeca-3-en-2-one (14): bp 97 °C (15 mm); IR (neat) 1670 (C=O); NMR 5.9–7.3 (m, 2 H, CH=CH), 2.1 (s, 3 H, CH_3CO); MS m/e 182 (M^+).

Acknowledgment. The authors are grateful to Dr. G. Passeri for his valuable help.

Registry No.—**2d**, 65899-17-4; **13**, 65899-18-5; **14**, 66142-11-8; C_8K, 12081-88-8; cyclohexylamine, 108-91-8; nonanal, 124-19-6; 1-phenylpropan-2-one, 103-79-7.

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Conformational Studies of Some 2-*exo*-Alkyl-3-benzyl-3-azabicyclo[3.3.1]nonanes

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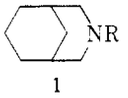
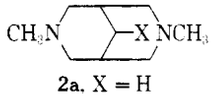
The conformations of three 3-benzyl-3-azabicyclo[3.3.1]nonanes substituted with 2-*exo*-alkyl groups have been studied by analysis of their proton and carbon-13 nuclear magnetic resonance spectra. These compounds were prepared by stereoselective alkylation of aldimmonium ion **4** with Grignard reagents. The presence of 2-methyl and 2-ethyl substituents was shown to cause the ring system to prefer a flattened double-chair conformation similar to that of the unsubstituted compound (**3a**). Introduction of a 2-isopropyl substituent, however, caused a change in favor of the chair–boat conformation.

Considerable attention has been directed toward synthesis and conformational analysis of substituted bicyclo[3.3.1]-nonanes and heterocyclic analogues, compounds which have potential as models for extension of the concepts and theories of stereochemistry.[1] In this connection, our interest has been centered on the 3-azabicyclo[3.3.1]nonane ring system (**1**). According to relative energy minima, **1** may exist in any of four conformations: double chair, chair–boat, boat–chair, and double boat. The most stable conformer of **1** is the double chair, as is the case with its *N*-alkyl analogues.[2] However, in this and in the conformationally similar diazabicyclic compound **2a**,[3a] minor structural modifications have been shown



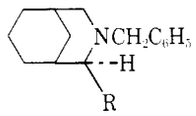
1



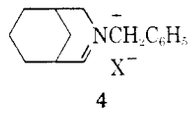
2a, X = H
b, X = OH

to cause conformational changes. For example, the methiodide of **1** (R = CH_3) and *N,N'*-dimethylbispidinol (**2b**) appear to prefer chair–boat conformations.[3b,c] While there have been a number of conformational studies of symmetrical derivatives of **1** and isomers, less information is available concerning the conformational preferences of unsymmetrical derivatives. Accordingly, we have investigated the effect of 2-*exo*-alkyl substituents on the conformation of **1**.

Among other methods, proton magnetic resonance (^{1}H NMR) spectrometry has proven to be effective in resolving configurational and conformational features in azabicyclic systems.[4] More recently, carbon-13 nuclear magnetic resonance (^{13}C NMR) spectrometry has been shown to be a particularly powerful tool in such studies.[5] In this paper, we report the synthesis of 3-benzyl-3-azabicyclo[3.3.1]nonane (**3a**) and three of its 2-*exo*-alkyl analogues (**3b–d**) and some conclusions regarding the preferred conformations of these last compounds as determined from analysis of their ^{1}H and ^{13}C NMR spectral features.



3a, R = H
b, R = CH_3
c, R = CH_2CH_3
d, R = *i*-C_3H_7



4

Results and Discussion

Compounds **3b–d** were each prepared from **3a** in two steps.[6] Oxidation of **3a** with bromine in methylene chloride[7] furnished aldimmonium salt **4** (X = bromide or perchlorate).

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