

PREPARATION AND REACTIONS OF  $\alpha$ -KETO-KETENE MERCAPTALS

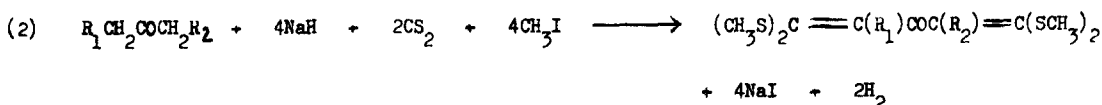
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The reaction of carbon disulphide with anions of compounds having two electron-withdrawing groups, like diethylmalonate and ethylacetoacetate has been known for a long time and recently was extensively studied<sup>(1-4)</sup>. The less activated aliphatic ketones react in several steps, with carbon disulphide and methyl iodide in the presence of various bases to yield  $\alpha$ -keto-ketene mercaptals.<sup>(5-10)</sup>

We have found that this series of reactions can be shortened by the use of carbon disulphide-methyl iodide-sodium hydride, a new combination not used simultaneously before. Addition of a ketone to this mixture is a fast reaction and accompanied by a methylene group is transformed into a ketene dimethyl mercaptal. The reaction occurs readily both with methylene and methyl groups and two such groups from both sides of a ketone react simultaneously (eqs. 1 and 2).



For example, 7.5 g 4-methoxyacetophenone (0.05 mole) is mixed with 3 g sodium hydride (80% in mineral oil, 0.1 mole), 6 g carbon disulphide (0.075 mole), 22.5 g methyl iodide (0.15 mole) and 80 ml of dry benzene. Dimethyl acetamide (10 ml) is added in portions and the mixture is stirred with occasional cooling for one hour. 40 g of ice and 200 ml water were added and the benzene extract of the mixture then yielded 8.2 g (80%) of 1-(4-methoxyphenyl)-3-dimercaptomethylpropen-1-one, m.p. 105°.

Results of experiments with several other ketones (mono- and di-substituted) are summarized in Tables I and II.

Table I

Results and spectral data for mono-substituted ketones<sup>a</sup> (eq. 1)

No.	Starting ketone	Yield(%)	mp/bp	C=O(cm <sup>-1</sup> )	λ max(μ)	(S-CH <sub>3</sub> )ppm
1	Diethylketone	30	94-6°/0.5mm	1645	305	2.20, 2.24
2	Pinacolone	45	162-4°/35mm	1635	317	2.20, 2.27
3	Cyclohexanone	23	118-22°/0.3mm	1615	310	2.20, 2.25
4	4-Methoxyacetophenone	80	103°	1595	345	2.25, 2.30
5	4-Chloroacetophenone	77	104°	1610	350	2.22, 2.27
6	4-Bromoacetophenone	75	108°	1610	350	2.22, 2.27
7	6-Methoxytetralone	60	78°	1590	355	2.30, 2.35
8	Desoxybenzoin	65	108°	1653	350	2.19, 2.25

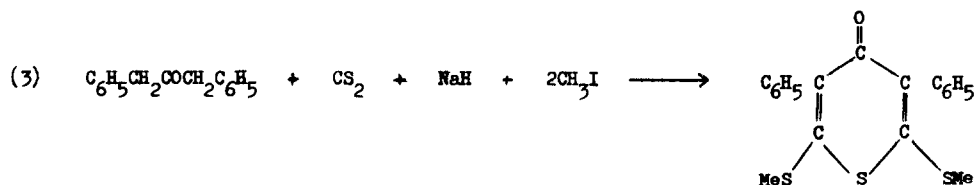
Table II

Results and spectral data for disubstituted ketones<sup>a</sup> (eq. 2)

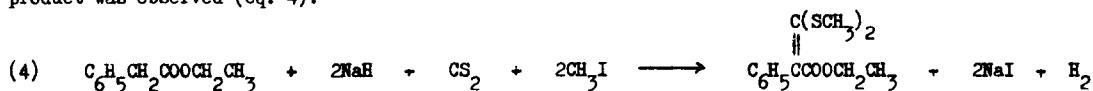
No.	Starting ketone	Yield(%)	mp/bp	C=O(cm <sup>-1</sup> )	max(μ)	(S-CH <sub>3</sub> )ppm
9	Acetone	33	134°	1590	365	2.40
10	Diethylketone	43	112°	1625	320	2.22, 2.27
11	Cyclohexanone	35	198-200°/0.3mm	1610	330	2.24, 2.29

<sup>a</sup> For all compounds good analyses were obtained.

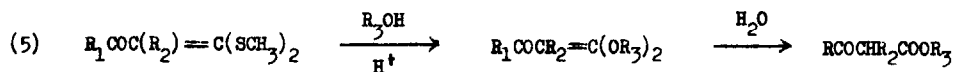
Dibenzylketone proved an exception giving a 1-thia- -pyrone derivative (eq. 3)



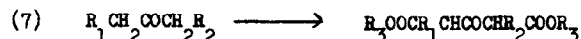
The reaction was also tried on simple esters. Here competition with a Claisen condensation was observed and esters like ethyl acetate and diethyl succinate gave very small yields of the corresponding ketene mercaptals. However, in the case of ethylphenylacetate 80% of the desired product was observed (eq. 4).



We have found that the dimethyl-mercaptal group is very quickly alcoholized in the presence of strong acids. By this reaction acetoacetic esters are obtained in good yields (eq. 5).



This reaction can be carried out without isolating the ketene-mercaptals (eqs. 6 and 7).



For example: To the benzene solution of 1-(4-methoxyphenyl)-3-dimercaptomethylpropen-1-one (former example), 20 ml ethanol and 1 g *p*-toluenesulphonic acid are added. The mixture is stirred for 2 hours at room temperature and refluxed for 15 min. After washing with bicarbonate the solution was evaporated and yielded 7.4 g (90%) of ethyl-4-methoxybenzoylacetate b.p. 139-142°/0.8 mm. Results with several other ketones are summarized in Table III.

Table III

Alcoholysis of dimethyl mercaptals prepared from ketones (eqs. 6 and 7)

Starting ketone	Product	b.p.	Yield
Acetophenone	Ethylbenzoylacetate	130-2°/1mm	90%
4-Methoxyacetophenone	Ethyl-4-methoxybenzoylacetate	139-42°/0.8mm	81%
Diethylketone	2,4-Dimethyl-3-ketoglutarate	131-4°/0.4mm	91%

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