

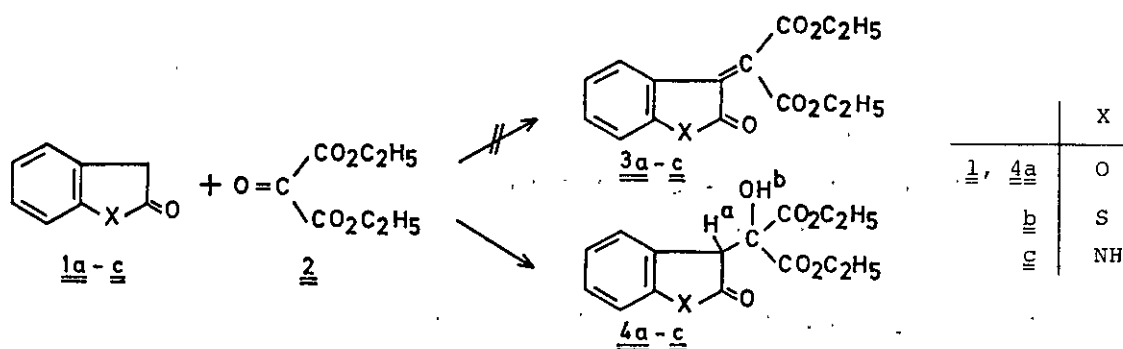
ADDITION OF DIETHYL MESOXALATE
TO BENZOFURANE-2(3H)-ONE, 1-BENZOTHIO-
PHENE-2(3H)-ONE AND 2-INDOLINONE

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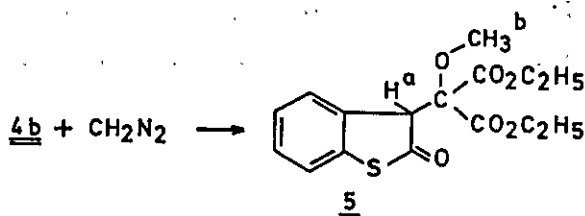
The condensation of a benzo-condensed lactone, thio-
lactone and lactam 1a-c with diethyl mesoxalate does not
yield α -methylene derivatives but only hydroxy compounds
4a-c, which cannot be dehydrated further.

Within the scope of our studies on the condensation of
lactones, thiolactones and lactams with ortho-esters^{1,2)}
and activated carbonyl compounds, we have also tried the
condensation with diethyl mesoxalate (2). Analogous to the
reaction with aldehyde or ketones^{3,4)}, we expected in connection
with the benzo[b]fused compounds substances 1a-c the corresponding
derivatives 3a-c. The reaction is effected by a slight excess of
the ester 2 without solvent and at higher temperature (Tab.).
However, it does not yield the expected condensation products
3a-c, but the stable adducts 4a-c.



Elimination of water from 4a-c to the α -[Bis(ethoxycarbonyl)methylene]-derivatives 3a-c, which in comparable reactions occurs spontaneously^{3,4)} cannot be attained even by heating and in the presence of acids, such as *p*-toluene-sulphonic acid. The same effect was observed with other adducts of dimethyl mesoxalate ester.⁵⁾ It is not clear whether the unexpected stability of the tertiary alcohols 4a-c can be due solely to the intramolecular hydrogen bond between the alcoholic proton H^b and the carbonyl groups. Even at high dilution, the IR-spectrum of 4a-c shows only a large, intense OH-band between 3400-3500 cm^{-1} . In the $^1\text{H-NMR}$ spectrum the proton H^b appears as a sharp singlet at $\tau=5.9$ and disappears when D_2O is added. The positions of both diastereoisomeric ethyl-ester groups vary slightly but distinctly ($\Delta\tau(\text{CH}_3)=0.05$ ppm; $\Delta\tau(\text{CH}_2)=0.02$ ppm).

It is of special interest that the alcoholic OH-group of 4b can be quickly methylated to the methyl ether 5 with diazomethane without adding acid catalysts as shown with 4b.



Substance	React. Temp. (°C)	% Yield	mp (°C)	Mol. Formula (Mol. Weight)	Analysis	
					C	H
<u>4a</u>	180	40	84	C ₁₅ H ₁₆ O ₇ (308.3)	calc. 58.44 found 58.63	5.23 5.13
<u>4b</u>	150	45	57	C ₁₅ H ₁₆ O ₆ S (324.3)	55.55 55.41	4.97 4.97
<u>4c</u>	120	35	113	C ₁₅ H ₁₇ NO ₆ (307.3)	58.63 58.43	5.58 5.58
<u>5</u>	10	95	98	C ₁₆ H ₁₈ O ₆ S (338.3)	56.80 57.02	5.36 5.45

Characteristic ¹H-NMR- and IR-Data of the Compounds 4a-c and 5

	NMR (CDCl ₃ ; τ -values)		IR (CHCl ₃ ; cm ⁻¹)		
	H ^a	H ^b	ν_{OH}	$\nu_{C=O(Ester)}$	$\nu_{C=O(Ring)}$
<u>4a</u>	5.30	5.85	3460	1740	1805
<u>4b</u>	5.24	5.95	3460	1730	1700
<u>4c</u>	5.53	5.65	3420	1740	1720
<u>5</u>	5.83	6.09	-	1720	1750

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