A Novel Practical Reaction of Diarylalkynes With Sulfur Trioxide: Oxidation to 1,2-Diketones

Victor O. Rogatchov,¹ Victor D. Filimonov,^{*1} Mehman S. Yusubov²

^a Department of Organic Chemistry, Tomsk Polytechnic University, Tomsk, 634034, Russia

^b Department of Chemistry Siberian Medical University, Tomsk, 634050, Russia Fax +7(3822)415235; E-mail: filim@org.chtd.tpu.edu.ru

Received 19 January 2001

Abstract: A new reaction of arylalkynes with the SO_3 -dioxane complex gives the corresponding aromatic 1,2-diketones in good yield.

Key words: alkynes, oxidations, ketones, sulfur trioxide

It is common knowledge that alkynes in acidic media, for example, in sulfuric acid, undergo hydration giving rise to the corresponding ketones.¹ Reactions of alkynes with the complex of SO₃ with dimethyl sulfide provided products of conjugated addition to triple bonds.² Terminal acetylenes are converted into corresponding sulfoacetylenes in the reaction with the SO₃-dioxane complex.³ Recently, we have disclosed that phenylacetylene in the reaction with the SO₃-dioxane complex gives rise to δ -sultones – 4,6-diphenyl-1,2-oxatiin.^{4,5}

In our attempts to extend this new reaction to some diarylalkynes (internal acetylenes), we have discovered that instead of formation of the sultone cycles, oxidation of triple bonds of the acetylenes into 1,2-diketones occurs. Although there are many reagents for oxidation of internal alkynes into 1,2-diketones, SO₃ has been unknown as an oxidant for this transformation (see review⁶). However, many of the known reagents for this purpose (e.g., KMnO₄, SeO₂, OsO₄, Tl(NO₃)₃, etc.) are toxic, rather expensive or require special reaction conditions.⁶ It is apparent that using SO₃ as an oxidant of alkynes is cheaper, safer and more convenient. To demonstrate the scope of the reaction, a series of acetylenic substrates 1a-h were subjected to oxidation by the SO₃-dioxane complex as a novel available reagent (Table).

So tolan (1a) is easily oxidized to benzil (2a) at 20-100 °C. Best yields of benzil (2a) in this reaction are achieved in dioxane as a solvent (Table). When chloroform or acetic anhydride have been used as solvents, the results were unsatisfactory. In most cases, the optimal temperature is 60 °C, though oxidation of tolan (1a) takes place at room temperature over a longer period. Temperature increase up to 100 °C resulted in strong acceleration of the oxidation reaction of tolan (1a), but the yield of benzil (2a) was reduced (Table, Scheme 1).

Sulfur trioxide in this reaction is reduced to SO_2 , the latter being fixed by qualitative probe with iodine. The oxidation reaction of alkyne **1a** by the SO_3 -dioxane complex has been found to be equally effective both in the presence and in the absence of air (argon medium). This significant fact demonstrates that sulfur trioxide is the true oxidant in the above reaction. The best preparative results (Table) were achieved when 4 equivalents of SO_3 per one equivalent of substrate **1a-c** was used.

It is important to note that the oxidation reaction with sulfur trioxide is very sensitive to the electronic nature of the acetylenic substrates and it probably has electrophilic character. Thus, methyltolan (**1b**) is oxidized just as fast as tolan (**1a**) with an almost quantitative yield. In contrast, alkyne **1c** containing the strong electron-withdrawing nitro-group is oxidized much slower and only provides a small yield of diketone **2c** (Table).



Scheme 1 a R=H, b R=CH3, c R=NO2

The reaction of the SO_3 -dioxane complex with dialkynes **1d**-**h** provides oxidation of one or both triple bonds depending on the structures of the substrates (Scheme 2). In the case of dialkynes **1d**, **e** with the close location of two

Synthesis 2001, No. 7, 01 06 2001. Article Identifier: 1437-210X,E;2001,0,07,1001,1003,ftx,en;E00601SS. © Georg Thieme Verlag Stuttgart · New York ISSN 0039-7881

Table Oxidation of Internal Alkynes by SO₃/C₄H₈O₂

Substrate	Temp. (°C)	Ratio of SO ₃ /sul strate (mol/mol)	b-Reaction time (min)	Product ^a	Yield ^b (%)	Mp (°C)	Lit. mp (°C)
1a	20	4	150	2a	57	94–95	
1a	60	2	120	2a	48	94–95	94–9511
1a	60	4	15	2a	99	94–95	
1a	100	4	5	2a	76	94–95	
1b	60	4	10	2b	92	29–30	3112
1c	60	4	120	2c	19	140–141	141-1427
1d	60	2	100	2d 3d	70 5	108–109 123–124	$\frac{106 - 107^{10}}{124 - 125^{10}}$
1e	60	2	100	2e 3e	37 16	174–175 192–193	- 193–194 ¹³
1f	60	8	30	3f	97	202-204	205-20613
1g	60	8	30	3g	98	105-106	106–107 ¹³
1h	60	8	30	3h	95	141–142	141-14214

^a All compounds give spectra (NMR, IR, MS) in accord with their proposed structures.

^b Yields refer to isolated, chromatographically pure products.



Scheme 2

triple bonds, we have observed that the SO_3 -dioxane complex oxidizes predominantly only one triple bond giving acetylenic diketones 2d, e. This circumstance not only allowed the successful oxidation of compound 1d to 1e (one

acetylene bond intact), but also led to the earlier unknown acetylene diketone 2e from alkyne 1e. Two moles of SO₃ per one mole of substrate 1d, e was used.

Synthesis 2001, No. 7, 1001-1003 ISSN 0039-7881 © Thieme Stuttgart · New York

Minor quantities of tetraketones **3d** and **3e** were also formed in the reaction of **1d**, **e** to diketones **2d** and **2e**. In the case of two- or tetra-fold increase of SO₃ per 1 mol of substrate **1d**, **e**, the formation of diketones **2d**, **e** dominates over the formation of tetraketones **3d**, **e**, the total yield of the oxidation products being considerably reduced. All attempts to oxidize the remaining triple bond of compound **2d** by means of SO₃-dioxane complex have failed, and tetraketone **3d** was obtained in negligible yield.

Most likely, the selective oxidation of only one triple bond in the compounds **1d**, **e** is the result of the inhibitory effect on the part of the electron-withdrawing COCOPh group in diketones **2d**, **e** as it took place in the case of oxidation of nitrotolan (**1c**). However, this selective oxidation of only one triple bond in diacetylenes **1d**, **e** by means of SO₃-dioxane complex is useful for organic synthesis. Only three oxidizers capable to transform selectively diacetylenes with isolated triple bonds into corresponding acetylenic 1,2-diketones–PhI(OCOCF₃)₂,⁷ I₂/DMSO,⁸ PdCl₂/ DMSO^{9,10} were known earlier.

In contrast, dialkynes 1f-h have more separated triple bonds, and the SO₃-dioxane complex easily oxidizes both triple bonds giving tetraketones 3f-h with almost quantitative yields (Table).

Thus, this new reaction of alkynes with SO_3 is of practical interest since it is a convenient and very cheap preparative method for synthesis of aromatic 1,2-diketones from aromatic alkynes.

IR spectra were taken on a UR-20 infrared spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX500 spectrometer. Uncorrected melting points were recorded on a Kofler apparatus.

Oxidation of Alkynes 1a-h by SO₃-dioxane Complex

A mixture of compounds **1a–h** (1 mmol) and SO₃-dioxane complex (4 mmol) was stirred at 60 °C for the times shown in the Table. The reaction mixture was poured into H_2O (50 mL) and extracted with Et₂O (50 mL). The solvent was removed in vacuo and the residue was purified and separated by chromatography (silica gel; benzenehexane, 1:1).

4-Phenylglyoxaloyl-7-(phenylethynyl)dibenzofuran (2e)

Mp: 174-175 °C.

IR (KBr): v = 1605, 1678 (C=O) cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 7.35 (m, 3H, Ar-H), 7.54 (m, 5H, Ar-H), 7.67 (m, 3H, Ar-H), 8.02 (d, 1H, *J* = 1.31 Hz, Ar-H), 8.03(m, 1H, Ar-H), 8.15 (m, 2H, Ar-H), 8.56 (dd, 1H, *J* = 0.52, 1.79 Hz, Ar-H).

¹³C NMR (80 MHz, CDCl₃): δ = 194.4 and 193.4 (C=O), 160.1, 156.3, 134.8, 132.9, 131.8, 131.4, 129.9, 129.5, 128.9, 128.5, 128.3, 128.2, 124.4, 124.3, 123.7, 123.5, 123.0, 118.9, 112.5, 112.1 (Ar-C), 89.6, 88.7 (alkynes).

Anal. Calcd. for $C_{28}H_{16}O_3$: C, 83.98; H, 4.02. Found: C, 84.01; H, 4.10.

Acknowledgement

We thank the Russian Foundation for Fundamental Researches (grant N 00–03–32812) for the financial support of this work.

References

- (1) Menashe, N.; Reshef, D.; Shvo, Y. J. Org. Chem. 1991, 56, 2912.
- (2) Lebedev, M. Y.; Balenkova, E. S. Zh. Org. Khim. **1991**, 27, 1388.
- (3) Zaborovski, Y. L.; Smirnov-Zamkov, I. V.; Staninec, V. I. Zh. Org. Khim. 1984, 20, 1774.
- (4) Yusubov, M. S.; Filimonov, V. D.; Rogachev, V. O. Zh. Org. Khim. 1996, 32, 1272.
- (5) Rogachev, V. O.; Yusubov, M. S.; Filimonov, V. D. Zh. Org. Khim. 1999, 35, 439.
- (6) Filimonov, V. D.; Yusubov, M. S.; Ki-Whan, C. Rus. Chem. Rev. 1998, 67, 725.
- (7) Vasil'eva, V. P.; Khalfina, I. L.; Karpitzkaya, L. G.; Merkushev, E. B. *Zh. Org. Khim.* **1987**, *23*, 2225.
- (8) Yusubov, M. S.; Filimonov, V. D. Synthesis **1991**, 131.
- (9) Ki-Whan, C.; Yusubov, M. S.; Filimonov, V. D. Synth. Commun. 1994, 24, 2119.
- (10) Yusubov, M. S.; Filimonov, V. D.; Vasilyeva, V. P.; Ki-Whan, C. *Synthesis* **1995**, 1234.
- (11) Aldrich Catalogue/Handbook of Fine Chemicals; 1988-1989.
- (12) Kwart, H.; Baevsky, M. J. Am. Chem. Soc. 1958, 80, 580.
- (13) Burke, W. J.; Bishop, I. L.; Warbunton, J. A. J. Org. Chem. 1962, 27, 4003.
- (14) Fuson, R. C.; Maynert, E. W.; Tan, Tzi-Lieh.; Trumbull, E.
 R.; Wassumund, F. W. J. Am. Chem. Soc. 1957, 79, 1938.

Downloaded by: Florida International University. Copyrighted material