

## REACTION OF TERTIARY $\alpha$ -SULFONYL CARBANION WITH $\alpha$ -BROMOCARBONYL COMPOUNDS

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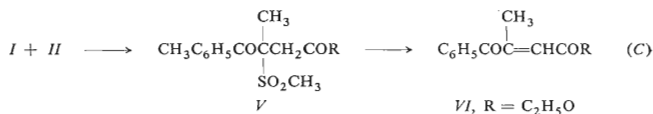
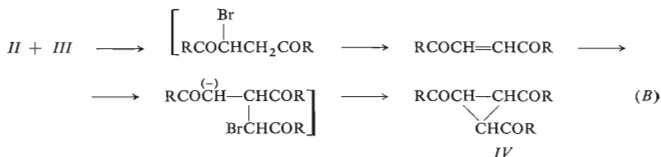
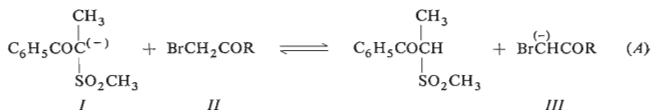
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The course of the reaction between the benzoylmethanesulfonylmethyl carbanion and  $\alpha$ -bromocarbonyl compounds in dimethyl sulfoxide is dependent on the nature of the substituent on the carbonyl group of the bromo ketone. The substituents with electron accepting properties give triacylcyclopropanes, while substituents with electron donating properties lead to formation of dioxosulfones.

In an attempt at the preparation of 1,4-diphenyl-2-methyl-1,4-butanedione we observed that the reaction of benzoylmethanesulfonylmethyl carbanion and  $\omega$ -bromoacetophenone does not lead to the expected dioxosulfone but to *trans*-tribenzoylcyclopropane<sup>1</sup>. From the structure of the isolated derivative it is evident that the mechanism of this reaction is different from that in which it is reacted with sulfonium ylides stabilised with a carbonyl on  $\alpha$ -halogenocarbonyl compounds. Two carbon atoms of the ylide take part in the latter reaction and only one carbon of the carbonyl component<sup>2-4</sup>. However, only carbanion *III*, generated from  $\omega$ -bromoacetophenone, can be the precursor of the symmetrical molecule of tribenzoylcyclopropane.  $\beta$ -Oxosulfonyl carbanion *I* takes part in the reaction only as a strong base similarly as, for example, sodium hydride in the reaction with  $\alpha$ -halo ketones<sup>5</sup>.

In view of the fact that the analogous reaction of  $\alpha$ -bromo ketones with secondary  $\alpha$ -sulfonyl carbanion<sup>1</sup> gives rise to a single product only, we endeavoured to determine whether the use of tertiary benzoylmethanesulfonylmethyl carbanion would lead to triacetylcyclopropanes in the same unambiguous way. The results summarized in Table I show that the reaction course is dependent on the equilibrium reaction between the sulfonyl carbanion and the bromocarbonyl compound  $R-COCH_2Br$  (Scheme 1, Equation (A)). The position of the equilibrium is determined mainly by electronic properties of substituent R. Substituents with electron acceptor effect (phenyl, 4-bromophenyl) favour the formation of the carbanion *III* which in view of its high nucleophilicity reacts immediately with bromo ketone *II*. Subsequent reactions giving rise to cyclopropane *IV* are evidently analogous to the mentioned reaction between sodium hydride and halo ketones<sup>5</sup>. We consider the carbene mechanism of the formation of cyclopropanes as improbable because in the reaction mix-



In compounds *II* and *IV* (Equation (B)): *a* R = C<sub>6</sub>H<sub>5</sub>; *b* R = 4-BrC<sub>6</sub>H<sub>4</sub>; *c* R = 3-(CH<sub>3</sub>O)-4-(C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>O)C<sub>6</sub>H<sub>3</sub>; *d* R = 3,4,5-(CH<sub>3</sub>O)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>.

In compounds *II* and *V* (Equation (C)): *a* R = 4-CH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>; *b* R = *t*-C<sub>4</sub>H<sub>9</sub>; *c* R = C<sub>2</sub>H<sub>5</sub>O.

ture which contains cyclohexene in addition to the usual reactants we were never able to prove the presence of the corresponding cyclopropane derivative. The fact that triaroylcyclopropanes are also formed from 3-methoxy-4-benzyloxy- and 3,4,5-trimethoxy- $\omega$ -bromoacetophenone may be probably explained by the partial delocalisation of the charge from carbon C<sub>(1)</sub> of the phenyl nucleus caused by the introduction of the methoxyl group into position *meta*. The carbonyl compounds with substituents with electron donor properties (tert-butyl, 4-methoxyphenyl, ethoxyl) afford carbanion *III* reluctantly and the sole reaction which takes place is nucleophilic substitution of the bromo ketone with sulfonyl carbanion. The expected cyclopropane derivative is not formed even when excess sulfonyl carbanion is used. In this case the sole reaction product was a mixture of *cis*- and *trans*-olefins *VI* which was formed by base-catalysed elimination of methanesulfonyl group<sup>6,7</sup>.

## EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Samples for analysis were dried at room temperature and 0.1 Torr for 8 hours. The infrared spectra were measured in chloroform on a UR-10 (Zeiss) spectrophotometer.

TABLE I  
Cyclopropanes IV and Dioxosulfones V

Compound	Yield %	M.p., °C	Composition (mol. w.)	Calculated/Found		
				% C	% H	% S
<i>IVa</i>	75	216—217 <sup>a</sup>	—	—	—	—
<i>IVb</i>	70	201—203	C <sub>24</sub> H <sub>15</sub> Br <sub>3</sub> O <sub>3</sub> (591.1)	48.76 48.59	2.56 2.64	— —
<i>IVc</i>	42	131—133	C <sub>48</sub> H <sub>42</sub> O <sub>9</sub> (762.8)	75.57 75.23	5.54 5.32	—
<i>IVd</i>	53	244—245	C <sub>33</sub> H <sub>36</sub> O <sub>12</sub> (624.6)	63.45 63.41	5.82 5.82	—
<i>Va</i>	42	124—125	C <sub>19</sub> H <sub>20</sub> O <sub>5</sub> S (360.4)	63.31 63.70	5.59 5.47	8.89 8.46
<i>Vb</i>	56	108—109	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub> S (310.4)	61.90 62.28	7.14 7.34	10.32 10.51
<i>Vc</i>	61	<sup>b</sup>	C <sub>14</sub> H <sub>18</sub> O <sub>5</sub> S (298.4)	56.36 56.51	6.08 6.00	10.75 10.64

<sup>a</sup> Literature<sup>B</sup> gives 215°C; <sup>b</sup> oil.

#### Reaction of 2-(Methanesulfonyl)propiophenone with $\alpha$ -Bromocarbonyl Compounds

A mixture of 2-(methanesulfonyl)propiophenone (0.5 mmol) and sodium hydride (0.5 mmol) in dimethyl sulfoxide (2.5 ml) was stirred at 20°C under nitrogen for 45 minutes. After dilution with tetrahydrofuran (2.5 ml) a solution of  $\alpha$ -bromocarbonyl compound (0.5 mmol) in tetrahydrofuran (10 ml) was added and stirred for three hours. The mixture was poured into ice-cold 0.5M-HCl (50 ml) and worked up in the conventional manner. The products were isolated by chromatography on silica gel with light petroleum-ether, and, with the exception of substance *Vc*, they were crystallised from a mixture of ethyl acetate and light petroleum. The yields, melting points and analyses of the substances prepared are listed in Table I. The structure of all derivatives prepared were corroborated by mass and IR spectra.

#### Ethyl 3-Methyl-4-oxo-4-phenyl-2-butenolate (*VI*)

A mixture of 2-(methanesulfonyl)propiophenone (1.5 mmol) and sodium hydride (1.5 mmol) in dimethyl sulfoxide (7.5 ml) was stirred at 20°C under nitrogen for 45 minutes. The mixture was diluted with 7.5 ml of tetrahydrofuran and then additioned (dropwise) with a solution of ethyl bromoacetate (0.5 mmol) in tetrahydrofuran (7.5 ml). After three hours' stirring the mixture was worked up in the usual manner. Chromatography on a silica gel column afforded dioxosulfone *Vc* (20%) and ethyl *trans*-3-methyl-4-oxo-4-phenyl-2-butenolate (43%). For C<sub>13</sub>H<sub>14</sub>O<sub>3</sub> (218.2) calculated: 71.54% C, 6.46% H; found: 71.46% C, 6.52% H; PMR: 1.28 (t, *J* = 7 Hz, 3-H) 4.22 (q, *J* = 7 Hz, 2-H), 2.40 (d, *J* = 1.55 Hz, 3-H), 6.14 (q, *J* = 1.55 Hz, 1-H), 7.30—7.90 (mt, 5-H).

Further ethyl *cis*-3-methyl-4-oxo-4-phenyl-2-butenolate was isolated in 37% yield. For  $C_{13}H_{14}O_3$  (218.2) calculated: 71.54% C, 6.46% H; found: 71.39% C, 6.42% H; PMR: 1.00 (t,  $J = 7$  Hz, 3-H), 2.11 (d,  $J = 1.6$  Hz, 3-H), 3.97 (q,  $J = 7$  Hz, 2-H), 6.00 (q,  $J = 1.6$  Hz, 1-H), 7.30–7.95 (mt, 5-H).

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