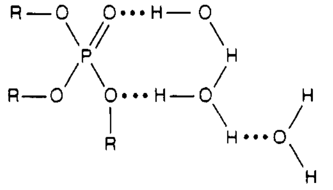
bisectors of the P–N–C planes (which correspond to the lone pair–N–P planes). These may be regarded as the angles of twist from maximal orbital overlap.

Multifunctional Acceptor Effects, a Caveat. The β values derived here are intended to be used as measures of the HBA basicities of the XYZP=O compounds acting as either solutes or solvents. There has been a complication, however, insofar as predictions of octanol/water partition coefficients or aqueous solubilities of $(RO)_3P{=}O$ and possibly $(RO)_2XP{=}O$ and $(RO)XYP{=}O$ compounds are concerned.

Using β values from Table I together with equations which we have reported for octanol/water partition coefficients[16] and aqueous solubilities[17] of organic nonelectrolytes has led to serious overpredictions of log K_{ow} and serious underpredictions of log S_w. We believe that this is because these compounds act as multifunctional hydrogen-bond acceptors in water, hydrogen bonding at both the P=O and R–O–P oxygens to either different or the same water clusters. In HBD solvents other than water,



such interactions at multiple HBA sites are very much less apt to occur. In water, however, *effective* $\sum\beta$ values rather than the β values reported here are required to predict solubility and partition properties of the trialkyl phosphates.

We have calculated from octanol/water partition constants[18] that $\sum\beta$ has values from 1.00 to 1.10 for methyl through *n*-butyl phosphates (compared to β = 0.77–0.82 in Table I). These values were confirmed by the finding that the $\sum\beta$ values for the trialkyl phosphates allowed the calculation of cyclohexane/water partition coefficients through the correlation equation for that bilayer system. This is strong confirmation, since the equation for cyclohexane/water partition has significantly larger m; $-s$, $-a$, and $-b$ coefficients in eq 2 than does that for octanol/water partition.

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(18) Unpublished results.

Mild and Regiospecific Reduction of Masked 1,3-Dicarbonyl Derivatives to Monocarbonyl Compounds and Primary and Secondary Amines

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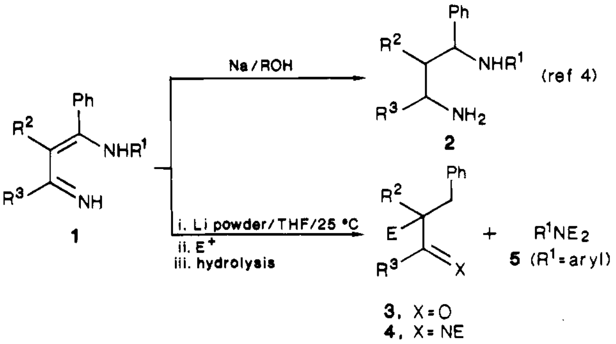
The regiospecific reduction of masked 1,3-dicarbonyl compounds to the corresponding saturated monocarbonyl **3** or iminic **4** compounds via 3-amino-2-alkenimines **1** is described. The formation of **3** or **4** can be explained in terms of a double reduction process from **1**. A simple method for the synthesis of primary and secondary amines **6** is also described.

We have been interested for some years in the readily available 3-amino-2-alkenimine systems **1**,[1,2] both as synthons in the preparation of a wide range of heterocycles[3] and in the preparation of β- and γ-difunctionalized compounds by reduction processes.[4–6] In particular, the reduction of **1** with sodium in *i*-PrOH as protic cosolvent led to a diastereoisomeric mixture of γ-diamines **2**[4] (Scheme I).

In connection with these studies, we now describe the behavior of systems **1**, direct precursors of the 1,3-dicarbonyl derivatives,[2] when treated with lithium metal in the absence of a proton source; this process allows the regiospecific reduction of **1** to saturated carbonyl or iminic compounds **3** and **4**.[7] In addition, a new method for the synthesis of amines of type **6** is also described.

Scheme I



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(7) Although the selective reduction of one of the carbonyl groups in 1,3-dioxo compounds has been widely studied in the preparation of β-hydroxy carbonyl compounds, especially from β-keto esters, only a few examples have been reported for the direct reduction of one of the >C=O groups to $=CH_2$ in 1,3-dicarbonyl compounds. See, for example: (a) Oishi, T.; Nakata, T. *Acc. Chem. Res.* **1984**, *17*, 338. (b) Coates, R. M.; Shaw, J. E. *J. Org. Chem.* **1970**, *35*, 2597 and 2601.

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Table I. Compounds 3 or 4 Obtained by Reaction of 1 with Lithium Metal

entry	compd	R^2	R^3	E	X	yield, %	mp or bp, °C
1	**3a**	CH_3	C_6H_5	H	O	80 (R^1 = C_6H_5)	97–100 (10^{-3} Torr)
2						83 (R^1 = p-$CH_3C_6H_4$)	
3	**3b**	CH_3	p-$CH_3C_6H_4$	H	O	80 (R^1 = C_6H_5)	92–96 (10^{-3} Torr)
4						90 (R^1 = p-$CH_3C_6H_4$)	
5	**3c**	CH_3	c-C_6H_{11}	H	O	85 (R^1 = C_6H_5)	82–86 (10^{-3} Torr)
6	**3d**	CH_3	CH_3	H	O	70 (R^1 = C_6H_5)	45–49 (10^{-3} Torr)
7	**3e**	H	C_6H_5	H	O	83 (R^1 = C_6H_5)	70–72
8						80 (R^1 = p-$CH_3C_6H_4$)	
9	**3f**	H	p-$CH_3C_6H_4$	H	O	78 (R^1 = C_6H_5)	62–64
10	**3g**	$C_6H_5CH_2$	p-$CH_3C_6H_4$	H	O	80 (R^1 = C_6H_5)	110–114 (10^{-3} Torr)
11	**3h**	$CH_2{=}CHCH_2$	C_6H_5	H	O	92 (R^1 = C_6H_5)	104–108 (10^{-3} Torr)
12	**3i**	CH_3	p-$CH_3C_6H_4$	CH_3	O	93[a] (R^1 = p-$CH_3C_6H_4$)	77–81 (10^{-3} Torr)
13	**3j**	CH_3	C_6H_5	CH_3	O	90[a] (R^1 = C_6H_5)	74–78 (10^{-3} Torr)
14	**3k**[d]	CH_3	C_6H_5	CH_2CH_3	O	85[c] (R^1 = p-$CH_3C_6H_4$)	oil[b]
15	**4a**[d]	CH_3	p-$CH_3C_6H_4$	CH_3	NCH_3	75 (R^1 = p-$CH_3C_6H_4$)	89–91
16	**4b**[d]	CH_3	C_6H_5	CH_3	NCH_3	81 (R^1 = C_6H_5)	oil[b]

[a] Yield in these cases from **4a** or **4b** (see Scheme III). [b] Not purified. [c] The corresponding imine **4** was not isolated. Overall yield from acid hydrolysis of the crude residue. Impurified with the α,β-unsaturated ketone $C_6H_5CH{=}C(CH_3)COC_6H_5$. [d] In the presence of i-Pr_2NH as protic cosolvent.

Results and Discussion

The treatment of **1** with an excess of lithium powder at room temperature for several hours (4–8 h) and in an inert solvent such as THF produces intense color changes leading, after addition of an electrophile EY (H_2O, MeOH, and RX) (ratio EY:1 ⩾ 3:1), to compounds **3** (or **4**) and amines **5** (R^1 = aryl). Yields are good,[8] and the process is regiospecific (see Scheme I and Table I).

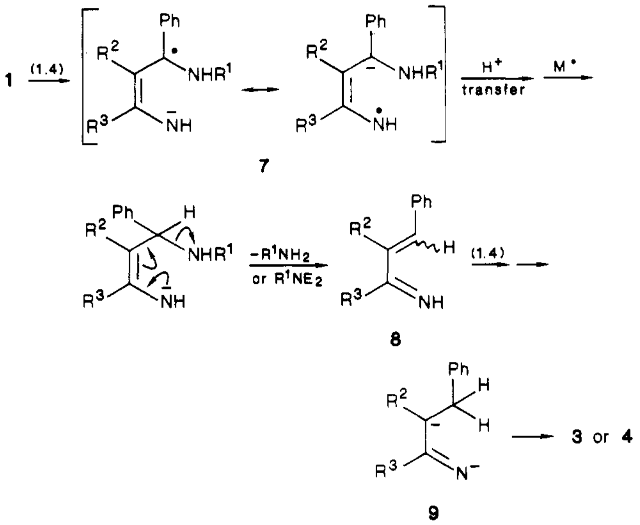
Similar results and also apparently complete regioselectivity are observed when the reaction is carried out in the presence of an amine, e.g., i-Pr_2NH, as protic cosolvent (see Table I, entries 14–16).

In some instances, independently of the lithium excess used, variable amounts (10–15%) of the starting material **1** were recovered (see, for example, entries 7–10, Table I). In others (entries 6, 14–16, Table I), small amounts of higher molecular weight, relatively nonvolatile substances, probably dimeric or polymeric materials, were formed.

Compounds **3** or **4** and **5** were easily separated and purified by distillation. Compounds **3** and **4** were characterized on the basis of their spectroscopic data and mass spectrometry. For instance, **3b** exhibits in the ^1H NMR (90 MHz) spectrum signals at δ 1.15 (d, 3 H), 2.60 (dd, 1 H, J = 13.5 and 7.5 Hz) and 3.15 (dd, 1 H, J = 13.5 and 6.0 Hz), which are assigned to CH_3CH and $PhCH_aH_b$ respectively. The corresponding carbon atoms appear in the ^{13}C NMR (20 MHz) spectrum at δ 16.90 (q) and 39.00 (t), and another characteristic signal appears at 195.10 (s), assignable to the CO group. Thus, the multiplicities of the signals and the coupling constants corroborate the proposed structure.

The formation of carbonyl or iminic compounds **3** and **4** can be explained by a double reduction with loss of amine **5**, following a mechanism similar to that suggested by Coates[7b] in the reduction of enol ethers of β-keto esters to saturated esters with lithium in liquid NH_3. In the present case, however, the proton source is, at least in most instances, provided by the 3-amino-2-alkenimine **1** (Scheme II).

Scheme II



Scheme III

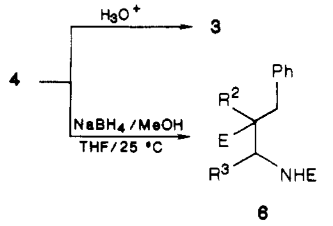


Table II. Amines 6 Obtained from 4[a] by Reduction with $NaBH_4/CH_3OH$

6	R^2	R^3	E	yield, %	mp or bp, °C
a	CH_3	C_6H_5	H	78[b]	70–76 (10^{-3} Torr)
b	H	p-$CH_3C_6H_4$	H	80	109–111
c	CH_3	C_6H_5	CH_3	74 (80)[c]	oil[d]

[a] **4** was obtained from **1** (R^1 = C_6H_5). [b] Obtained as a 59:41 (^1H NMR (300 MHz) of the crude residue) mixture of diastereoisomers. [c] Yield obtained by reduction of **4** with Na/i-PrOH/THF/25 °C. [d] Characterized as its hydrochloride, **6c**·HCl, mp 277–279 °C (ethanol).

The formation of compounds **4** and **6** (see below and Tables I and II) supports the proposed mechanism.[9] Furthermore, in some cases (compounds **3d** and **3k**, Table I) small amounts (⩽10%) of the corresponding α,β-unsaturated ketone, PhCH=C(Me)COR^3, were identified by GC/MS.

When the electrophile used was MeI, imine **4** (E = Me) (entries 15, 16, Table I) was isolated. On the contrary, when EY was H_2O, the imine **4** (E = H) initially formed

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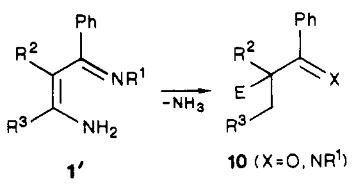
[8] The chemical yield of the process is influenced by the nature of the metal. Thus, lower chemical yields (⩽50%) referred to compounds **3** or **4** were obtained when the metal used was sodium or potassium. Olano, B. Ph.D. Thesis, University of Oviedo, 1985.

[9] In the sequence **8** → **3** (or **4**), a more gradual process is possible, in which an anion-radical, monoanion, electrophile addition followed by a further reaction takes place instead of dianion **9** formation.

Scheme IV



decomposed and the corresponding ketones **3** were isolated instead.

However, when the electrophile used was anhydrous methanol instead of water, a solution of the unstable imine **4** (E = H) was formed in situ. The subsequent reduction with $NaBH_4$/MeOH/THF at room temperature for several hours gave rise to the corresponding amines **6a,b** in high yields (see Scheme III, Table II). In the case of the reaction of **1** (R^2 = Me, R^1 = R^3 = Ph), the amine **6a** was isolated as a mixture of two diastereoisomers at an approximate ratio of 1.5:1.

On the other hand, the reduction of **4** (E = Me, Et) with $NaBH_4$/MeOH or Na/*i*-PrOH at 25 °C, or its acid hydrolysis with 2 N H_2SO_4 in THF, produced, as expected, the amine **6c** and ketones **3i–k** respectively (see Scheme III and Tables I and II).

Finally, with unsymmetrical 3-amino-2-alkenimines **1** (i.e., $R^3 \neq$ Ph and especially in cases where R^3 = aryl, e.g., entries 3, 9, 10, Table I), two different regioisomers **3** and **10** may be formed by way of the two possible tautomer forms ($\mathbf{1} \rightleftharpoons \mathbf{1'}$) of the starting compounds, i.e., $\mathbf{1} \rightarrow \mathbf{3}$ and $\mathbf{1'} \rightarrow \mathbf{10}$ (Schemes I and IV).

The high regioselectivity observed during the reduction (in all cases investigated, the compounds **3** or **4** were the sole regioisomers detected) suggests that the reaction has taken place exclusively through the tautomer form **1** giving rise to the ketone **3**. The structure of **3** can be unequivocally ascertained by the study of its mass spectrum. Thus, for instance, for **3b**, the base peak, *m/e* 119, is assigned to the ion *p*-TolC≡O:$^+$ resulting in the usual fragmentation of aryl alkyl ketones. Moreover, the ion *m/e* 105, which would correspond to the same fragmentation (PhC≡O:$^+$) for the regioisomer from the tautomer form **1′**, was not observed in the mass spectrum of the crude reaction product.

Conclusions

This paper describes a simple method that, for the first time, to our knowledge, allows the selective reduction of one of the ketone groups of an unsymmetrically substituted 1,3-diketone to a methylene group, via the systems **1**. Moreover, the sequence **1** (R^2 = H) → **1** (R^2 = alkyl)^2 → **3** appears as a new strategy for the regioselective alkylation of unsymmetrically substituted dialkyl ketones. Finally, the regiospecificity observed along with the simplicity of the process makes this method a suitable procedure for the synthesis of ketones and amines of type **3** and **6**.

Experimental Section

General Methods. Melting points are uncorrected. Infrared spectra were recorded with a Pye-Unicam SP-1000 spectrophotometer. The ^1H NMR spectra were determined on a Varian FT-80A or a Brücker AC-300 spectrometer with internal tetramethylsilane as the reference. The ^{13}C NMR spectra were determined on a Varian FT-80A or a Brücker AC-300 instrument. GC–mass spectra were taken on a Hewlett-Packard 5930A spectrometer. Microanalyses were performed on a Perkin-Elmer Model 240 instrument.

Materials. 3-Amino-2-alkenimines **1** were prepared according to literature methods.[1,2] All reactions were run under argon. All organic extracts were dried over anhydrous sodium sulfate. Tetrahydrofuran (THF) was distilled from sodium benzophenone under argon prior to use. Methanol was distilled over magnesium turnings/iodine under argon prior to use.[10] All other reagents were commercially available and were used as received.

General Preparative Procedure for Ketones 3a–h. A solution of **1** (10 mmol) in anhydrous THF (20 mL) was added dropwise to a mixture of Li powder (0.35 g, 50 mmol) and anhydrous THF (20 mL) at room temperature. When the addition was complete, the yellow solution was stirred at room temperature for several hours (4–8 h). The yellow color slowly changed to deep purple. The resulting dark suspension was filtered off to give the corresponding solution of the intermediate **9** and then treated with H_2O (30–40 mmol). The mixture was stirred for 1–2 h, 2 N H_2SO_4 (100 mL) was added, and then the mixture was extracted with ether; the organic layer was dried over sodium sulfate and filtered, the solvents were removed, and the residue was distilled under reduced pressure (see Table I) to afford the products **3**.

The aqueous layer was then treated with KOH until basic, extracted with ether, and evaporated. Amines **5** (R^1NH_2) were distilled and identified.

2-Methyl-3-phenyl-1-*p*-tolyl-1-propanone (3b): IR (Nujol) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (d, 3 H), 2.20 (s, 3 H), 2.60 (dd, 1 H, *J* = 13.5 and 7.5 Hz), 3.15 (dd, 1 H, *J* = 13.5 and 6.0 Hz), 3.65 (m, 1 H), 6.80–8.00 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 195.10, 142.85, 139.60, 133.65, 128.90–125.65, 41.80, 39.00, 20.75, 16.90; MS, *m/e* 238 (M^+), 119, 91. Anal. Calcd for $C_{17}H_{18}O$: C, 85.71; H, 7.56. Found: C, 85.81; H, 7.41.

3-Methyl-4-phenyl-2-butanone (3d): IR (film) 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (d, 3 H), 2.00 (s, 3 H), 2.35–3.10 (complex, 2 H + 1 H), 7.10–7.50 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 188.90, 141.00, 140.55, 131.50–127.00, 48.95, 39.10, 28.60, 16.10; MS, *m/e* 162 (M^+), 147, 91, 77, 43. Anal. Calcd for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.19; H, 8.72.

3-Phenyl-1-*p*-tolyl-1-propanone (3f): IR (Nujol) 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 3.00 (m, 4 H), 6.90–7.80 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 203.10, 143.15, 140.90, 133.85, 129.00–121.00, 39.30, 29.00, 20.75; MS, *m/e* 224 (M^+), 119, 91. Anal. Calcd for $C_{16}H_{16}O$: C, 85.71; H, 7.14. Found: C, 85.62; H, 7.21.

2-Benzyl-3-phenyl-1-*p*-tolyl-1-propanone (3g): IR (Nujol) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 2.72 (dd, 2 H, *J* = 13.5 and 6.0 Hz), 3.05 (dd, 2 H, *J* = 13.5 and 7.5 Hz), 3.94 (m, 1 H), 6.95–7.60 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 197.20, 144.50, 140.80, 135.90, 130.50–126.80, 51.00, 39.07, 21.92; MS, *m/e* 223 ($M^+ - 91$), 119, 91. Anal. Calcd for $C_{23}H_{22}O$: C, 87.89; H, 7.00. Found: C, 88.07; H, 7.08.

2-Benzyl-1-phenyl-4-penten-1-one (3h): IR (Nujol) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 (m, 1 H), 2.47 (m, 1 H), 2.74 (dd, 1 H, *J* = 13.5 and 6.0 Hz), 3.04 (dd, 1 H, *J* = 13.5 and 7.5 Hz), 3.71 (m, 1 H), 4.93 (m, 2 H), 5.68 (m, 1 H), 6.90–7.85 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 197.50, 140.25, 137.80, 136.00, 131.90, 129.00–126.20, 117.00, 47.50, 37.30, 36.05; MS, *m/e* 250 (M^+), 209, 105, 77. Anal. Calcd for $C_{18}H_{18}O$: C, 86.40; H, 7.20. Found: C, 86.51; H, 7.29.

Spectral data for compounds **3a**, **3c**, and **3e** are included as supplementary material.

General Preparative Procedure for Imines 4. A solution of **1** (10 mmol) in 20 mL of anhydrous THF was added dropwise to a stirred suspension of Li powder (0.35 g, 50 mmol) in 20 mL of THF and 5 mL of *i*-Pr_2NH at room temperature. The subsequent operations were the same as those for compounds **3a–h**. To the resulting solution was then added the corresponding alkyl halide (40 mmol), and the mixture was stirred for 2–4 h, treated with ice-cooled, concentrated KOH until basic, and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), filtered, and evaporated. The residue was distilled under reduced pressure (0.001 Torr) to afford the compounds **4** and the amines **5** (R^1NE_2), which were easily separated. The yields are given in Table I.

***N*-(2,2-Dimethyl-3-phenyl-1-*p*-tolylpropylidene)methylamine (4a)**: purified by recrystallization from *n*-hexane; IR (Nujol) 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (s, 6 H), 2.35 (s, 3 H), 2.85 (s, 2 H), 2.90 (s, 3 H), 6.50–7.35 (m, 9 H); ^{13}C NMR ($CDCl_3$)

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(10) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. In *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980; p 320.

δ 180.10, 139.10, 136.90, 134.45, 130.82–125.85, 46.55, 43.70, 40,67, 26.22, 21.00; MS, *m/e* 265 (M^+), 132, 91. Anal. Calcd for $C_{19}H_{23}N$: C, 86.04; H, 8.68; N, 5.28. Found: C, 85.97; H, 8.60; N, 5.32.

Spectral data for compounds **4b** are included as supplementary material.

Treatment of 4 with 2 N Sulfuric Acid. Preparation of 2,2-Dimethyl-3-phenyl-1-*p*-tolyl-1-propanone (3i). A solution of **4a** (5 mmol) in THF (50 mL) was heated with 2 N H_2SO_4 (10 mL) at 50 °C for 1 h. The solution was slowly poured into ice-cooled water, extracted with ether, and evaporated. The residue was distilled under reduced pressure to yield **3i**: IR (film) 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 6 H), 2.35 (s, 3 H), 3.05 (s, 2 H), 7.00–8.00 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 191.20, 141.53, 139.00, 137.10, 131.43–127.03, 49.73, 47.25, 27.03, 22.23. Anal. Calcd for $C_{18}H_{20}O$: C, 85.71; H, 7.94. Found: C, 85.60; H, 8.02.

Spectral data for compounds **3j** and **3k** are included as supplementary material.

Preparation of *N*-(2,2-Dimethyl-1,3-diphenylpropyl)methylamine (6c). Method A. Reduction of 4b with $NaBH_4$/MeOH. To a solution of imine **4b** (5 mmol) in anhydrous THF (20 mL) and anhydrous methanol (10 mL) was slowly added $NaBH_4$ (1.85 g, 50 mmol) with stirring in an ice bath. After being stirred for 4 h at room temperature, the solution was poured into 3 N KOH and extracted with ether. The extract was dried over sodium sulfate and evaporated. The resulting crude product was distilled under reduced pressure. Amine **6c** was obtained and characterized as its hydrochloride.

Method B. Reduction of 4b with Na/*i*-PrOH. A solution of **4b** (5 mmol) in anhydrous THF (20 mL) and anhydrous *i*-PrOH (10 mL) was added dropwise to a mixture of Na (2.0 g, 86 mmol) and anhydrous THF (10 mL) at room temperature. The subsequent operations were the same as those for method A. Amine **6c** was obtained and characterized as its hydrochloride. Yields and melting points are given in Table II.

6c·HCl: IR (Nujol) 3200–2500, 1590, 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 3 H), 1.20 (s, 3 H), 2.60 (br t, 3 H) (+D_2O, s, 3 H), 2.75 (d, 1 H, J = 12.5 Hz), 3.05 (d, 1 H, J = 12.5 Hz), 3.85 (br, 1 H) (+D_2O, s, 1 H), 7.00–7.70 (m, 10 H), 9.70 (br, s, N H); ^{13}C NMR ($CDCl_3$) δ 136.95, 132.41–126.26, 74.13, 44.96, 38.52, 33.30, 24.60, 23.80. Anal. Calcd for $C_{18}H_{24}NCl$: C, 74.61; H, 8.29; N, 4.84. Found: C, 74.57; H, 8.40; N, 4.73.

Preparation of (3-Phenyl-1-*p*-tolylpropyl)amine (6b). To a solution of **9** (R^2 = H, R^3 = *p*-tolyl) (see general preparative procedure for ketones **3a–h**) were slowly added anhydrous methanol (10 mL) and $NaBH_4$ (3.73 g, 100 mmol) with stirring in an ice bath. The subsequent operations were the same as those for method A (see above). Aniline (R^1NH_2) was distilled and the amine **6b** (80%) purified by recrystallization from *n*-hexane: mp 109–11 °C; ^{1}H NMR ($CDCl_3$) δ 0.60 (br s, NH), 0.75 (q, 2 H), 1.09 (s, 3 H), 1.33 (m, 2 H), 2.60 (t, 1 H), 5.85–6.18 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 145.01, 143.80, 137.10, 130.5–126.7, 56.10, 41.91, 33.30, 21.52; MS, *m/e* 225 (M^+), 208, 120, 91, 77. Anal. Calcd for $C_{16}H_{19}N$: C, 85.33; H, 8.44; N, 6.22. Found: C, 85.12; H, 8.51; N, 6.29.

Spectral data for compound **6a** are included as supplementary material.

Supplementary Material Available: Spectral and analytical data for compounds **3a,c,e,j,k**, **4b**, and **6a** (2 pages). Ordering information is given on any current masthead page.

Selective Formation of Five-Membered Heterocyclic Products by Anodic Oxidation of Alkyl Isothiocyanates (RNCS) in Dichloromethane and Their Thermal Isomerization and Decomposition[1]

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Anodic oxidation of primary and secondary alkyl isothiocyanates (RNCS) in dichloromethane yielded two isomers of five-membered heterocyclic products, 4-alkyl-5-(alkylimino)-1,2,4-dithiazolidine-3-one **2** and 2,4-dialkyl-5-oxo-1,2,4-thiadiazolidine-3-thione **3**. Their relative ratio was found to be dependent on the length or bulkiness of the alkyl group in RNCS. Isomer **2** was favorable for R = Me and Et and exclusive for R = *n*-Pr, *n*-Bu, and cyclohexyl. Upon GLC injection (at 150–200 °C), compounds of type **2** isomerized completely to **3** (when R = Me, Et), mostly to **3** and partially decomposed to RN=C=NR (**11**) (when R = *n*-Pr, *n*-Bu), and exclusively decomposed to **11** for R = cyclohexyl. Tertiary RNCS did not yield cyclic products but instead underwent chlorination to substitute a hydrogen (or "NCS" group) by chlorine. Plausible mechanistic schemes are suggested and discussed.

Introduction

The anodic oxidation of the cumulene functionality either in allenic hydrocarbons or in some selective heteroallenes was described before.[2,3] Recently we reported on the anodic oxidation of alkyl isocyanates and alkyl isothiocyanates in acetonitrile.[4] It was found that the former were oxidized at relatively high anodic potentials (3–3.2V vs Ag/Ag$^+$) while the latter at significantly lower ones (2–2.2 V). As to the outcome of their preparative controlled potential electrolysis, each family of compounds afforded an entirely different spectrum of products. RNCO derivatives gave low yield mixtures of products which stemmed mainly from C–NCO bond cleavage accompanied (or followed by) with nucleophilic attack by either water or acetonitrile to form carbonyl derivatives or amides, respectively. Under dry conditions, the major products involved mono-, di-, and tricyanomethylation and a loss of the cumulene functionality. RNCS derivatives were found to undergo three types of processes which their relative ratio was highly dependent on the nature of the alkyl group: (a) exclusive formation of five-membered

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