Generation and Rearrangements of Ylides from Tertiary Amines and α-Diazo Ketones − Very High Catalytic Activity of [RuCl(η^5-C_5H_5)(PPh_3)$_2$]

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The reaction of *N,N*-dimethyl-2-propen-1-amine, *N,N*-dimethylbenzylamine and *N,N*-dimethyl-2-propyn-1-amine with the α-diazo ketones N_2CHCOR [R = Me (**2a**), Et (**2b**), *n*Pr (**2c**), *i*Pr (**2d**), $(CH_2)_{10}Me$ (**2e**), $(CH_2)_{14}Me$ (**2f**) or Ph (**2g**)] in a 1:1 molar ratio, catalysed by the complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**) (1% mol), have been investigated. Noticeably, the corresponding α-amino ketones **3a**–**g**, **4a**–**g** and **5a**–**g** are readily and quantitatively formed by rearrangement of transient nitrogen ylides. Compounds **3**–**5**, most of which have not yet been reported, have been isolated and fully characterised by IR, ^1H and ^{13}C NMR spectroscopy and GC-MS. It has been proved that complex **1** is an excellent and specific catalyst for the generation of nitrogen ylides from diazo carbonyls.

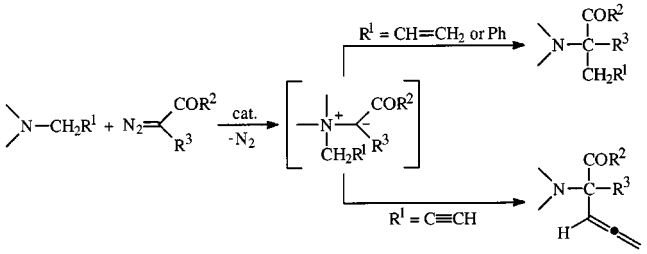
Introduction

The formation of ylides and their transformations have received considerable attention in the last two decades, owing to their great versatility in the synthesis of natural products and other complex molecules.[1] Of particular interest to us, the transient ammonium ylides generated from reaction between tertiary amines and diazo carbonyl compounds generally undergo rearrangement processes to afford *N,N*-dialkylamino esters or ketones.[1]

Until now, the metal complexes [$Rh_2(CH_3CO_2)_4$],[2−4] [$Rh_6(CO)_{16}$],[2] and [Cu(acac)$_2$][5] (acac = acetylacetonate), have been used in the nitrogen ylide formation process, decomposing the diazo compound catalytically, with resulting dinitrogen extrusion and formation of a reactive electrophilic metal-carbene. This species is then readily attacked by the nitrogen atom of the amine, affording a metal-coordinated ylide. The subsequent dissociation of the ylide, through cleavage of the metal−carbon bond, regenerates the catalyst. Copper powder has also been used as a catalyst in some studies,[4,6] owing to its low cost.

We have recently discovered that the commercially available, half-sandwich complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**) displays catalytic activity in several processes involving diazo carbonyl compounds. Thus, **1** induces insertion of α-diazo carbonyl compounds into the N−H bond of amines[7] and the S−H bond of thiols.[7] Furthermore, **1** has also been conveniently employed in the cyclopropanation of styrenes with ethyl diazoacetate (EDA),[8] and is also the best catalyst to date for stereoselective carbene-carbene coupling starting from diazo carbonyl compounds.[9]

As part of an ongoing program directed towards investigation of the catalytic potential of half-sandwich cyclopentadienyl ruthenium complexes, we tested complex **1** in the generation of ammonium ylides from tertiary amines and α-diazo ketones. In this paper we report on studies of the reactions between the α-diazo ketones N_2CHCOR [R = Me, Et, *n*Pr, *i*Pr, $(CH_2)_{10}Me$, $(CH_2)_{14}Me$ or Ph] and *N,N*-dimethyl-2-propen-1-amine (*N*-allyldimethylamine, ADMA), *N,N*-dimethylbenzylamine (DMBA) and *N,N*-dimethyl-2-propyn-1-amine (*N,N*-dimethylpropargylamine, DMPA). Such amines have already been shown to be suitable precursors for generating transient ammonium ylides,[2−4,6] which readily rearrange by a [1,2] Stevens shift or [2,3] sigmatropic rearrangement (Scheme 1). This study establishes that complex **1** represents a useful alternative to rhodium(II) acetate or copper-based catalysts for a carbenoid-based approach to ylide generation, with significant potential for applications in organic synthesis.



Scheme 1

Results and Discussion

To establish the catalytic efficacy of complex **1** in the generation of nitrogen ylides, the α-diazo ketones N_2CHCOR [R = Me (**2a**), Et (**2b**), *n*Pr (**2c**), *i*Pr (**2d**), $(CH_2)_{10}Me$ (**2e**), $(CH_2)_{14}Me$ (**2f**) or Ph (**2g**)] were tested by treatment with ADMA, DMBA and DMPA in a chloroform solution containing a catalytic amount of **1**. The reactions were performed at 60 °C, because in previous studies we had found that at this temperature complex **1** generates the 16-electron

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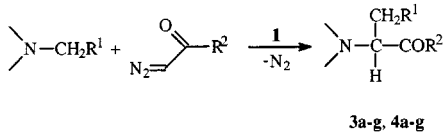
species [RuCl(η^5-C_5H_5)(PPh_3)], which, in the presence of the diazo carbonyl compound, affords a very reactive carbene intermediate.[10,11]

The reaction mixtures were analysed by ^1H and ^{13}C NMR spectroscopy and by GC-MS techniques. The samples were prepared by adding a $CDCl_3$ solution of the diazo compound to a $CDCl_3$ solution containing a stoichiometric amount of amine and 1 mol% of **1** at 60 °C. The ^1H and ^{13}C NMR spectra of all samples unequivocally indicated quantitative conversion of reactants into products **3a−g**, **4a−g** and **5a−g** (from ADMA, DMBA and DMPA, respectively). All these compounds were prepared and isolated in very high yield (>90%). Their ^1H NMR spectra are listed in Tables 1−3 for clarity.

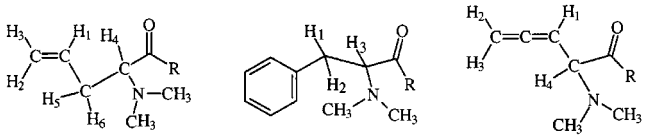
It is noteworthy that reaction of both ADMA and DMPA occurs without observable cycloaddition to the carbon−carbon double or triple bond. The only side-process observed is benzyl dimerisation in the case of DMBA — traces of 1,2-diphenylethane have been detected by GCMS in a few samples. Such a finding provides further evidence that the [1,2] Stevens rearrangement proceeds via radical intermediates.[12]

The formation of products **3a−g** and **4a−g** is shown in Scheme 2. The most striking feature of such compounds is the presence of a chiral carbon atom (C*) in their skeletons. Because of this, the hydrogens of the CH_2 group bound to the C* atom are diastereotopic. Consequently, protons H_5 and H_6 in compounds **3** (Figure 1) are magnetically nonequivalent, and rather strongly coupled with each other (J_{56} = ca. −14 Hz, Table 1). Analogously, in the ^1H NMR spectra of compounds **4**, a typical ABC spectral pattern (J_{12} = ca. −13 Hz, Table 2) is found for the CH_2C^*H framework (Figure 1).



R^1 = CH=CH_2 **3** or Ph **4**; R^2 = Me **a**, Et **b**, *n* Pr **c**, *i* Pr **d**, $(CH_2)_{10}$Me **e**, $(CH_2)_{14}$Me **f** or Ph **g**

Scheme 2



3 **4** **5**

Figure 1

Table 1. ^1H NMR spectroscopic data of compounds **3a−g**

Compound[a][b]	δH_1	δH_2	δH_3	δH_4	δH_5	δH_6	$J_{1,2}$ Hz	$J_{1,3}$ Hz	$J_{1,5}$ Hz	$J_{1,6}$ Hz	$J_{2,3}$ Hz	$J_{2,5}$ Hz	$J_{2,6}$ Hz	$J_{3,5}$ Hz	$J_{3,6}$ Hz	$J_{4,5}$ Hz	$J_{4,6}$ Hz	$J_{5,6}$ Hz
3a	5.73	5.07	5.03	3.01	2.39	2.35	17.0	10.1	7.1	7.0	1.7	−1.2	−1.3	−1.4	−1.4	8.9	5.1	−14.1
3b	5.72	5.06	5.01	3.09	2.43	2.30	17.1	10.1	7.0	7.0	1.9	−0.9	−1.2	−1.4	−1.4	8.9	5.0	−14.1
3c	5.72	5.06	5.01	3.07	2.50	2.33	17.1	10.2	7.2	6.9	1.7	−1.1	−1.0	−1.5	−1.6	8.9	5.1	−14.2
3d	5.72	5.07	5.02	3.32	2.46	2.27	17.1	10.1	7.0	7.1	1.6	−0.9	−1.4	−1.0	−1.4	8.9	4.7	−13.7
3e	5.72	5.06	5.01	3.07	2.42	2.31	17.1	10.2	7.2	7.0	1.8	−1.0	−1.0	−1.4	−1.5	9.0	4.8	−13.8
3f	5.72	5.06	5.01	3.07	2.41	2.34	17.1	10.2	7.2	7.2	1.7	−1.0	−1.1	−1.6	−1.7	9.4	4.2	−14.4
3g	5.76	5.06	4.99	4.10	2.65	2.42	17.1	10.2	7.0	7.0	2.0	−1.7	−1.7	−1.0	−1.0	9.0	4.8	−14.0

[a] In $CDCl_3$ solution; the numbering of the nuclei is given in Figure 1; J_{14}, J_{24}, and J_{34} = 0.0 Hz. − [b] Additional δ values (multiplicity given as: s = singlet, d = doublet, t = triplet, q = quadruplet, st = septuplet, m = multiplet, tq = triplet of quadruplets): **3a**, 2.17 (s, CH_3) 2.29 (s, NCH_3); **3b**, 1.01 (t, CH_3), 2.27 (s, NCH_3), 2.48 (q, CH_2), 2.52 (q, CH_2); **3c**, 0.91 (t, CH_3), 1.61 (tq, CH_2), 2.29 (s, NCH_3), 2.47 (t, CH_2), 2.49 (t, CH_2); **3d**, 1.03 (d, CH_3), 1.07 (d, CH_3), 2.30 (s, NCH_3), 2.88 (st, CH); **3e**, 0.88 (t, CH_3), 1.2−1.7 (m, CH_2), 2.29 (s, NCH_3), 2.47 (t, CH_2), 2.49 (t, CH_2); **3f**, 0.88 (t, CH_3), 1.2−1.7 (m, CH_2), 2.28 (s, NCH_3), 2.47 (t, CH_2), 2.49 (t, CH_2); **3g**, 2.35 (s, NCH_3), 7.1−8.1 (m, C_6H_5).

Table 2. ^1H NMR spectroscopic data of compounds **4a−g**

Compound[a][b]	δH_1	δH_2	δH_3	J_{12}/Hz	J_{13}/Hz	J_{23}/Hz	NCH_3	Ph
4a	2.83	2.97	3.34	−13.3	4.1	9.5	2.34	7.1−7.4
4b	2.83	3.00	3.38	−13.1	4.1	9.7	2.35	7.1−7.4
4c	2.81	3.00	3.36	−13.0	3.9	9.8	2.35	7.1−7.4
4d	2.77	3.02	3.53	−12.8	3.6	10.0	2.36	7.1−7.4
4e	2.80	2.99	3.36	−13.0	3.9	9.7	2.34	7.1−7.4
4f	2.80	3.00	3.37	−13.1	4.0	9.8	2.34	7.1−7.4
4g	2.87	3.21	4.26	−13.1	3.8	9.7	2.33	7.1−7.9

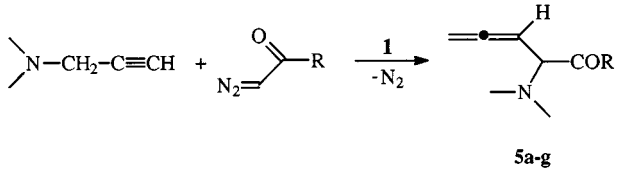
[a] In $CDCl_3$ solution; the numbering of the nuclei is given in Figure 1. − [b] Additional δ values (multiplicity given as: s = singlet, d = doublet, t = triplet, q = quadruplet, st = septuplet, m = multiplet, tq = triplet of quadruplets): **4a**, 2.05 (s, CH_3); **4b**, 0.89 (t, CH_3), 2.47 (q, CH_2), 2.56 (q, CH_2); **4c**, 0.77 (t, CH_3), 1.43 (tq, CH_2), 2.42 (t, CH_2), 2.50 (t, CH_2) **4d**, 0.66 (d, CH_3), 0.98 (d, CH_3), 2.64 (st, CH); **4e**, 0.88 (t, CH_3), 1.1−1.6 (m, CH_2), 2.42 (m, CH_2); **4f**, 0.89 (t, CH_3), 1.1−1.6 (m, CH_2), 2.43 (m, CH_2).

Table 3. ^{1}H NMR spectroscopic data of compounds **5a−g**

Compound[a][b]	δH_1	δH_2	δH_3	δH_4	J_{12}/Hz	J_{13}/Hz	J_{14}/Hz	J_{23}/Hz	J_{24}/Hz	J_{34}/Hz
5a	5.17	4.83	4.81	3.49	6.7	6.8	9.2	−11.3	1.0	1.2
5b	5.18	4.81	4.80	3.53	6.6	6.6	9.3	−11.3	1.0	1.1
5c	5.17	4.81	4.80	3.51	6.5	6.7	9.3	−11.4	1.0	1.1
5d	5.17	4.81	4.80	3.71	6.6	6.7	9.3	−11.1	0.9	1.2
5e	5.17	4.80	4.79	3.51	6.7	6.6	9.3	−11.2	0.9	1.2
5f	5.18	4.80	4.79	3.51	6.4	6.8	9.3	−11.4	0.9	1.2
5g	5.43	4.79	4.75	4.47	6.6	6.6	9.3	−11.2	1.0	1.0

[a] In $CDCl_3$ solution; the numbering of the nuclei is given in Figure 1. − [b] Additional δ values (multiplicity given as: s = singlet, d = doublet, t = triplet, q = quadruplet, s*t* = septet, m = multiplet, dt = doublet of triplets, tq = triplet of quadruplets): **5a**, 2.29 (s, NCH_3), 2.17 (s, CH_3); **5b**, 2.21 (s, NCH_3), 0.88 (t, CH_3), 2.35 (q, CH_2); **5c**, 2.29 (s, NCH_3), 0.91 (t, CH_3), 2.49 (dt, CH_2), 1.61 (tq, CH_2); **5d**, 2.30 (s, NCH_3), 1.03 (d, CH_3), 1.07 (d, CH_3), 2.88 (*st*, CH); **5e**, 2.22 (s, NCH_3), 0.81 (t, CH_3), 2.42 (dt, CH_2), 1.1−1.6 (m, CH_2); **5f**, 2.28 (s, NCH_3), 0.88 (t, CH_3), 2.48 (dt, CH_2, 1.2−1.7 (m, CH_2); **5g**, 2.37 (s, NCH_3), 7.4−8.1 (m, C_6H_5).

Scheme 3 illustrates the reaction of DMPA, leading to products **5a−g**. As previously established,[3] the ylides generated from the reaction between DMPA and α-diazo carbonyl compounds undergo a [2,3] sigmatropic rearrangement, with formation of allenes **5a−g**. In such compounds, the presence of the chiral carbon atom makes the $=CH_2$ protons (H_2 and H_3 in Figure 1) diastereotopic. Protons H_2 and H_3 exhibit very similar chemical shifts, and a coupling constant of ca. −11 Hz (Table 3). We found that all allenes **5a−g** underwent a slow, thermally induced isomerisation process. Therefore, to avoid formation of mixtures of isomers, the length of time for addition of α-diazo ketones to DMPA was strictly controlled. A reaction time of about 15 min was accordingly found sufficient to achieve complete conversion into allenes **5a−g** without formation of appreciable amounts of by-products.

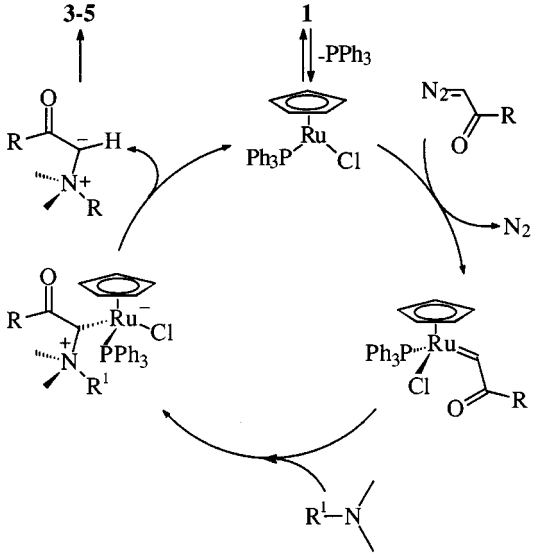


R = Me **a**, Et **b**, *n* Pr **c**, *i* Pr **d**, $(CH_2)_{10}$Me **e**, $(CH_2)_{14}$Me **f** or Ph **g**

Scheme 3

The findings reported in this paper are in line with those previously obtained for reactions of diazo compounds promoted by **1**,[7−11] and can be rationalised in terms of the catalytic cycle depicted in Scheme 4, accounting for the formation of the α-amino ketones **3−5**.

It should be noted that, unlike the α-diazo ketones, EDA did not react with any of the amines used in this work. The ^{1}H NMR spectra indicated that a quantitative conversion into diethyl maleate (99%) and diethyl fumarate always occurred,[9] the amine present in solution remaining entirely unchanged. These results confirm the very different behaviour, in reactions catalysed by complex **1,** of EDA with respect to α-diazo ketones. Indeed, we have found that α-diazo ketones give almost quantitative carbene insertion into



Scheme 4

the N−H bond of amines, whereas EDA affords complex mixtures containing very low amounts of insertion product.[7]

Conclusion

We have demonstrated that, in the presence of **1**, suitable tertiary amines and α-diazo ketones can be converted readily and quantitatively into transient ammonium ylides, which rapidly rearrange to give α-amino ketones. It should be stressed that complex **1** is a commercially available chemical and is used in low, catalytic amount (1 mol%). In comparison with the other catalysts[2−6] used to promote the formation of nitrogen ylides, complex **1** is very efficient and no excess of amine is necessary; nor are long reaction times. In contrast, previous studies had found that both high amine/diazo compound ratios (up to 10) and very slow addition of the diazo compound to the amine were needed to reduce the formation of by-products.[2−4,6]

Our results suggest some points concerning the reactivity of the reaction intermediates in metal-catalysed transformations of diazo compounds. The metal carbene arising from

the decomposition of α-diazo ketones reacts selectively with tertiary amines, with quantitative formation of ylides and without formation of enediones by the competing carbene-carbene coupling reaction. In contrast, the latter is the only reaction observed in the case of EDA, which is converted overwhelmingly into diethyl maleate. Furthermore, in the case of ADMA and DMPA, no competition between ylide generation and cycloaddition reactions has been observed.

Experimental Section

Materials and Methods: All solvents were purified using standard procedures and stored over molecular sieves under an argon atmosphere. Ethyl diazoacetate, DMBA, DMPA and the chemicals used for the preparation of the diazo ketones were purchased from Aldrich Chemical Co, ADMA was purchased from Fluka (Aldrich). The diazo ketones **2a−g** were prepared and purified as previously described.[9] Catalyst [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**) was synthesised according to a literature procedure.[13]

^{1}H (200.13 MHz) and ^{13}C{^{1}H} (50.32 MHz) NMR spectra were recorded on a Bruker AC 200 F QNP spectrometer; chemical shifts for both nuclei are referenced to $SiMe_4$. NMR spectral simulations were performed on an Aspect 2000 computer, using the program P.A.N.I.C. (Bruker Spectrospin AG). Infrared (IR) spectra were recorded on a Nicolet Magna 550 FT spectrophotometer. The GCMS analyses were performed with a Fisons TRIO 2000 gas chromatograph-mass spectrometer working in the positive ion 70 eV electron impact mode. Injector temperature was kept at 250 °C and the column (Supelco® SE-54, 30 m long, 0.25 mm i.d., coated with a 0.5 μm phenyl methyl silicone rubber film) temperature was programmed from 50 °C to 310 °C with a gradient of 10 °C/min.

Preparation of the Samples for NMR and GCMS Analysis: At 60 °C, a 5 mm diameter NMR tube was charged with a $CDCl_3$ solution (0.2 mL) of amine (0.2 mmol) and complex **1** (2 mg). A $CDCl_3$ solution (0.2 mL) of the diazo carbonyl compound (0.2 mmol) was then added over 15 min. After evolution of nitrogen ended, the tube was cooled and transferred into the probe of the NMR spectrometer. The samples used for GCMS analysis were prepared from these solutions by dilution with diethyl ether.

General Procedure for the Synthesis of Compounds 3−5:[14] Under an argon atmosphere, a chloroform solution (15 mL) containing 2 mmol of the appropriate diazo ketone **2a−g** was added dropwise over 15 min to a chloroform solution (15 mL) containing 2 mmol of amine (ADMA, 170 mg; DMBA, 270 mg; DMPA, 166 mg) and **1** (15 mg; ca. 20 μmol) at 60 °C. After removal of solvent, the residue was taken up in ethyl ether, the mixture was filtered and the solid material discarded. Elimination of the solvent in vacuo gave pure products as a yellow solid (**4g**) or oil. For clarity, the ^{1}H NMR spectroscopic data of compounds **3−5** have been collected in Table 1, Table 2, and Table 3.

3-Dimethylamino-5-hexen-2-one (3a): Yield: 260 mg (92%). − IR (neat): $\tilde{\nu}$ = 1637 (C=C), 1712 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 27.98 (CH_3), 30.60 (CH_2), 42.18 (NCH_3), 74.28 (CH), 116.93 (=CH_2), 134.62 (=CH), 209.20 (CO). − MS; *m/z* (%) = 141 (0.4) [M$^+$], 100 (10), 98 (100), 68 (9), 55 (19), 44 (17), 42 (14).

4-Dimethylamino-6-hepten-3-one (3b): Yield: 279 mg (90%). − IR (neat): $\tilde{\nu}$ = 1639 (C=C), 1715 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 7.25 (CH_3), 30.25 (CH_2), 34.10 (CH_2), 41.96 (NCH_3), 72.98 (CH), 116.74 (=CH_2), 133.47 (=CH), 211.33 (CO). − MS; *m/z* (%): 155 (1) [M$^+$], 114 (23), 99 (34), 98 (100), 83 (16), 82 (20), 68 (15), 55 (37), 44 (39), 42 (36).

5-Dimethylamino-7-octen-4-one (3c): Yield: 315 mg (93%). − IR (neat): $\tilde{\nu}$ = 1636 (C=C), 1713 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 16.98 (CH_3), 17.15 (CH_2), 30.22 (CH_2), 42.16 (NCH_3), 43.05 (CH_2), 73.28 (CH), 117.79 (=CH_2), 134.86 (=CH), 210.99 (CO). − MS; *m/z* (%): 169 (0.2) [M$^+$], 128 (5), 99 (39), 98 (100), 55 (8), 44 (8) 42 (6).

4-Dimethylamino-2-methyl-6-hepten-3-one (3d): Yield: 311 mg (92%). − IR (neat): $\tilde{\nu}$ = 1638 (C=C), 1712 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 17.75 (CH_3), 18.37 (CH_3), 28.71 (CH_2), 38.60 (CH), 41.73 (NCH_3), 70.75 (CH), 116.83 (=CH_2), 135.15 (=CH), 213.52 (CO). − MS; *m/z:* 169 (0.4) [M$^+$], 128 (13), 99 (81), 98 (100), 55 (20), 44 (22) 42 (21).

4-Dimethylamino-1-hexadecen-5-one (3e): Yield: 524 mg (93%). − IR (neat): $\tilde{\nu}$ = 1639 (C=C), 1714 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 13.97 (CH_3), 22.55 (CH_2), 23.37 (CH_2), 29.13 (CH_2), 29.20 (CH_2), 29.33 (CH_2), 29.49 (CH_2), 30.15 (CH_2), 31.79 (CH_2), 41.08 (CH_2), 42.12 (NCH_3), 73.26 (CH), 116.90 (=CH_2), 134.91 (=CH), 210.99 (CO). − MS; *m/z* (%): 281 (1) [M$^+$], 240 (15), 99 (64), 98 (100), 55 (20), 44 (18), 43 (17) 42 (18) 41 (18).

4-Dimethylamino-1-eicosen-5-one (3f): Yield: 634 mg (94%). − IR (neat): $\tilde{\nu}$ = 1636 (C=C), 1717 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 14.03 (CH_3), 22.60 (CH_2), 23.41 (CH_2), 29.29 (CH_2), 29.37 (CH_2), 29.42 (CH_2), 29.59 (CH_2), 31.84 (CH_2), 41.14 (CH_2), 42.17 (NCH_3), 73.31 (CH), 116.95 (=CH_2), 134.95 (=CH), 211.04 (CO). − MS; *m/z* (%): 337 (3) [M$^+$], 297 (22), 99 (56), 98 (100), 55 (24), 44 (25), 43 (43) 42 (27), 41 (29).

2-Dimethylamino-1-phenyl-4-penten-1-one (3g): Yield: 370 mg (91%). − IR (neat): $\tilde{\nu}$ = 1636 (C=C), 1682 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 29.63 (CH_2), 41.70 (NCH_3), 67.69 (CH), 117.17 (=CH_2), 128.49 (C_{Ph}), 132.90 (C_{Ph}), 135.03 (=CH), 137.15 (C_{Ph}), 199.01 (CO). − MS; *m/z* (%): 203 (0.2) [M$^+$], 162 (19), 105 (24), 99 (32), 98 (100), 77 (30), 55 (26), 44 (34), 42 (39).

3-Dimethylamino-4-phenylbutan-2-one (4a): Yield: 344 mg (90%). − IR (neat): $\tilde{\nu}$ = 1705 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 29.23 (CH_3), 30.97 (CH_2), 42.00 (NCH_3), 75.43 (CH), 126.07 (C_{Ph}), 128.12 (C_{Ph}), 129. 05 (C_{Ph}), 138.66 (C_{Ph}), 208.79 (CO). − MS; *m/z* (%): 191 (0.1) [M$^+$], 149 (18), 148 (100), 133 (32), 105 (8), 100 (9), 91 (7).

2-Dimethylamino-1-phenylpentan-3-one (4b): Yield: 374 mg (91%) − IR (neat): $\tilde{\nu}$ = 1707 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 7.35 (CH_3), 31.31 (CH_2), 35.68 (CH_2), 42.01 (NCH_3), 74.45 (CH), 126.04 (C_{Ph}), 128.34 (C_{Ph}), 129. 27 (C_{Ph}), 139.08 (C_{Ph}), 211.26 (CO). − MS; *m/z* (%): 205 (0.1) [M$^+$], 149 (24), 148 (100), 133 (24), 114 (8), 105 (6), 91 (6).

2-Dimethylamino-1-phenylhexan-3-one (4c): Yield: 404 mg (92%). − IR (neat): $\tilde{\nu}$ = 1707 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 13.68 (CH_3), 16.87 (CH_2), 30.96 (CH_2), 42.10 (NCH_3), 44.44 (CH_2), 74.62 (CH), 126.14 (C_{Ph}), 128.45 (C_{Ph}), 129. 34 (C_{Ph}), 139.30 (C_{Ph}), 210.64 (CO). − MS; *m/z* (%): 219 (0.2) [M$^+$], 149 (100), 148 (99), 134 (18), 133 (21), 105 (7), 91 (12).

4-Methyl-2-dimethylamino-1-phenylpentan-3-one (4d): Yield: 395 mg (90%). − IR (neat): $\tilde{\nu}$ = 1704 cm^{-1} (C=O). − ^{13}C{^{1}H} NMR ($CDCl_3$, 295 K): δ = 17.26 (CH_3), 17.75 (CH_3), 29.73 (CH_2),

39.27 (CH), 41.56 (NCH_3), 72.37 (CH), 125.77 (C_{Ph}), 128.09 (C_{Ph}), 129. 14 (C_{Ph}), 139.14 (C_{Ph}), 212.66 (CO). − MS; *m/z* (%): 219 (0.3) [M^+], 149 (85), 148 (100), 133 (57), 128 (22), 105 (19), 91 (23), 43 (23), 42 (33).

2-Dimethylamino-1-phenyltetradecan-3-one (4e): Yield: 609 mg (92%). − IR (neat): $\tilde{\nu}$ = 1706 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 13.94 (CH_3), 22.52 (CH_2), 23.23 (CH_2), 28.91 (CH_2), 29.20 (CH_2), 29.27 (CH_2), 30.69 (CH_2), 31.76 (CH_2), 41.84 (NCH_3), 42.25 (CH_2), 74.39 (CH), 125.87 (C_{Ph}), 128.08 (C_{Ph}), 129.11 (C_{Ph}), 139.08 (C_{Ph}), 210.37 (CO). − MS; *m/z* (%): 331 (0.4) [M^+], 240 (18), 149 (68), 148 (100), 133 (29), 91 (12), 43 (16), 42 (14).

2-Dimethylamino-1-phenyloctadecan-3-one (4f): Yield: 729 mg (94%). − IR (neat): $\tilde{\nu}$ = 1709 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 14.06 (CH_3), 22.65 (CH_2), 23.34 (CH_2), 29.07 (CH_2), 29.32 (CH_2), 29.39 (CH_2), 29.55 (CH_2), 29.66 (CH_2), 30.89 (CH_2), 31.88 (CH_2), 42.10 (NCH_3), 44.44 (CH_2), 74.62 (CH), 126.02 (C_{Ph}), 128.36 (C_{Ph}), 129. 24 (C_{Ph}), 139.22 (C_{Ph}), 210.63 (CO). − MS; *m/z* (%): 387 (0.3) [M^+], 174 (4), 149 (14), 148 (100), 133 (5), 91 (2), 43 (2).

2-Dimethylamino-1,3-diphenylpropan-1-one (4g): Yield: 481 mg (95%). − IR (nujol): $\tilde{\nu}$ = 1662 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 30.30 (CH_2), 41.52 (NCH_3), 69.38 (CH), 126.01 (C_{Ph}), 128.36 (C_{Ph}), 128.39 (C_{Ph}), 128.45 (C_{Ph}), 129.34 (C_{Ph}), 132.81 (C_{Ph}), 137. 26 (C_{Ph}), 139.18 (C_{Ph}), 198.57 (CO). − MS; *m/z* (%): 253 (0.2) [M^+], 149 (35), 148 (100), 133 (30), 105 (24), 91 (16), 77 (20), 42 (14). − $C_{17}H_{19}NO$ (253.34): calcd. C 80.60, H 7.56, N 5.53; found C 80.23, H 7.64, N 5.39.

3-Dimethylamino-4,5-hexadien-2-one (5a): Yield: 253 mg (91%). − IR (neat): $\tilde{\nu}$ = 1952 (C=C=C), 1714 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 26.75 (CH_3), 42.47 (NCH_3), 75.45 (CH), 75.69 (=CH_2), 84.63 (=CH), 207.14 (=C=), 209.86 (CO). − MS; *m/z* (%): 139 (6) [M^+], 100 (12), 96 (100), 94 (36), 81 (33), 80 (30), 68 (10), 42 (29).

4-Dimethylamino-5,6-heptadien-3-one (5b): Yield: 285 mg (93%). − IR (neat): $\tilde{\nu}$ = 1951 (C=C=C), 1717 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 7.51 (CH_3), 32.67 (CH_2), 42.32 (NCH_3), 74.62 (CH), 75.17 (=CH_2), 84.63 (=CH), 209.36 (=C=), 209.48 (CO). − MS; *m/z* (%): 153 (48) [M^+], 138 (46), 124 (33), 110 (15), 96 (100), 82 (21), 81 (89), 55 (24), 42 (14).

5-Dimethylamino-6,7-octadien-4-one (5c): Yield: 308 mg (92%). − IR (neat): $\tilde{\nu}$ = 1949 (C=C=C), 1712 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 13.59 (CH_3), 16.98 (CH_2), 41.47 (CH_2), 42.46 (NCH_3), 74.94 (CH), 75.27 (=CH_2), 84.66 (=CH), 208.81 (=C=), 209.65 (CO). − MS; *m/z* (%): 167 (38) [M^+], 152 (20), 138 (35), 124 (32), 96 (100), 81 (67), 55 (17).

4-Dimethylamino-2-methyl-5,6-heptadien-3-one (5d): Yield: 301 mg (90%). − IR (neat): $\tilde{\nu}$ = 1948 (C=C=C), 1714 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 18.38 (CH_3), 37.85 (CH), 42.38 (NCH_3), 72.88 (CH), 75.14 (=CH_2), 84.60 (=CH), 209.67 (=C=), 212.07 (CO). − MS; *m/z* (%): 167 (29) [M^+], 152 (42), 124 (23), 96 (100), 81 (58), 55 (13).

4-Dimethylamino-1,2-hexadecadien-5-one (5e): Yield: 530 mg (95%). − IR (neat): $\tilde{\nu}$ = 1947 (C=C=C), 1716 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 13.89 (CH_3), 22.47 (CH_2), 23.52 (CH_2), 29.05 (CH_2), 29.13 (CH_2), 29.22 (CH_2), 29.28 (CH_2), 31.70 (CH_2), 39.50 (CH_2), 42.39 (NCH_3), 74.87 (CH), 75.14 (=CH_2), 84.62 (=CH), 208.78 (=C=), 209.61 (CO). − MS; *m/z* (%): 279 (22) [M^+], 264 (26), 236 (31), 166 (21), 153 (50), 152 (48), 140 (91), 139 (100), 138 (42), 124 (76), 110 (26).

4-Dimethylamino-1,2-eicosadien-5-one (5f): Yield: 650 mg (97%). − IR (neat): $\tilde{\nu}$ = 1952 (C=C=C), 1713 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 13.93 (CH_3), 22.52 (CH_2), 23.55 (CH_2), 29.09 (CH_2), 29.20 (CH_2), 29.25 (CH_2), 29.32 (CH_2), 29.46 (CH_2), 29.50 (CH_2), 29.52 (CH_2), 31.76 (CH_2), 39.54 (CH_2), 42.43 (NCH_3), 74.91 (CH), 75.19 (=CH_2), 84.67 (=CH), 208.84 (=C=), 209.65 (CO). − MS; *m/z* (%): 335 (37) [M^+], 321 (25), 292 (27), 153 (28), 152 (33), 140 (31), 139 (57), 138 (31), 124 (100), 110 (20).

3-Dimethylamino-1-phenyl-3,4-pentadien-1-one (5g): Yield: 370 mg (92%). − IR (neat): $\tilde{\nu}$ = 1954 (C=C=C), 1678 cm^{-1} (C=O). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 295 K): δ = 42.10 (NCH_3), 70.46 (CH), 75.26 (=CH_2), 84.52 (=CH), 128.33 (C_{Ph}), 128.83 (C_{Ph}), 133.00 (C_{Ph}), 135.85 (C_{Ph}), 197.23 (=C=), 209.79 (CO). − MS; *m/z* (%): 201 (71) [M^+], 186 (28), 172 (26), 158 (48), 128 (21), 105 (24), 96 (100), 81 (69), 77 (27), 55 (18).

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