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ALLENES AND ACETYLENES—XXIII[1]

SYNTHESIS OF α-ALLENIC AMINES VIA ALLENIC IMINES OBTAINED FROM ORGANOCOPPER REACTIONS[2]

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Abstract—N-2,3-Alkadienyldiphenylmethanimines 5a-h are formed in moderate yields in 1,3-substitution reactions (S_N2') of propargylic sulfonates with an organocopper reagent derived from metalated N-methyldiphenylmethanimine 1 and Me_2S·CuBr. The imines can be readily hydrolyzed to primary α-allenic amines. Alkylation of the imines with methyl fluorosulfonate followed by hydrolysis gives N-methyl-substituted secondary α-allenic amines.

It is known that N-methyldiphenylmethanimine 1 can be metalated by n-BuLi[3] or by lithium diisopropylamide (LDA)[4] to give 3,3-diphenyl-2-azaallyllithium 2 (eqn 1). Compound 2 can be used as an aminomethyl equivalent. Thus, 2 reacts with ketones and aldehydes to give after hydrolysis aminoalcohols and with organic halides to give primary amines.[3,4] It is well known that various types of allenes can be prepared by, formally, S_N2' reactions of several propargylic derivatives with various types of organocopper reagents.[5]

We report here the transformation of 2 to the organocopper reagent 3, which contains a functionalized ligand.† Reactions of this reagent with propargylic sulfonates give allenic imines which can be easily converted to primary and secondary α-allenic amines. α-Allenic amines have biological interest as irreversible, mechanism-based inhibitors of mitochondrial monoamine oxidase (MAO).[7] MAO is an enzyme which plays an important role in the oxidative deamination of transmitter amines in many types of cells.[8] MAO-inhibitors can be used clinically, mainly in the treatment of depression.[9]

α-Allenic amines have hitherto been prepared by the following methods: (i) reaction of 2,3-alkadienyl chlorides[10] or mesylates[11] with amines, (ii) addition of secondary amines to alkenynes,[12] (iii) organocuprate reactions of acetylenic aminoethers,[13] (iv) addition of organometallic reagents to enynamines,[14] (v) reaction of gem-dibromcyclopropanamines with BuLi,[15] (vi) pyrolysis of certain Diels–Alder adducts.[16]

However, many of these methods are not generally employed and are tedious and give low yields. Furthermore, some methods involve α-allenic alcohols as starting materials, compounds which are sometimes difficult to obtain. In contrast, the method described herein offers a very short and simple way of preparing many primary and N-Me substituted α-allenic amines. Furthermore, the new organocopper reagent 3, which is an aminomethyl anion equivalent, might find other applications in organic synthesis.

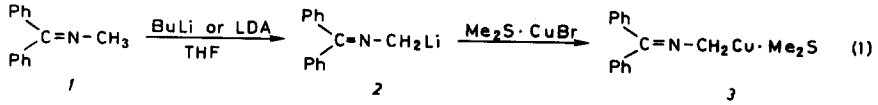
†For other organocopper reagents containing functionalized ligands, see ref. 6.

RESULTS AND DISCUSSION

Formation of allenic imines

In preliminary studies, we noticed the formation of the allenic imine **5a** when reacting the organocopper reagent 3, derived from metalated N-methyldiphenylmethanimine 1 and one equivalent of Me_2S·CuBr in tetrahydrofuran (THF) at −60° (eqn 1), with the propargylic tosylate **4a** (eqn 2, Table 1).

This result prompted us to undertake a systematic investigation of the reaction of propargylic sulfonates with the organocopper reagent 3. We chose to use the propargylic mesylates **4b–h**, because they are usually more easily obtained than the corresponding tosylates, and reacted them with 3. The results of these reactions



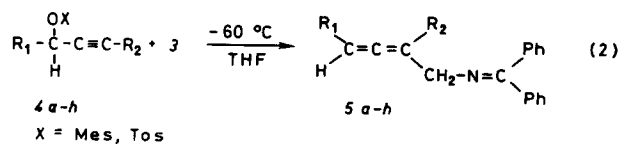


Table 1, Reactions of sulfonates 4 with 3 (eqn 2)

Entry	Sulfonate 4	X	R_1	R_2	Allenimine 5	Isolated yield (%)[a]
1	4a	Tos	CH_3	H	5a	32
2	4b	Mes	CH_3	CH_3	5b	39
3	4c	Mes	C_3H_7	H	5c	49
4	4d	Mes	H	C_4H_9	5d	31
5	4e	Mes	H	CH_2-Ph	5e	33
6	4f	Mes	H	Ph	5f	14
7	4g	Mes	H	CH_3	5g	40
8	4h	Mes	CH_3	C_6H_{13}	5h	54
9[b]	4c	Mes	C_3H_7	H	5c	30
10[b]	4h	Mes	CH_3	C_6H_{13}	5h	40
11[c]	4a	Tos	CH_3	H	5a	0
12[d]	4b	Mes	CH_3	CH_3	5b	5
13[e]	4h	Mes	CH_3	C_6H_{13}	5h	43

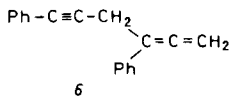
[a]Based on N-methyldiphenylmethanimine.
[b]0.5 equivalents of CuBr · Me_2S was used.
[c]Ether was used as solvent.
[d]Cu(I)Br was used.
[e]LDA was used as metalating reagent.

are summarized in Table 1.† These results indicate that the reaction depicted in eqn 2 is a general one and can be used as a general synthetic method for allenic imines and hence for α-allenic amines. The yields are low to moderate, varying from 14% (entry 6) to 54% (entry 8). The relatively low yields may be explained by known and unknown side reactions (see below). However, the method is easy to use and utilizes readily available starting materials.

The purification of the allenic imines on silica gel columns, using a standard column chromatography technique, was accompanied by considerable losses of material due to hydrolysis. This was indicated by the presence of benzophenone in the eluate when eluting the allene **5a**. Pretreatment of the silica gel with either triethylamine or methanolic potassium carbonate did not prevent the hydrolysis. Most of the decomposition of the allenic imines on the silica column, however, can be avoided by using a flash-chromatography technique.[17]

Insufficient metalation of the imine **1** led in some cases to formation of allenic hydrocarbons from the reaction of butylcopper (from BuLi) with the sulfonate. Kauffmann *et al.* have reported a deuterium incorporation of 85% upon deuterolysis of metalated **1** with use of LDA as the metalating agent.[4] We obtained a deuterium incorporation of 85–90%, as determined by NMR, when using BuLi as the metalating agent in one control experiment.

The dienyne **6** was isolated in a yield of about 15% from one reaction (entry 6). A possible explanation for its formation is coupling of the sulfonate **4f** with a hypothetical allenylcopper compound **7** formed by a side



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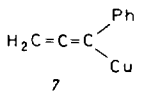

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reaction (reduction) of the sulfonate **4f**. There is ample precedence in the literature for reductions of propargylic and allylic substrates in reactions of the organocuprate type. A mechanism for the allylic case, which nicely fits the present finding that only the conjugated sulfonate **4f** underwent reduction and further reactions, has been proposed.[18]

We noticed in all reactions the formation of some unknown polymeric material, which, together with the discussed side reactions, explains the relatively low yields obtained.

In our experience, the time required for complete formation of the copper reagent **3** is 5–10 min. Longer reaction times only lowered the yield, indicating that **3** decomposes on standing.

It is essential to use a polar solvent such as THF or hexamethylphosphoramide/benzene when metalating **1**.[3] Ether gives rise to polymers[3] (see entry 11).

LDA and BuLi are roughly equivalent as metalating agents for **1**. However, the total yield was somewhat lower when LDA was used (see entries 8 and 13). Also, as the use of BuLi involves a simpler experimental technique, we chose BuLi as the metalating agent throughout the study. In the preparation of the organocopper reagent, it is preferable to use the dimethylsulfide complex of CuBr,[19] instead of CuBr alone. Thus, CuBr or CuI as the copper source dramatically decreased the yield of **5** (entry 12). No other soluble copper complexes were tested.

Attempts to use only 0.5 equivalents of CuBr·Me_2S led to decreased yields (entries 9 and 10).

†For experimental details see the Experimental section.

Attempts were made to metalate N-ethyldiphenylmethanimine **8**[20] and N-isopropyldiphenylmethanimine **9**,[20] with the aim of obtaining a method for preparation of α-substituted allenic amines. However, these failed, since the imines seemed to be largely unaffected by BuLi or LDA at −60° in THF (eqn 3). When we metalated **8** at 0° with BuLi, a complex reaction mixture was obtained after deuterolysis. Preliminary results indicate, however, that the imine **8** reacts with BuLi in THF at −30°, since a low yield of 2-hydroxy-2-phenylethylamine was obtained after addition of benzaldehyde followed by acidic work-up.

The imine-forming reaction (eqn 2) was shown to be 100% regioselective, since in no case were acetylenic imines obtained. The same high regioselectivity has been observed in reactions of propargylic tosylates[21] or sulfinates[22] with heterocuprates derived from RMgX and CuBr or CuBr·LiBr in THF.

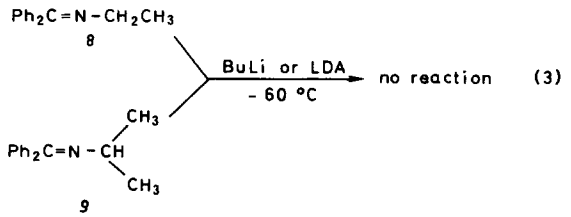
It has been reported that copper(I)derivatives of metalated dialkylalkane phosphonates react with 2-alkynyl bromides, chlorides or benzene sulfonates in THF to give dialkyl-2,3-alkadiene phosphonates.[23] The best results were obtained when bromide was used as the leaving group. This is in contrast to our findings, since propargylic bromides gave very poor results (not shown in the Table); similarly poor results were obtained in reactions of propargylic bromides with RMgX/CuBr.[21]

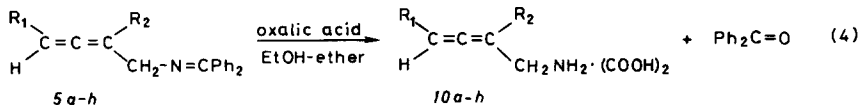
Hydrolysis of allenic imines

After some experimentation it was found that the allenic imines could be most conveniently hydrolyzed by using oxalic acid in ethanol–ether. The allenic amine oxalates thus obtained can simply be filtered off from the reaction mixture. The method gives practically quantitative yields of the allenic amine oxalates **10a–h** (Table 2, eqn 4).

Alkylation of allenic imines with methyl fluorosulfonate

It has long been known that N-Me substituted secondary amines can be synthesized by alkylation of imines with MeI.[24] Our attempts to alkylate **5a** with MeI failed. However, when using the very reactive alkylating reagent methyl fluorosulfonate, we noticed a smooth alkylation of **5** in dichloromethane at 0°. Hydrolysis of the immonium compounds thus obtained afforded the amines **11** in high yields (eqn 5, Table 3).





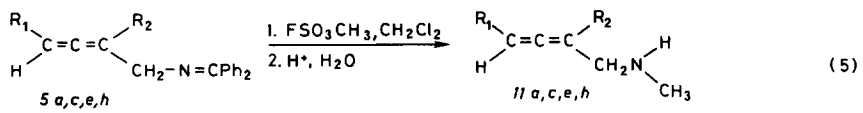


Table 2. Primary allenamines **10** from **5** (eqn 4)

Allenimine 5	R_1	R_2	Allenamine oxalate 10[a]
5a	CH_3	H	10a
5b	CH_3	CH_3	10b
5c	C_3H_7	H	10c
5d	H	C_4H_9	10d
5e	H	CH_2Ph	10e
5f	H	Ph	10f
5g	H	CH_3	10g
5h	CH_3	C_6H_{13}	10h

[a] Yields: 90–100 %

Table 3. N-Methylallenamines 11 from reactions of 5 with methyl fluorosulfonate (eqn 5)

Allenimine 5	R^1	R^2	N-Methyl-allenamine 11	Isolated yield (%)
5a	CH_3	H	11a	85[a]
5c	C_3H_7	H	11c	85[a]
5e	H	CH_2Ph	11e	85
5h	CH_3	C_6H_{13}	11h	75

[a] Isolated as oxalates

$$Ph\text{-}CH_2Cu + Br\text{-}C{\equiv}C\text{-}CH_2OTHP \xrightarrow[2.\ H^+]{1.\ THF/ether} Ph\text{-}CH_2\text{-}C{\equiv}C\text{-}CH_2OH \qquad (6)$$

Comments on the synthesis of 4-phenyl-2-butyn-1-ol (12)

It is very difficult to achieve nucleophilic substitution in benzyl halides by using alkynides, since a number of side reactions occur.[25] Consequently, the synthesis of such a simple compound as 4-phenyl-2-butynol is not as straightforward as one might presume. It has been prepared in a rather high yield by reaction of phenylmagnesium halide with 4-chloro-2-butyn-1-ol in ether.[26] However, in this case the acetylenic alcohol was contaminated with substantial amounts of 2-phenyl-2,3-butadienol. Normant has reported, as a footnote, that the coupling between n-BuCu and Br–C≡C–R (R = alkyl) in THF gives n-Bu–C≡C–R in a 70% yield.[27a] These findings have recently been published in a full paper.[27b] Normant's first observation together with our own experience of copper–organic chemistry encouraged us to react a benzyl–copper reagent, derived from benzylmagnesium chloride, CuBr and Me_2S, with the 2-tetrahydropyranyl (THP) ether of 3-bromo proparagyl alcohol (eqn 6). We observed the desired coupling and 12 was obtained in a yield of 58% after hydrolysis.[32]

EXPERIMENTAL

General methods and materials. ^{1}H NMR spectra were recorded at 60 MHz with a Perkin-Elmer R-12 spectrometer or at 100 MHz with a JEOL JNM-FX 100 spectrometer. Chemical shift values are expressed as δ (parts per million) relative to TMS as an internal standard. IR spectra were obtained on a Perkin–Elmer Infracord 157 G spectrophotometer, using liquid films between NaCl disks. Mass spectra were run on an LKB 9000 mass spectrometer generally at 70 eV, using a direct inlet system. M.ps were taken in open capillary tubes and are uncorrected.

Elemental analyses were performed by the Microanalytical Laboratory, Royal Agricultural College, Uppsala. The progress of all reactions and the purity of all compounds were determined by tlc, using Merck silica gel 60 F_{254} (0.2 mm) sheets. Preparative column chromatography was performed on Merck silica gel 60 (230–400 mesh), using light petroleum–ethyl acetate (9:1) as the eluent, unless otherwise indicated. THF was distilled from LAH. n-BuLi in hexane was purchased from Merck and the concentration was determined by titrating diphenylacetic acid with BuLi.[28] All organocopper reactions were performed in an atmosphere of argon or nitrogen.

Preparation of starting materials. The following compounds were prepared as described in the given references: Cu(I)Br·Me_2S,[19] N-methyldiphenylmethanimine 1,[20] 4-methylbenzenesulfonate ester of 3-butyn-2-ol **4a**,[29] mesylate of 1-hexyn-3-ol **4c**,[30] mesylate of 3-decyn-2-ol **4h**,[31] acetylenic alcohols[25] (except for 12).

4-Phenyl-2-butyn-1-ol 12. A Grignard reagent, derived from Mg (3.2 g, 0.13 mol) and benzyl chloride (15.0 ml, 0.13 mol) in ether (100 ml) and THF (10 ml), was cooled to −30°. To the well-stirred soln were added THF (100 ml) and Me_2S (5 ml). CuBr (9.4 g, 0.065 mol) was then added over a 5-min period. The yellow-black soln was cooled to −45° and stirred for 15 min. A soln of Br–C≡C–CH_2OTHP (14.3 g, 0.065 mol) in THF (20 ml), prepared according to a general procedure,[25] was then added dropwise over a 10-min period. After 2.5 hr, when the temp was −10°, the mixture was quenched with satd NH_4Claq (150 ml). Extraction with ether (3 × 150 ml) gave 19.5 g of a crude product, which was treated with *p*-toluenesulfonic acid (0.5 g) in MeOH for a period of 12 hr. After treatment with an excess of K_2CO_3, the solvent was removed under vacuum. The residue was chromatographed on a silica gel 60 column, using ether:light petroleum (1:1) as the eluent, to give 5.5 g (58%) of 12. NMR ($CDCl_3$) 7.28 (s, 5H), 4.21 (t, 2H), 3.54 (t, 2H), 3.12 (broad s, 1H).

General procedure for preparation of mesylates of acetylenic alcohols

To a stirred soln of an acetylenic alcohol (0.050 mol), Et_3N (6.1 g, 0.060 mol) and CH_2Cl_2 (50 ml) at −20° was added 6.3 g (0.055 mol) of methane sulfonylchloride over a period of 10 min. The soln was stirred for another 30 min. After addition of CH_2Cl_2 (50 ml), the organic phase was washed with water (4 × 15 ml), dried over $MgSO_4$ and concentrated *in vacuo*. The mesylates were purified on silica gel 60, with ether:light petroleum (1:1) as the eluent, or used without further pruification. They were characterized by NMR.

Mesylate of 3-pentyn-2-ol **4b**, yield: 77%. NMR ($CDCl_3$) 5.04–5.43 (m, 1H), 3.09 (s, 3H), 1.89 (d, $^5J \sim 2.5$ Hz, 3H), 1.59 (d, $^3J \sim 7$ Hz, 3H).

Mesylate of 2-heptyn-1-ol **4d**, yield: 85%. NMR ($CDCl_3$) 4.78 (t, $^5J \sim 2.5$ Hz, 2H), 3.06 (S, 3H), 2.04–2.43 (m, 2H), 1.26–1.65 (m, 4H), 0.91 (t, 3H).

Mesylate of 4-phenyl-2-butyn-1-ol **4e**, purified on silica gel, yield: 80%. NMR ($CDCl_3$) 7.32 (s, 5H), 4.74 (t, $^5J \sim 2.5$ Hz, 2H), 3.53 (t, $^5J \sim 2.5$ Hz, 2H) 2.88 (s, 3H).

Mesylate of 3-phenyl-2-propyn-1-ol **4f**, purified on silica gel, yield: 90%. NMR ($CDCl_3$) 7.22 (s, 5H), 4.88 (s, 2H), 2.96 (s, 3H).

Mesylate of 2-butyn-1-ol **4g**, purified on silica gel, yield: 87%. NMR ($CDCl_3$) 4.78 (q, $^5J \sim 2.5$ Hz, 2H), 3.09 (s, 3H), 1.88 (t, $^5J \sim 2.5$ Hz, 3H).

General procedure for preparation of allenic imines

A stirred soln of n-BuLi in hexane (5.25 mmol) and THF (25 ml) under argon was cooled to −60° and a soln of 1 (0.98 g, 5.0 mmol) in THF (5 ml) was added with a syringe over a 10-min

period. The dark red soln was stirred for 20–30 min at −60°. CuBr·Me_2S (1.08 g, 5.25 mmol) was added over a 2-min period and the mixture was stirred for 5 min at −60°. A soln of **4a–h** (5.25 mmol) in THF (2 ml) was then added with a syringe over a 5-min period. The mixture was stirred at about −50° for 45 min. Light petroleum (50 ml) was added and the mixture was suction-filtered through celite and the cake was washed with light petroleum (25 ml). The organic phase was carefully washed with sat. NH_4Claq and dried over Na_2SO_4 and K_2CO_3. The solvent was removed under vacuum. Flash chromatography on a silica gel 60 column gave **5a–h** (contaminated by 5–15% benzophenone). The allenic imines were characterized by NMR and IR.

N - 2,3 - *Pentadienyldiphenylmethanimine* **5a**, yield: 32%. IR (film) 1960 cm^{-1}. NMR ($CDCl_3$) 6.95–7.65 (m, 10H), 4.85–5.45 (m, 2H), 3.96 (dd, $^3J \sim 6$ Hz, $^5J \sim 3$ Hz, 2H), 1.60 (dd, $^3J \sim 6.5$ Hz, $^5J \sim 3$ Hz, 3H).

N - (2 - *Methyl* - 2,3 - *pentadienyl)diphenylmethanimine* **5b**, yield: 39%. IR (film) 1960 cm^{-1}. NMR ($CDCl_3$) 6.96–7.76 (m, 10H), 4.80-5.26 (m, 1H), 3.91 (d, $^5J \sim 3$ Hz, 2H), 1.77 (d, $^5J \sim 3$ Hz, 3H), 1.57 (d $^3J \sim 7$ Hz, 3H).

N - 2,3 - *Heptadienyldiphenylmethanimine* **5c**, yield: 49%, IR (film) 1960 cm^{-1}. NMR ($CDCl_3$) 7.00–7.70 (m, 10H), 4.93–5.50 (m, 2H), 3.95 (dd $^3J \sim 6$ Hz, $^5J \sim 3$ Hz, 2H), 1.70–2.10 (m, 2H), 1.10–1.60 (m, 2H), 0.86 (t, 3H).

N - (2 - *Butyl* - 2,3 - *butadienyl)diphenylmethanimine* **5d**, yield: 31%. IR (film) 1950 cm^{-1}. NMR ($CDCl_3$) 6.96–7.68 (m, 10H), 4.50–4.78 (m, 2H), 3.92 (t, 2H), 1.78–2.28 (m, 2H), 1.16–1.58 (m, 4H), 0.87 (t, 3H).

N - (2 - *Benzyl* - 2,3 - *butadienyl)diphenylmethanimine* **5e**, yield: 33%. IR (film) 1955 cm^{-1}. NMR ($CDCl_3$) 6.90–7.85 (m, 15H), 4.52–4.76 (m, 2H), 3.88 (t, 2H), 3.49 (t, 3H).

N - (2 - *Phenyl* - 2,3 - *butadienyl)diphenylmethanimine* **5f**, yield: 14%. NMR ($CDCl_3$) 7.08–7.80 (m, 15H), 5.07 (t, $^5J \sim 3$ Hz, 2H), 4.39 (t, $^5J \sim 3$ Hz, 2H).

N - (2 - *Methyl* - 2,3 - *butadienyl)diphenylmethanimine* **5g**, yield: 40%. IR (film) 1960 cm^{-1}. NMR ($CDCl_3$) 7.02–7.78 (m, 10H), 4.50–4.83 (m, 2H), 3.92 (t, 2H), 1.68 (t, 3H).

N - (2 - *Hexyl* - 2,3 - *pentadienyl)diphenylmethanimine* **5h**, yield: 54%. IR (film) 1960 cm^{-1}. NMR ($CDCl_3$) 7.02–7.74 (m, 10H), 4.82–5.28 (m, 1H), 3.94 (d, $^5J \sim 3$ Hz, 2H), 1.85–2.38 (m, 1.63 (d, $^3J \sim 7$ Hz, 3H), 1.04–1.60 (m, 8H), 0.88 (t, 3H).

General procedure for preparation of allenic amines from allenic imines

A soln of an allenic imine (**5a–5h**, 1.0 eq.), oxalic acid (1.1–1.5 eq.), ether (30 ml) and 95% EtOH (5 ml) was stirred at room temp. for 2–5 hr. The allenic amine oxalates **10a–h** were filtered off. The oxalates were recrystallized from EtOH–ether and characterized by NMR and mass spectroscopy (recorded as free amines).

2,3-*Pentadienylaminium hydrogen oxalate* **10a**, m.p. 126–127°. NMR (D_2O) 5.18–5.60 (m, 2H), 3.52 (t, 2H), 1.66 (dd, $^3J = 7.3$ Hz, $^5J = 3.4$ Hz, 3H). MS: *m/e* (rel. int. %) 83 (5), 82 (62), 67 (11), 53 (11), 51 (10), 46 (57), 45 (100), 44 (21), 41 (15), 39 (24).

2-*Methyl*-2,3-*pentadienylaminium hydrogen oxalate* **10b**, m.p. 150–151°. NMR (D_2O) 5.30–5.53 (m, 1H), 3.43 (d, 2H), 1.70 (d, $^5J = 3.9$ Hz, 3H), 1.65 (d, $^3J = 7.3$ Hz, 3H). MS: *m/e* (rel. int. %) 97 (11), 96 (37), 82 (37), 81 (9), 80 (9), 67 (15), 53 (17), 46 (57), 45 (100), 44 (41), 42 (10), 41 (30), 40 (11), 39 (39).

2,3-*Heptadienylaminium hydrogen oxalate* **10c**, *m.p.* 145–146°. NMR (liberated amine, $CDCl_3$) 5.03–5.43 (m, 2H), 3.24 (t, 2H), 1.74–2.21 (m, 2H), 1.12–1.70 (m, 4H), 0.92 (t, 3H). MS: *m/e* (rel. int. %) 111 (0.2), 110 (2), 83 (8), 82 (100), 77 (10), 67 (13), 53 (12), 51 (9), 46 (54), 45 (92), 44 (24), 41 (24), 39 (29).

2 - *Butyl* - 2,3 - *butadienylaminium hydrogen oxalate* **10d**, m.p. 164–165°. NMR (liberated amine, $CDCl_3$) 4.64–4.90 (m, 2H), 3.13 (t, 2H), 1.70–2.16 (m, 2H), 1.13–1.60 (m, 6H), 1.90 (t, 3H). MS: *m/e* (rel. int. %) 125 (0.8), 124 (9), 110 (30), 100 (14), 83 (36), 82 (12), 69 (16), 67 (10), 55 (10), 53 (13), 52 (10), 51 (12), 46 (58), 45 (100), 44 (20), 41 (30), 39 (38).

2 - *Benzyl* - 2,3 - *butadienylaminium hydrogen oxalate* **10e**, m.p. 156–157°. NMR (liberated amine, $CDCl_3$) 7.15 (s, 5H), 4.68–4.80 (m, 2H), 3.23 (t, 2H), 3.01 (t, 2H), 1.43 (s, 2H). MS: *m/e* (rel. int. %) 159 (27), 158 (100), 144 (47), 142 (25), 128 (35), 115 (21), 91 (50), 65 (24), 51 (30), 46 (38), 45 (68), 44 (23), 39 (25).

2 - *Phenyl* - 2,3 - *butadienylaminium hydrogen oxalate* **10f**, m.p. 160° (dec.) This compound could not be recrystallized. NMR (liberated amine, $CDCl_3$) 7.28 (s, 5H), 5.05 (t, 3H), 3.62 (t, 2H), 1.45 (s, 2H). MS: *m/e* (rel. int. %) 145 (40), 144 (100), 143 (13), 130 (13), 128 (11), 117 (10), 116 (21), 115 (50), 89 (16), 63 (18), 46 (24), 45 (40), 39 (10).

2 - *Methyl* - 2,3 - *butadienylaminium hydrogen oxalate* **10g**, m.p. 169–171°. NMR (D_2O) 4.92–5.27 (m, 2H), 3.47 (t, $^5J = 3.4$ Hz, 2H), 1.73 (t, $^5J = 3.4$ Hz, 3H). MS: *m/e* (rel. int. %) 83 (47), 82 (14), 68 (11), 67 (11), 55 (16), 53 (15), 51 (20), 50 (17), 46 (25), 45 (45), 44 (100), 42 (20), 41 (22), 39 (35).

2 - *Hexyl* - 2,3 - *pentadienylaminium hydrogen oxalate* **10h**, m.p. 139–140°. NMR (liberated amine, $CDCl_3$) 4.88–5.40 (m, 1H), 3.00–3.20 (m, 2H), 1.66 (d, $^3J \sim 7$ Hz, 3H), 1.06–2.08 (m, 12H), 0.88 (t, 3H). MS: *m/e* (rel. int. %, only ≥ 20%) 167 (8), 138 (60), 124 (42), 110 (20), 98 (21), 97 (48), 96 (41), 84 (44), 82 (46), 81 (24), 80 (26), 79 (31), 77 (27), 71 (25), 68 (43), 67 (42), 66 (22), 65 (24), 55 (35), 53 (32), 46 (40), 45 (71), 44 (55), 43 (34), 41 (100), 39 (63).

General procedure for alkylation of allenic imines **5a, c, e, h** *with methyl fluorosulfonate*

N - *Methyl* - 2 - *hexyl* - 2,3 - *pentadienylamine* **11h**. To a stirred soln of **5h** (1.10 g, 3.3 mmol) and CH_2Cl_2 (40 ml) at 0° was added 0.40 ml (0.57 g, 5.0 mmol) of methyl fluorosulfonate. The mixture was stirred for 30 min at 0° and the solvent was removed under vacuum. The residue was treated with dil HCl (0.1 M, 40 ml) and the mixture was shaken vigorously for 2 min. The aqueous phase was washed with ether (2 × 30 ml), made basic with Na_2CO_3 and extracted with ether (3 × 40 ml). The organic phase was dried over Na_2SO_4–K_2CO_3 and the solvent was removed under vacuum. Purification on silica gel 60 (eluent: ether–MeOH 9:1) gave 0.45 g (75%) of **11h**. NMR ($CDCl_3$) 4.94–5.35 (m, 1H), 2.90-3.26 (m, 2H), 2.40 (s, 3H), 1.78–2.16 (m, 2H), 1.65 (d, $^3J \sim 7$ Hz, 3H), 1.00–1.60 (m, 9H), 0.88 (t, 3H). **11h** was converted to an oxalate which, after recrystallization from EtOH, had a m.p. of 176–177°.Found: C 61.9; H 9.2; N 5.0. Calc. for $C_{14}H_{25}NO_4$: C 62.0; H 9.3; N 5.2%).

N - *Methyl* - 2 - *benzyl* - 2,3 - *butadienylamine* **11e**. The procedure was similar to that for **11h**, yield: 85%. NMR ($CDCl_3$) 7.22 (s, 5H), 4.65–4.90 (m, 2H), 3.32 (t, 2H), 3.09 (t, 2H), 2.38 (s, 3H), 1.52 (s, 1H). Oxalate of **11e**: m.p. 174–176°. (Found: C 63.8; H 6.5; N 5.3. Calc. for $C_{14}H_{17}NO_4$: C 63.9; H 6.5; N 5.3%).

N - *Methyl* - 2,3 - *heptadienylamine* **11c**. This compound was prepared in the same way as **11h**. Instead of being purified on silica gel, **11c** was precipitated directly from the ether soln, yield 85%, m.p. (after recrystallization from EtOH–ether) 162–163°. NMR (liberated amine, $CDCl_3$) 4.97–5.25 (m, 2H), 3.05–3.32 (m, 2H), 2.42 (s, 3H), 1.96 (s, 1H), 1.15–2.20 (m, 4H), 0.91 (t, 3H). (Found: C 55.7; H 7.9; N 6.4. Calc. for $C_{10}H_{17}NO_4$: C 55.8; H 8.0; N 6.5%).

N-*Methyl*-2,3-*pentadienylamine* **11a**. The procedure was similar to that for **11h** except for the workup procedure. After removal of CH_2Cl_2, ether (40 ml) and water (2 ml) were added. The mixture was stirred for a 60-min period and an excess of K_2CO_3–Na_2SO_4 was added. Filtration and treatment of the etheral soln with oxalic acid gave **11a** in a yield of 85%, m.p. (recrystallized from EtOH) 145–146°. NMR (D_2O) 5.10–5.58 (m, 2H), 3.54 (dd, $^3J = 5.9$ Hz, $^5J = 2.9$ Hz, 2H), 2.70 (s, 3H), 1.66 (dd, $^3J = 7.3$, $^5J = 3.4$, 3H). (Found: C 51.5; H 7.0; N 7.4. Calc. for $C_8H_{13}NO_4$: C 51.3; H 7.0; N 7.5%).

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