Letters to the Editor

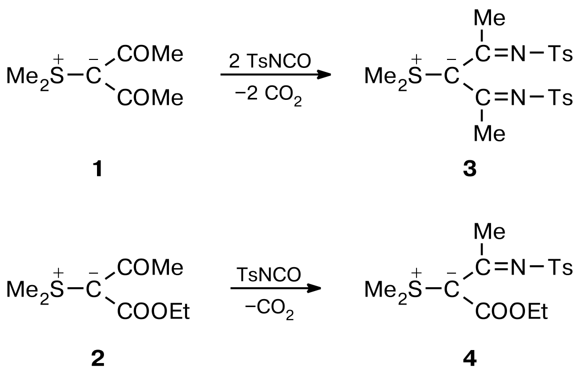
A new reaction of sulfur ylides. Imination of dimethylsulfonium ketoylides with tosyl isocyanate

Yu. G. Gololobov,* I. R. Golding, P. V. Petrovskii, and Z. S. Klemenkova

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 119991 Moscow, Russian Federation.
E-mail: Yugol@ineos.ac.ru

Reactions of double stabilized ylides with isocyanates that occur with retention of the ylide structure are not described.[1] We found that tosyl isocyanate reacts with the acetyl groups of ketoylides **1** and **2** with CO_2 evolution and substitution of the carbonyl O atom by the tosylimino group. This reaction does not involve the $S^+—C^-$ bond and, according to the data of the ^1H NMR spectra, stable sulfur ylides **3** and **4** are formed in ~100% yields (Scheme 1).

Scheme 1



The completeness of the transformations considered was monitored using ^1H NMR spectroscopy by the disappearance of signals from protons of the Me groups in the COMe fragments of ylides **1** and **2** and by an increase in the intensity of signals from protons of the MeC(=N)Ts groups in ylides **3** and **4**. The composition and structure of previously undescribed ylides **3** and **4** were confirmed by the data of elemental analysis, ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and mass spectrometry.

IR spectra were recorded on a Magna-IR 750 instrument (Nicolet) in pellets with KBr. ^1H and ^{13}C NMR spectra were obtained on a Bruker AMX-400 spectrometer (400.26 and 100.68 MHz) in $CDCl_3$. Reactions were carried out in dry nitrogen. Solvents were used after purification and drying. Mass spectra were obtained on an MS 890 instrument (Kratos).

Dimethylsulfonium diacetylmethylide (1) was synthesized using a known procedure.[2]

Dimethylsulfonium acetyl(carbethoxy)methylide (2) was synthesized using a known procedure[2] as semihydrate, m.p. 60—62.5 °C (*cf.* Ref. 2: 58—60 °C). Found (%): C, 48.30; H, 7.65; S, 15.98. $C_8H_{15}O_{3.5}S$. Calculated (%): C, 48.22; H, 7.59; S, 16.09. IR, ν/cm^{-1}: 1545 (C=O, MeC(O)); 1677 (C=O, CO_2Et); 3360 (OH). ^1H NMR, δ: 1.27 (t, 3 H, $\underline{Me}CH_2$, J = 7.2 Hz); 1.79 (s, 1 H, H_2O); 2.38 (s, 3 H, MeCO); 2.89 (s, 6 H, Me_2S); 4.14 (q, 2 H, $MeC\underline{H}_2$, J = 7.2 Hz).

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Dimethylsulfonium bis(1-tosyliminoethyl)methylide (3). A solution of ylide **1** (0.24 g, 1.5 mmol) in $CHCl_3$ (1 mL) was added dropwise to a solution of TsNCO (0.74 g, 3.7 mmol) in $CHCl_3$ (4 mL) at 10 °C. The mixture was stored for 1 day at ~20 °C, refluxed for 3 h, cooled, and poured into hexane (20 mL). A precipitate was separated and twice recrystallized from a THF—Et_2O (5 : 1) mixture. Compound **3** was obtained as colorless crystals in 46% yield (0.32 g), m.p. 162—163 °C. Found (%): C, 54.26; H, 5.70; N, 5.82; S, 20.45. $C_{21}H_{26}N_2O_4S_3$. Calculated (%): C, 54.04; H, 5.62; N, 6.00; S, 20.61. IR, ν/cm^{-1}: 1142, 1270 (SO_2); 1521 (C=N, by analogy with ylides Ph_3P=CHC(R)=NTs)[3]; 1597 (arom.). ^{1}H NMR, δ: 2.40 (s, 6 H, 2 Me (Ts)); 2.70 (s, 6 H, 2 MeCNTs); 2.89 (s, 6 H, Me_2S); 7.26 (d, 4 H, H arom., *J* = 8.0 Hz); 7.55 (d, 4 H, H arom., *J* = 8.0 Hz). ^{13}C NMR, δ: 21.36 (MeCNTs); 24.48 (Me (Ts)); 27.07 (MeS); 88.78 (ylide C); 126.21, 129.29 (CH arom.); 140.00, 142.51 (C arom.); 175.64 (C=N). MS (EI, 70 eV), *m/z*: 404 $[M - SMe_2]^+$.

Dimethylsulfonium carbethoxy(1-tosyliminoethyl)methylide (4). A solution of TsNCO (0.65 g, 3.3 mmol) in $CHCl_3$ (4 mL) was added dropwise to a solution of ylide **2** semihydrate (0.35 g, 1.7 mmol) in $CHCl_3$ (1 mL) at 10 °C. The mixture was stored for 1 day at ~20 °C, refluxed for 6 h, cooled, and poured into hexane (20 mL). A precipitate was separated and twice recrystallized from toluene. Compound **4** was obtained as colorless crystals in 62% yield (0.37 g), m.p. 182—184 °C. Found (%): C, 52.33; H, 6.10; N, 3.94; S, 18.53. $C_{15}H_{21}NO_4S_2$. Calculated (%): C, 52.45; H, 6.16; N, 4.07; S, 18.67. IR, ν/cm^{-1} : 1137, 1265 (SO_2); 1491 (sh, C=N); 1599 (arom.); 1674 (C(O), CO_2Et). ^{1}H NMR, δ: 1.24 (t, 3 H, $MeCH_2$, *J* = 7.2 Hz); 2.40 (s, 3 H, Me (Ts)); 2.69 (s, 3 H, MeCNTs); 2.92 (s, 6 H, Me_2S); 4.14 (q, 2 H, $MeCH_2$, *J* = 7.2 Hz); 7.24 (d, 4 H, H arom., *J* = 8.0 Hz); 7.77 (d, 4 H, H arom., *J* = 8.0 Hz). ^{13}C NMR, δ: 14.39 ($MeCH_2$); 21.36 (MeCNTs); 22.27 (Me (Ts)); 26.27 (MeS); 60.11 ($MeCH_2$); 70.45 (ylide C); 126.24, 129.18 (CH arom.); 141.14, 141.78 (C arom.); 165.55 (C=O); 177.18 (C=N). MS (EI, 70 eV), *m/z*: 343 $[M]^+$.

References

1. I. D. Sadekov, V. I. Minkin, V. V. Semenov, and S. A. Shevelev, *Usp. Khim.*, 1981, **50**, 313 [*Russ. Chem. Rev.*, 1981, **50** (Engl. Transl.)].
2. A. F. Cook and J. P. Moffatt, *J. Am. Chem. Soc.*, 1968, **90**, 740.
3. H. Yoshida, T. Ogata, and S. Inokawa, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 3315.

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