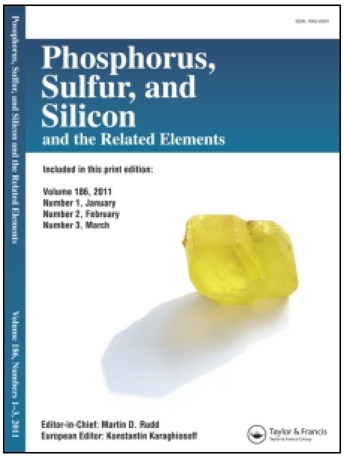
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTION OF BENZOYLACETONE WITH CHLOROSULFONIC ACID

Jatinder P. Bassin[a]
[a] Department of Chemistry, American University of Beirut, Beirut, Lebanon

To cite this Article Bassin, Jatinder P.(1996) 'REACTION OF BENZOYLACETONE WITH CHLOROSULFONIC ACID', Phosphorus, Sulfur, and Silicon and the Related Elements, 112: 1, 285 — 287

To link to this Article: DOI: 10.1080/10426509608046371

URL: http://dx.doi.org/10.1080/10426509608046371

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus, Sulfur, and Silicon, 1996, Vol. 112, pp. 285–287
Reprints available directly from the publisher
Photocopying permitted by license only

© 1996 OPA (Overseas Publishers Association)
Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

Communication

REACTION OF BENZOYLACETONE WITH CHLOROSULFONIC ACID

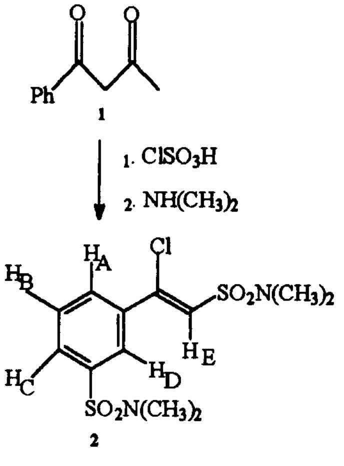
JATINDER P. BASSIN
Department of Chemistry, American University of Beirut, Beirut, Lebanon

(Received July 13, 1995; in final form November 1, 1995)

Key words: Benzoylacetone, chlorosulfonic acid.

Downloaded At: 19:11 28 January 2011

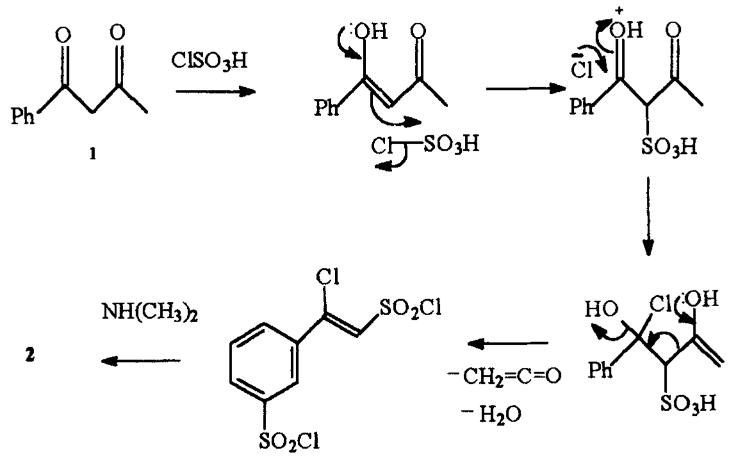
The work described in this paper forms part of our general research program concerned with the synthesis and biological properties of sulfonyl derivatives.[1-3] Previous work has demonstrated that benzalacetone with excess chlorosulfonic acid did not afford the expected 4,ω-disulfonyl chloride, but resulted in the formation of styrene-4,β-disulfonyl chloride.[4,5] In view of these interesting results, we decided to examine the reaction of benzoylacetone **1** with chlorosulfonic acid. The reaction of benzoylacetone **1** with a large excess of chlorosulfonic acid produced a gum which was treated with aqueous dimethylamine (Scheme 1). The resulting product **2** was identified by micro analytical and spectral data.



Scheme 1.

The mass spectrum of **2** showed the molecular ion, M/Z 352/354 indicating the presence of a chlorine atom, and fragment ions 317, 308, and 244 corresponding to loss of Cl, NMe_2, and SO_2NMe_2 respectively. The ^1H NMR analysis revealed aromatic protons (δ 8.1–7.0) and aliphatic protons (δ 3.0 and δ 2.8) which were assigned to the NMe_2 groups. The aromatic protons H_B and H_D both appeared as triplets from the coupling with protons H_A and H_C with coupling constant values 9.0 Hz and 2.4 Hz respectively. Proton H_A and H_C both appeared as multiplets owing to coupling with protons H_B and H_D. The presence of the vinylic chloride is supported by the absence of an E-alkenyl group (singlet due to the proton H_E) coupling as previously reported.[4] The structure of the product could therefore be assigned as **2**. The ^{13}C NMR spectrum of **2** showed ten chemical shifts, of which three were assigned to the quaternary carbon atoms on the basis of DEPT-135 technique, further confirming the structure of **2**.

Previous studies[6] have shown that reaction of certain substituted acetophenones with chlorosulfonic acid generated α-chloro-β-chlorosulfonylstyrenes, contrary to reports by Weston and Suter.[7] In the reaction of benzalacetone with chlorosulfonic acid Cremlyn *et al.*[4] postulated the formation of β-chlorosulfonylstyrene by first enolization followed by ω-chlorosulfonation and then migration of the sulfonyl moiety with elimination of ketene. Because of the additional activation provided by the styryl group, they suggested that side-chain substitution follows ring substitution. It is also likely that side-chain substitution follows ring substitution with **1** analogous to benzalacetone, i.e. *meta* substitution in the ring due to the influence of the carbonyl group. However, in the reaction of **1** with chlorosulfonic acid, direct sulfonation occurs on the methylene carbon (enol form) and the reaction then likely proceeds via the chlorohydrin intermediate: Scheme 2. Attempts to obtain the monosulfonyl chloride by reaction of **1** with chlorosulfonic acid (3 molar equivalents) in thionyl chloride were unsuccessful.



Scheme 2

EXPERIMENTAL

Melting points were determined using a Gallenkamp electric apparatus and are uncorrected. The NMR spectra were recorded with a Brucker AC250 spectrometer using tetramethylsilane as internal standard and deuterochloroform as solvent. IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer. Mass spectra were obtained with a VG micromass V15 spectrometer operating at 70 ev.

Downloaded At: 19:11 28 January 2011

α-Chloro-styrene-bis-3,β(N,N-dimethylsulfonamide) **2.** Benzoylacetone (5.0 g, 0.031 moles) was gradually added to Chlorosulfonic acid (36.0 g, 0.31 moles) at 0°. The mixture was heated on a water bath for 3 hours. It was slowly added to ice-water and the resulting sticky gum was directly treated with aqueous dimethylamine to yield the product **2**, which was recrystallised from ethanol, 3.9 g (33%), m.p. 133°; IR (KBr) ν_{max} 1600 (C=C stretch), 1340, 1160 (SO_2 stretch) cm^{-1}; ^1H NMR ($CHCl_3$-d) δ 7.65–8.10 (multiplet, 4H, aromatic protons), δ 7.03 (singlet, CH=CCl), δ 2.8, 3.0 (12H, SO_2NMe_2); MS m/z 352,354 M^+, 317 (M^+-Cl), 244 (M^+-SO_2NMe_2).

Anal. Calcd. for $C_{12}H_{17}ClN_2O_4S_2$: C, 41.0; H, 4.8; N, 8.0. Found: C, 41.3; H, 4.5; N, 7.8.

ACKNOWLEDGEMENTS

Thanks to Professor R. J. Cremlyn (University of Hertfordshire) for the use of his facilities and for his stimulating discussions. The award of a research grant by the American University of Beirut is acknowledged. Thanks are also due to Naim Maalouf for experimental assistance.

REFERENCES

1. R. J. Cremlyn, J. P. Bassin, S. Graham and D. Saunders, *Phosphorus, Sulfur and Silicon*, **84**, 135 (1993).
2. J. P. Bassin, R. J. Cremlyn, J. M. Lynch and F. J. Swinbourne, *Phosphorus, Sulfur and Silicon*, **78**, 55 (1993).
3. R. J. Cremlyn, J. P. Bassin, S. Farouk, M. Potterton and T. Mattu, *Phosphorus, Sulfur and Silicon*, **73**, 107 (1992).
4. R. J. Cremlyn, F. J. Swinbourne and Mrs. L. Goodman, *Phosphorus, Sulfur and Silicon*, **28**, 395 (1986).
5. R. J. Cremlyn, F. J. Swinbourne, P. A. Carter and L. Ellis, *Phosphorus and Sulfur*, **47**, 265 (1990).
6. D. D. Chapman, *Heterocycles*, **21**, 597 (1984).
7. A. W. Weston and C. M. Suter, *J. Am. Chem. Soc.*, **61**, 389 (1939).

Downloaded At: 19:11 28 January 2011