Tetrahedron Letters No. 1, pp 107 - 110, 1974. Pergamon Press. Printed in Great Britain.

GENERATION OF THE DIANION OF PHENYLSULFINYL ACETONE AND ITS REACTIONS

Isao Kuwajima and Hiroyuki Iwasawa
Laboratory of Organic Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo

(Received in Japan 25 October 1973; received in UK for publication 26 November 1973)

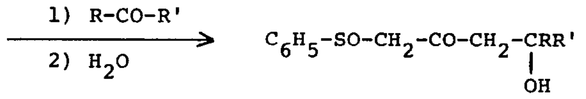
Much attention has recently been focussed on the method involving regiospecific introduction of alkyl group into the carbon atom neighboring to the carbonyl group. In connection with the studies of the reactions of β-keto sulfides[1] and β-keto sulfoxides,[2] we have examined the generation of the dianion of phenylsulfinyl acetone and the reactions with various electrophiles under the consideration that it would afford a useful synthetic way to the carbonyl compounds because of the easily removable character of sulfinyl group of β-keto sulfoxides[3] and of the expected different reactivities between the two carbanionic sites.[4]

For the generation of the dianion, phenylsulfinyl acetone was added to a suspension of sodium hydride (slight excess) in tetrahydrofuran under argon atmosphere, followed by treatment with an equimolar amount of n-butyllithium at 0° for 10—15 min. To the resulting red-colored solution was added tetrahydrofuran solution of benzophenone and it kept stirring for 4 hr at room temperature, which gave the corresponding addition product, 1,1-diphenyl-4-phenylsulfinyl-butan-1-ol-3-one (m.p. 133-4°, Anal. Calcd for $C_{22}H_{20}O_3S$: C, 72.51; H, 5.53; S, 8.78. Found: C, 72.75; H, 5.68; S, 8.75. nmr($CDCl_3$): 6.6τ (s, 2H), 6.2τ (s, 2H), and 2.4—2.7τ (m, 15H). ir(KBr): 3250, 1680 and 1030 cm^{-1}.) in 91% yield after purification with silica gel tlc separation of the reaction mixture.

Removal of phenylsulfinyl group from the product could easily be carried out by the Corey's procedure[3] to yield the corresponding 1,1-diphenyl-1-hydroxy-3-butanone nearly quantitatively.

Similarly, the corresponding addition products were obtained in good yields by treating the dianion (I) of phenylsulfinyl acetone with the other carbonyl compounds under similar reaction condition (see Table I).

$$C_6H_5\text{-SO-}CH_2\text{-CO-}CH_3 \xrightarrow[\text{2) } C_4H_9Li]{\text{1) NaH}} \left[C_6H_5\text{-SO-}\bar{C}H\text{-CO-}\bar{C}H_2\right] \quad Li^+ \quad Na^+$$



$$\xrightarrow[\text{2) } H_2O]{\text{1) R-CO-R'}} C_6H_5\text{-SO-}CH_2\text{-CO-}CH_2\text{-}\underset{\displaystyle OH}{\underset{|}{C}}RR'$$

Further, it was also shown that the dianion (I) reacted smoothly with alkyl halides to yield the corresponding substitution products in good yield (see Table II). For example, treatment of the dianion (I) with n-hexyl bromide at room temperature for 3 hr led to the formation of 1-phenylsulfinyl-2-nonanone (m.p. 75°. Anal. Calcd for $C_{15}H_{22}O_2S$: C, 67.64; H, 8.33; S, 12.02. Found: C, 67.91; H, 8.27; S, 11.94. nmr($CDCl_3$): 9.0τ (t, 3H), 8.6—8.9τ (m, 10H), 7.45τ (t, 2H), 4.2τ (d, 2H) and 2.3—2.5τ (m, 5H). ir(KBr): 2900, 2820, 1710 and 1030 cm^{-1}) in 79% yield.

$$\text{(I)} \quad + \quad \text{R-Hal} \longrightarrow C_6H_5SO\text{-}CH_2\text{-CO-}CH_2\text{-R}$$

Finally, we have examined the reaction of the dianion (I) with α,β-unsaturated carbonyl compounds and it was found that 1,4-addition reaction took place exclusively in the case of the reaction with α,β-unsaturated ester such as methyl crotonate, but 1,2-addition products were only isolated from the reactions with α,β-unsaturated ketone as shown in Table I.

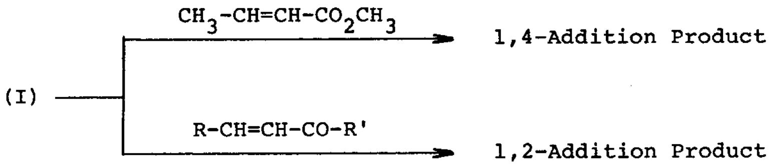


Table I. The Reactions of the Dianion (I) with Carbonyl Compounds

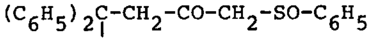
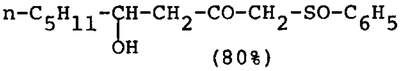
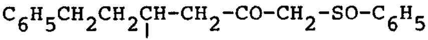
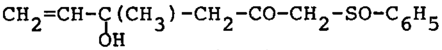
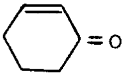
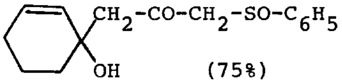
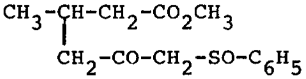
Carbonyl Compound	Reaction Condition		Product (Yield, %)
$(C_6H_5)_2C=O$	Room Temp.	4 hr	 $(C_6H_5)_2\underset{OH}{C}-CH_2-CO-CH_2-SO-C_6H_5$ (91%)
$n-C_5H_{11}-CHO$	Room Temp.	4 hr	 $n-C_5H_{11}-\underset{OH}{CH}-CH_2-CO-CH_2-SO-C_6H_5$ (80%)
$C_6H_5CH_2CH_2CHO$	Room Temp.	4 hr	 $C_6H_5CH_2CH_2\underset{OH}{CH}-CH_2-CO-CH_2-SO-C_6H_5$ (77%)
$CH_2=CH-CO-CH_3$	-40°	3 hr	 $CH_2=CH-\underset{OH}{C}(CH_3)-CH_2-CO-CH_2-SO-C_6H_5$ (65%)
	-40°	3 hr	 (75%)
$CH_3CH=CH-CO_2CH_3$	-40°	3 hr	 $CH_3-\underset{CH_2-CO-CH_2-SO-C_6H_5}{CH}-CH_2-CO_2CH_3$ (66%)

Table II. The Reactions of the Dianion (I) with Alkyl Halides

Halides	Reaction Condition		Product (Yield, %)
$n-C_6H_{13}-Br$	Room Temp.	3 hr	$n-C_6H_{13}-CH_2-CO-CH_2-SO-C_6H_5$ (79%)
$C_6H_5-CH_2-Br$	Room Temp.	4 hr	$C_6H_5CH_2-CH_2-CO-CH_2-SO-C_6H_5$ (73%)
$CH_2=CH-CH_2Br$	0°	5 hr	$CH_2=CH-CH_2-CH_2-CO-CH_2-SO-C_6H_5$ (64%)

References

1) I. Kuwajima and Y. Kurata, Chemistry Letters, 291 (1972).

2) I. Kuwajima and Y. Fukuda, Tetrahedron Letters, 327 (1973).

3) E. J. Corey and M. Chaykovsky, J. Amer. Chem. Soc., 87, 1345 (1965); G. A. Russell and G. J. Mikol, ibid., 88, 5498 (1966).

4) L. Weiler, ibid., 92, 6702 (1970); P. A. Grieco and C. S. Pogonowski, ibid., 95, 3071 (1973). See also, Org. Synthesis, 47, 92 (1967).