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Ylide Chemistry

A Direct Ylide Transfer to Carbonyl Derivatives and Heteroaromatic Compounds**

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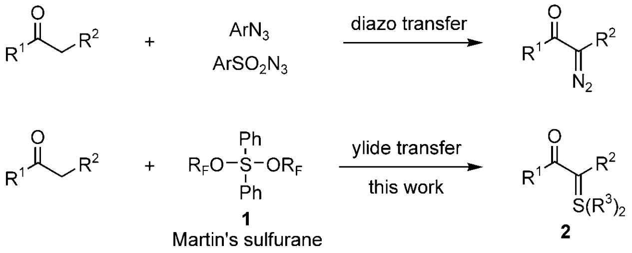
Since the pioneering work of Corey et al. and Johnson et al. in the 1960s,[1] sulfonium and sulfoxonium ylides have occupied a prominent place as cornerstone, textbook reagents in organic chemistry.[2] In addition to the construction of simple small rings such as epoxides,[3] cyclopropanes,[4] and aziridines,[5] new methods to access more complex architectures through cascade cyclizations using sulfonium ylides with suitable reagents have also been developed in recent years.[6] Perhaps less well-known but equally interesting are reports highlighting antimicrobial properties of sulfur ylides.[7] More recently, increased interest has focused on the potential of sulfonium/sulfoxonium ylides to behave as metal carbene precursors under suitable conditions.[8] Indeed, whilst the arena of carbenoid donors to metals is almost exclusively dominated by α-diazocarbonyl derivatives,[9] their toxic and hazardous nature has long plagued applications to synthesis. In particular, the rapid evolution of nitrogen gas upon their decomposition is prone to generate uncontrolled exotherms that limit their suitability for large-scale processing.[8e]

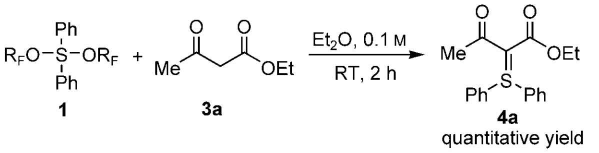
It is particularly intriguing to note that, whereas α-diazocarbonyl compounds are typically synthesized in a single step by one out of a number of so-called "diazo transfer reactions",[10] the analogous concept of "ylide transfer" has been scarcely developed (Scheme 1).[11] In fact, standard technology for preparation of sulfonium and sulfoxonium ylides is still essentially the same as that introduced by Corey et al. and Yao and co-workers more than 40 years ago,[12] and entails deprotonation of a sulfonium/sulfoxonium salt (which must be prepared by a substitution reaction) by a strong base. Ironically, the most competitive process to the aforementioned method is perhaps the decomposition of diazo compounds in the presence of sulfides to produce sulfonium ylides—with its own shortcomings, such as the requirement for (often) stoichiometric amounts of metal salts and the prior synthesis and handling of toxic and explosive diazo compounds.[13] Herein, we report on simple, high-yielding ylide transfer reactions of Martin's sulfurane (**1**; Scheme 1) that allow direct access to aliphatic and aromatic ylide derivatives with interesting structural properties.



Scheme 1. Comparison of the synthesis of diazocarbonyl compounds and carbonyl-stabilized sulfur ylides. R^1–R^3 = alkyl, aryl, electron-withdrawing groups; $R_F = C_6H_5(CF_3)_2C$.

Martin's sulfurane (**1**), named after the scientist whose group was the first to prepare it in 1971,[14] is widely used as a reagent for dehydration (mostly of alcohols) in organic synthesis.[15,16] We speculated that **1** might behave as a ylide transfer reagent to suitable carbonyl derivatives, thus yielding diphenylsulfonium ylides (**2**, R^3 = Ph). To the best of our knowledge, Martin's sulfurane (**1**) has not been previously employed for this purpose.[17]

To test this hypothesis, we began our study using readily available ethyl acetoacetate **3a** as a model substrate for reaction with **1**. Gratifyingly, treatment of **3a** with 1.5 equivalents of **1** in diethyl ether afforded a single compound in quantitative yield [Eq. (1)]. After careful analysis, the product was found to have a structure consistent with **4a** (as additionally supported by NMR spectroscopy and high-resolution mass spectrometry). Unambiguous proof of structure and geometry was achieved by single-crystal X-ray analysis (Figure 1).[18]



(1)

Encouraged by this result, we investigated the scope of this ylide transfer reaction. As compiled in Scheme 2, a broad variety of substrates afforded the corresponding sulfonium ylides in good to excellent yields. Different ketoesters (**3a**–**d**) including tetronic acid **3i** reacted smoothly with **1**. The reactions of acyclic (**3e**–**g**) and cyclic (**3h**) diketones bearing aromatic or aliphatic groups gave the corresponding ylides (**4e**–**h**) in good to quantitative yields. Pleasingly, dimethyl

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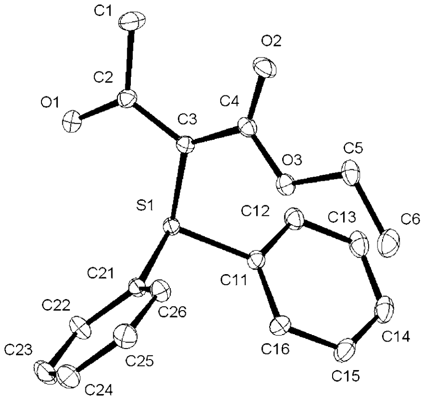
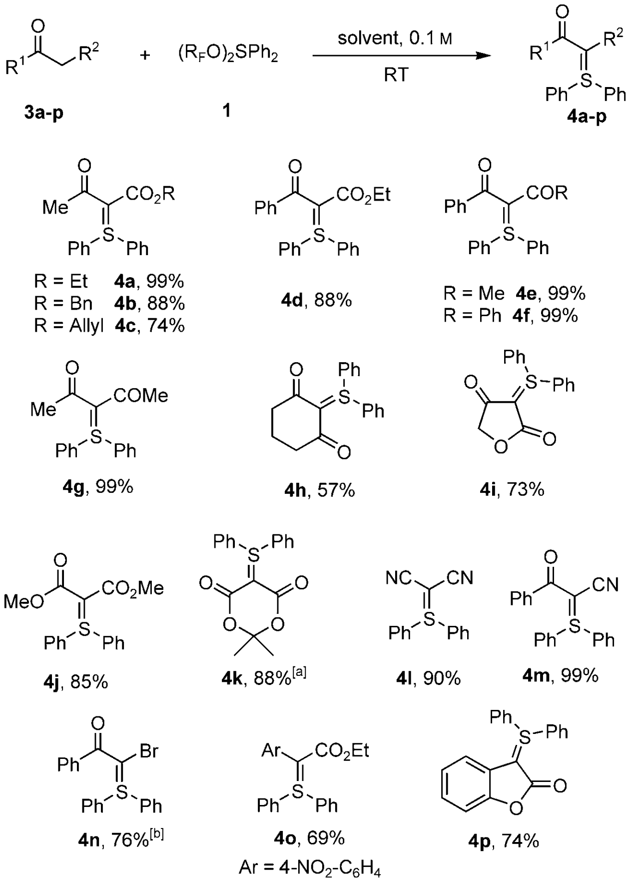


Figure 1. X-ray crystal structure for **4a**. The thermal ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity.

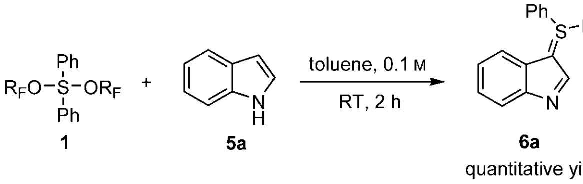


Scheme 2. Direct ylide transfer to active methylene compounds using **1**. Yields refer to pure, isolated compounds. All reactions were run in diethyl ether using 1.5 equivalents of **1** unless mentioned otherwise. [a] Solvent was chloroform. [b] Solvent was dichloromethane.

malonate (**3j**) and the analogous malononitrile (**3l**) and Meldrum's acid (**3k**) were perfect candidates for this reaction, furnishing **4j–l** in high yields. Furthermore, for acetophenones **3m,n** and phenylacetate derivatives **3o,p**, the corresponding ylides **4m,n** and **4o,p** were also obtained in high yields. Compound **4n**, derived from α-bromoacetophenone, merits notice because of the fact that its ylidic carbon atom bears a leaving group. Similar compounds are reported as potent fungicides, and previous preparations relied on bromination/deprotonation of the pre-synthesized, unsubstituted ylides.[19] In sharp contrast, **4n** is available in a single step through the present methodology.[20]

It is worthhwile noting at this juncture that sulfurane **1** appears to be particularly effective in this ylide transfer process; alternative methods (e.g., combinations of sulfoxides and diverse dehydrating reagents) are known[11] to be plagued by low yields, harsh reaction conditions, and somewhat narrow substrate scopes. Mechanistically, the reactions in Scheme 2 may proceed either by initial deprotonation of the carbonyl derivative by dissociated Martin's sulfurane with subsequent attack on sulfur, or direct nucleophilic displacement by an enol tautomer.

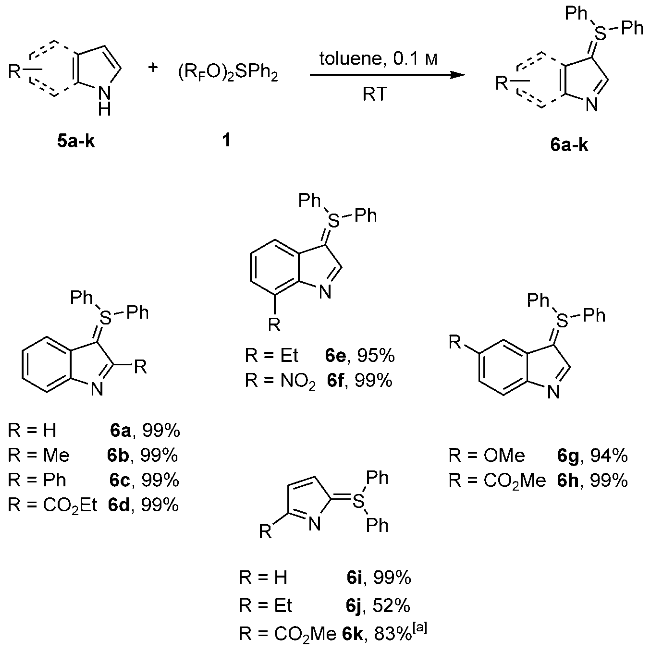
Intrigued by the simplicity of this procedure, we then set our sights on more challenging classes of substrates. In particular, we hypothesized that the powerful ylide transfer ability of sulfurane **1** might be amenable to Friedel–Crafts-like dearomatization of suitable heterocycles. Indole **5a** reacted smoothly with **1** within 2 hours at room temperature, affording the indole-3-sulfonium ylide **6a** in quantitative yield [Eq. (2)].[21] Once again, the strikingly facile access to this compound encouraged us to examine related substrates in more detail.

 (2)

As can be seen, this reaction appears to possess a broad scope (Scheme 3). Indoles **5a–h** bearing substituents ranging from electron-donating to electron-neutral and strong electron-withdrawing groups were tolerated. Moreover, considerable flexibility is allowed regarding the substituent location. All the ylides **6a–h** were obtained in quantitative yields.

In addition, pyrrole (**5i**) and its derivatives **5j,k** also performed competently in this reaction. As might be expected, pyrrole 2-sulfonium ylide **6i** was obtained as the exclusive regioisomer.[22] Interestingly, the presence of an ester substituent as in **5k** led to the production of small amounts of the 4-sulfonium ylide isomer, presumably owing to the strong *meta*-directing effect of the ester moiety. The robustness of this reaction is additionally apparent from the ease of scale-up: indole derivative **5d** was easily converted into the corresponding sulfonium ylide **6d** on a multigram scale.[23]

In addition to the crystal structure of **4a**, the crystal structures of **4g**, **4j**, **4l**, **4n**, and **4m** were determined,[24] and they reveal an interesting trend, which is noticeable in the geometry about the ylidic carbon atom. Whereas **4m**, containing electron-withdrawing groups ($R^1 = CN$ and $R^2 = COPh$), has a relatively long S=C distance of 1.734(1) Å and a large C-C(=S)-C angle of 126.4(1)°, **4n**, having the weaker

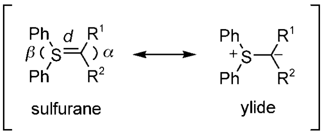


Scheme 3. Direct ylide transfer to heteroaromatic compounds using **1**. Yields refer to pure, isolated compounds. All reactions were run in toluene using 1.5 equivalents of **1** unless mentioned otherwise. [a] 16% of the 4-sulfonium ylide was also obtained.

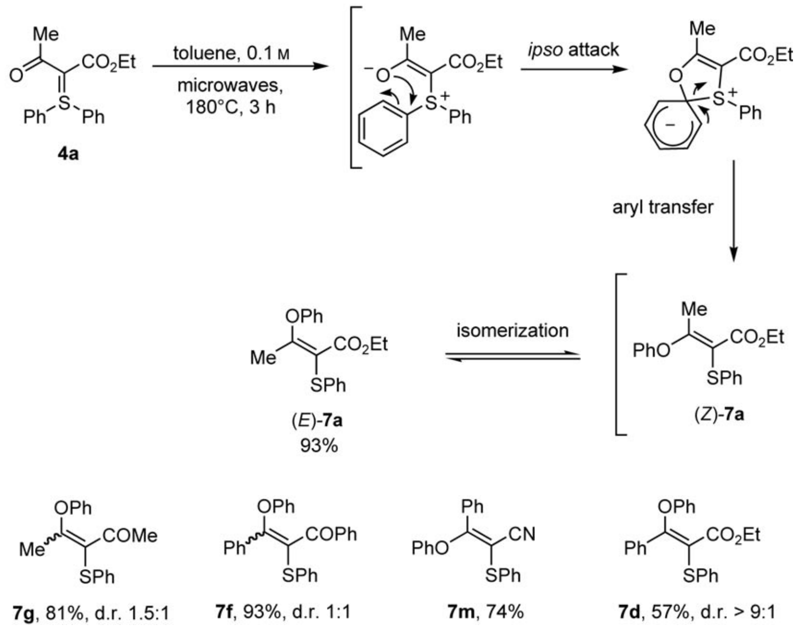
electron-withdrawing group ($R^1 = Br$), has a shorter S=C distance of 1.688(2) Å and a smaller C-C(=S)-C angle of 118.1(2)° (Table 1). Consistent with build-up of negative charge on the ylidic C, the C atom in **4n** is slightly pyramidal (0.15 Å out of the plane through S, Br, and C(=O)(Ph)), indicating that this C atom is very basic; that is, the ylidic resonance form dominates. In contrast, the angles around the S atom remain essentially constant down the series, suggesting that little electron density is transferred from the ylidic C back to S.[25] In the case of **4g**, the structure of a selenurane analogue has been determined,[26] wherein the C-C(=X)-C angle is significantly larger (134.10° cf. av. 126.9(2)°). Interestingly, not only is the angle larger in the selenurane, but in contrast to **4g**, which contains *E*- and *Z*-configured carbonyl groups in each of the two independent molecules in the unit cell, both carbonyl oxygen atoms point towards the Se (*Z*, *Z*). Clearly, the geometry of the ylide is particularly sensitive to the electronic situation at the carbanion.

The structural complexity of the prepared compounds gives rise to unusual reactivity profiles. For instance, thermolysis of compound **4a** triggers a clean migration of a phenyl group from S to O, thus leading to (*E*)-**7a** (Scheme 4). This migration correlates with the short distance between the ketocarbonyl oxygen atom and the diphenylsulfur ylide that is observed in the crystal structure.[24] We thus believe that this rearrangement proceeds by *ipso*-attack of a negatively charged oxygen atom onto the proximal, activated aromatic ring (Scheme 4).[27,28] This intriguing behavior was not unique to **4a**, and other analogues (Scheme 4) also smoothly isomerized into their tetrasubstituted olefin counterparts **7d**–**m**. The geometries of the final products were variable, likely resulting from facile *E*/*Z* isomerization of the push–pull olefins formed.[29]

Table 1: The dependence of S=C distances and R^1-C-R^2 angles upon substituents R^1 and R^2.



Compd.	R^1	R^2	d [Å]	α [°]	β [°]
4n	Br	COPh	1.688(2)	118.1(2)	101.8(1)
4l	CN	CN	1.718(1)	121.8(1)	103.2(4)
4j	COOMe	COOMe	1.724(2)	121.0(2)	104.5(1)
4g	COMe	COMe	1.729(1)	126.5(1)	105.0(1)
			1.723(1)	127.3(1)	105.2(1)
4a	COMe	COOEt	1.7300(6)	126.25(5)	105.65(3)
4m	CN	COPh	1.734(1)	126.4(1)	102.8(1)



Scheme 4. Phenyl migration from S to O for **4a**.

In summary, we have developed a new ylide transfer reaction. This process allows a direct, operationally simple synthesis of sulfur ylides from active methylene compounds and heteroaromatics, and provides a powerful sulfur equivalent to the well-known diazo transfer reactions. Indeed, **1** appears uniquely suited to direct, high-yielding syntheses of sulfur ylides and the reactions described herein should find broad applications in synthesis. Furthermore, we have uncovered a pronounced impact of the electron density variations upon the ylide geometry which may influence future synthetic planning and discovery for new transformations of sulfur ylides.

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[1] a) A. W. Johnson, R. B. Lacount, *Chem. Ind.* **1958**, 1440; b) A. W. Johnson, R. B. Lacount, *J. Am. Chem. Soc.* **1961**, *83*, 417; c) E. J. Corey, M. Chaykovsky, *J. Am. Chem. Soc.* **1962**, *84*, 3782; d) A. W. Johnson, V. J. Hruby, J. L. Williams, *J. Am. Chem. Soc.* **1964**, *86*, 918; e) E. J. Corey, M. Chaykovsky, *J. Am. Chem. Soc.* **1965**, *87*, 1353.

[2] a) M. B. Smith, J. March, *Advanced Organic Chemistry*, Wiley, New York, **2001**; b) F. A. Carey, R. J. Sundberg, *Advanced Organic Chemistry Part B: Reactions and Synthesis*; Kluwer Academic, New York, **2001**. For selected reviews, see: c) B. M. Trost, L. S. Melvin, *Sulfur Ylides*, Academic Press, New York, **1975**; d) A.-H. Li, L.-X. Dai, V. K. Aggarwal, *Chem. Rev.* **1997**, *97*, 2341; e) V. K. Aggarwal, C. L. Winn, *Acc. Chem. Res.* **2004**, *37*, 611; f) Y. Tang, S. Ye, X.-L. Sun, *Synlett* **2005**, 2720; g) E. M. McGarrigle, E. L. Meyers, O. Illa, M. A. Shaw, S. L. Riches, V. K. Aggarwal, *Chem. Rev.* **2007**, *107*, 5841.

[3] For selected examples, see: a) V. K. Aggarwal, E. Alonso, G. Hynd, K. M. Lydon, M. J. Palmer, M. Porcelloni, J. R. Studley, *Angew. Chem.* **2001**, *113*, 1479; *Angew. Chem. Int. Ed.* **2001**, *40*, 1430; b) M. Davoust, J.-F. Brière, P. Metzner, *Org. Biomol. Chem.* **2006**, *4*, 3048; c) V. K. Aggarwal, J. P. H. Charmant, D. Fuentes, J. N. Harvey, G. Hynd, D. Ohara, W. Picoul, R. Robiette, C. Smith, J.-L. Vasse, C. L. Winn, *J. Am. Chem. Soc.* **2006**, *128*, 2105; d) D. M. Badine, C. Hebach, V. K. Aggarwal, *Chem. Asian J.* **2006**, *1*, 438; e) O. Illa, M. Arshad, A. Ros, E. M. McGarrigle, V. K. Aggarval, *J. Am. Chem. Soc.* **2010**, *132*, 1828.

[4] For recent examples, see: a) V. K. Aggarwal, E. Alonso, G. Fang, M. Ferrara, G. Hynd, M. Porcelloni, *Angew. Chem.* **2001**, *113*, 1482; *Angew. Chem. Int. Ed.* **2001**, *40*, 1433; b) R. K. Kunz, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2005**, *127*, 3240; c) V. K. Aggarwal, E. Grange, *Chem. Eur. J.* **2006**, *12*, 568.

[5] See: a) A.-H. Li, Y.-G. Zhou, L.-X. Dai, X.-L. Hou, L.-J. Xia, L. Lin, *Angew. Chem.* **1997**, *109*, 1375; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1317; b) ref. [4a]; c) D. Morton, D. Pearson, R. A. Field, R. A. Stockman, *Org. Lett.* **2004**, *6*, 2377; d) D. Morton, D. Pearson, R. A. Field, R. A. Stockman, *Chem. Commun.* **2006**, 1833; e) R. Robiette, *J. Org. Chem.* **2006**, *71*, 2726.

[6] a) M. G. Unthank, N. Hussain, V. K. Aggarwal, *Angew. Chem.* **2006**, *118*, 7224; *Angew. Chem. Int. Ed.* **2006**, *45*, 7066; b) X.-L. Sun, Y. Tang, *Acc. Chem. Res.* **2008**, *41*, 937; c) L.-Q. Lu, Y.-J. Cao, X.-P. Liu, J. An, C.-J. Yao, Z.-J. Ming, W.-J. Xiao, *J. Am. Chem. Soc.* **2008**, *130*, 6946; d) L.-Q. Lu, F. Li, J. An, J.-J. Zhang, X.-L. An, Q.-L. Hua, W.-J. Xiao, *Angew. Chem.* **2009**, *121*, 9706; *Angew. Chem. Int. Ed.* **2009**, *48*, 9542.

[7] G. R. Reddy, G. R. Reddy, S. Sarada, *Biochem. Int.* **1989**, *19*, 215.

[8] Sulfonium ylides: a) P. Müller, D. Fernandez, P. Nury, J.-C. Rossier, *Helv. Chim. Acta* **1999**, *82*, 935; b) M. Gandelman, B. Rybtchinski, N. Ashkenazi, R. M. Gauvin, D. Milstein, *J. Am. Chem. Soc.* **2001**, *123*, 5372; c) M. Gandelman, K. M. Naing, B. Rybtchinski, E. Poverenov, Y. Ben-David, N. Ashkenazi, R. M. Gauvin, D. Milstein, *J. Am. Chem. Soc.* **2005**, *127*, 15265. Sulfoxonium ylides: d) J. E. Baldwin, R. M. Adlington, C. R. A. Godfrey, D. W. Gollin, G. J. Vaughan, *J. Chem. Soc. Chem. Commun.* **1993**, 1434; e) I. K. Mangion, I. K. Nwamba, M. Shevlin, M. A. Huffan, *Org. Lett.* **2009**, *11*, 3566.

[9] a) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, **1998**; b) M. P. Doyle, D. C. Forbes, *Chem. Rev.* **1998**, *98*, 911; c) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417; d) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704, and references therein.

[10] a) M. Regitz, G. Maas, *Diazo Compounds – Properties and Synthesis*, Academic Press, Orlando, **1986**; b) G. Maas, *Angew. Chem.* **2009**, *121*, 8332; *Angew. Chem. Int. Ed.* **2009**, *48*, 8186.

[11] a) A. Hochrainer, F. Wessely, *Tetrahedron Lett.* **1965**, *6*, 721; b) A. F. Cook, J. G. Moffatt, *J. Am. Chem. Soc.* **1968**, *90*, 740; c) K. Friedrich, J. Rieser, *Justus Liebigs Ann. Chem.* **1976**, 641; d) K. Schank, C. Schuhknecht, *Synthesis* **1978**, 678; e) S. Katayama, T. Watanabe, M. Yamahuchi, *Chem. Pharm. Bull.* **1990**, *38*, 3314 .

[12] a) See ref. [1b]; b) A. J. Speziale, C. C. Tung, K. W. Ratts, A. Yao, *J. Am. Chem. Soc.* **1965**, *87*, 3460; for platinum- and gold-catalyzed in situ generation of sulfur ylides, see: c) P. W. Davies, S. J. C. Albrecht, *Angew. Chem.* **2009**, *121*, 8522; *Angew. Chem. Int. Ed.* **2009**, *48*, 8372.

[13] For selected examples, see: a) W. Ando, T. Yagihara, S. Tozune, T. Migita, *J. Am. Chem. Soc.* **1969**, *91*, 2786; b) W. Ando, T. Yagihara, S. Tozune, I. Imai, J. Suzuki, T. Toyama, S. Nakaido, T. Migita, *J. Org. Chem.* **1972**, *37*, 1721; c) M. Ma, L. Peng, C. Li, X. Zhang, J. Wang, *J. Am. Chem. Soc.* **2005**, *127*, 15016; d) S. C. Valdez, J. L. Leighton, *J. Am. Chem. Soc.* **2009**, *131*, 14638. For variations employing in situ-generated diazo compounds, see: e) V. K. Aggarwal, A. Thompson, R. V. H. Jones, M. C. H. Standen, *J. Org. Chem.* **1996**, *61*, 8368; f) V. K. Aggarwal, E. Alonso, I. Bae, G. Hynd, K. M. Lydon, M. J. Palmer, M. Patel, M. Porcelloni, J. Richardson, R. A. Stenson, J. R. Studley, J. Vasse, C. L. Winn, *J. Am. Chem. Soc.* **2003**, *125*, 10926.

[14] a) J. C. Martin, R. J. Arhart, *J. Am. Chem. Soc.* **1971**, *93*, 2339; b) J. C. Martin, R. J. Arhart, *J. Am. Chem. Soc.* **1971**, *93*, 2341; c) I. C. Paul, J. C. Martin, E. F. Perozzi, *J. Am. Chem. Soc.* **1971**, *93*, 6674; d) R. J. Arhart, J. C. Martin, *J. Am. Chem. Soc.* **1972**, *94*, 4997; e) I. C. Paul, J. C. Martin, E. F. Perozzi, *J. Am. Chem. Soc.* **1972**, *94*, 5010; f) J. C. Martin, R. J. Arhart, J. A. Franz, E. F. Perozzi, L. J. Kaplan, *Org. Synth.* **1977**, *57*, 22.

[15] a) J. C. Martin, R. J. Arhart, *J. Am. Chem. Soc.* **1971**, *93*, 4327; b) J. C. Martin, R. J. Arhart, *J. Am. Chem. Soc.* **1972**, *94*, 5003; c) J. C. Martin, J. A. Franz, R. J. Arhart, *J. Am. Chem. Soc.* **1974**, *96*, 4604; d) J. A. Franz, J. C. Martin, *J. Am. Chem. Soc.* **1975**, *97*, 583.

[16] For selected applications of **1** as a dehydrating reagent in total synthesis, see: a) P. S. Baran, J. M. Richter, *J. Am. Chem. Soc.* **2004**, *126*, 7450; b) A. Kuramochi, H. Usuda, K. Yamatsugu, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2005**, *127*, 14200; c) K. C. Nicolaou, Q.-Y. Toh, D. Y.-K. Chen, *J. Am. Chem. Soc.* **2008**, *130*, 11292; d) J. M. Richter, Y. Ishihara, T. Masuda, B. W. Whitefield, T. Llamas, A. Pohjakallio, P. S. Baran, *J. Am. Chem. Soc.* **2008**, *130*, 17938; e) K. C. Nicolaou, H. Zhang, A. Ortiz, P. Dagneau, *Angew. Chem.* **2008**, *120*, 8733; *Angew. Chem. Int. Ed.* **2008**, *47*, 8605; f) M. Movassaghi, M. Tjandra, J. Qi, *J. Am. Chem. Soc.* **2009**, *131*, 9648.

[17] For pioneering work on carbonyl-stabilized sulfonium ylides, see: a) ref. [8b]; b) K. W. Ratts, A. N. Yao, *J. Org. Chem.* **1966**, *31*, 1185; c) B. M. Trost, *J. Am. Chem. Soc.* **1967**, *89*, 138; d) H. Nozaki, K. Nakamura, M. Takaku, *Tetrahedron* **1969**, *25*, 3675; e) L. Field, H.-K. Chu, *J. Org. Chem.* **1977**, *42*, 1768; f) J. Galloy, W. H. Watson, D. Craig, C. Guidry, M. Morgan, R. McKeller Jr. , A. L. Ternay, G. Martin, *J. Heterocycl. Chem.* **1983**, *20*, 399; g) S. Furukawa, J. Igarashi, M. Watanabe, T. Kinoshita, *Chem. Pharm. Bull.* **1990**, *38*, 227.

[18] Interestingly, a survey of solvents indicated that this process was particularly tolerant with respect to the reaction medium. A broad range of solvents, ranging from toluene to acetonitrile, all

allowed the formation of **4a** in excellent yields. See the Supporting Information for details.

[19] a) K. W. Ratts, A. N. Yao, *J. Org. Chem.* **1966**, *31*, 1689; b) K. W. Ratts (Monsanto Co.), US 3538229, **1970**.

[20] Analogous diazo compounds are not common in the literature. For a rare example, see: V. M. Balci, R. Schalenbach, E. Vogel, *Angew. Chem.* **1981**, *93*, 816; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 809.

[21] a) G. D. Daves, Jr., W. R. Anderson, Jr., M. V. Pickering, *J. Chem. Soc. Chem. Commun.* **1974**, 301; b) K. H. Park, G. A. Gray, G. D. Daves, Jr., *J. Am. Chem. Soc.* **1978**, *100*, 7475; c) K. H. Park, G. D. Daves, Jr., *J. Org. Chem.* **1980**, *45*, 780; d) K. Hartke, D. Strangemann, *Heterocycles* **1986**, *24*, 2399; e) K. Hartke, D. Teuber, H.-D. Gerber, *Tetrahedron* **1988**, *44*, 3261; f) H. H. Wendebourg, K. Hartke, *Synthesis* **1989**, 329; g) A. Fürstner, M. Alcarazo, K. Radkowski, C. W. Lehmann, *Angew. Chem.* **2008**, *120*, 8426; *Angew. Chem. Int. Ed.* **2008**, *47*, 8302.

[22] The one-step synthesis reported herein is a significant improvement from previous reports. Compounds related to **6a–k** were previously accessible only through (often lengthy) multistep sequences. See references [21c] and [21d].

[23] The amounts of sulfurane **1** could be reduced to 1.0 equivalents with only a marginal decrease in yield. For example, reaction of **3a** with 1.0 equivalents of **1** gave ylide **4a** in 85 % yield. See the Supporting Information for details.

[24] CCDC 776545 (**4a**), 776546 (**4g**), 776547 (**4j**), 776548 (**4l**), 776550 (**4m**), 776549 (**4n**), 785393 (**4o**), 776551 (**6d**), 776552 (**6k**), 776553 (**7m**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[25] This agrees with theoretical studies which exclude the role of d orbitals in hypercoordinate molecules in second-row elements: see: E. Magnusson, *J. Am. Chem. Soc.* **1990**, *112*, 7940.

[26] K.-T. H. Wei, I. C. Paul, M.-M. Y. Chang, J. I. Musher, *J. Am. Chem. Soc.* **1974**, *96*, 4099.

[27] Such a process is mechanistically related to the Smiles rearrangement: a) J. F. Burnett, R. E. Zalher, *Chem. Rev.* **1951**, *49*, 273; b) W. E. Truce, E. M. Kreider, W. W. Brand, *Org. React.* **1970**, *18*, 99.

[28] a) M. Takaku, Y. Hayasi, H. Nozaki, *Tetrahedron* **1970**, *26*, 1243. For Grignard reagent-initiated rearrangements, see ref. [17d]; b) For recent reviews on sulfur-mediated rearrangements, see: *Topics in Current Chemistry*, Springer, Berlin, **2007**, *274* and *275*.

[29] The geometry of (***E***)-**7a** was determined through NOE experiments. See the Supporting Information for details.