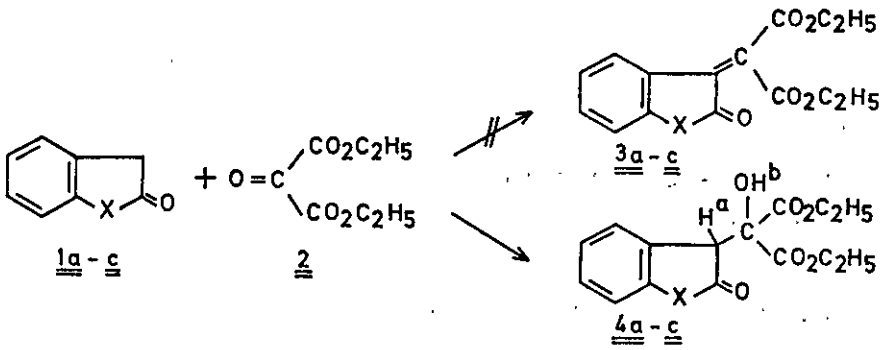
ADDITION OF DIETHYL MESOXALATE TO BENZOFURANE-2(3H)-ONE, 1-BENZOTHIOPHENE-2(3H)-ONE AND 2-INDOLINONE

Heinz Wolfers, Udo Kraatz and Friedhelm Korte

Institut für Ökologische Chemie der TU München and Institut für Ökologische Chemie der Gesellschaft für Strahlen- und Umweltforschung mbH München, D-805 Freising-Weihenstephan, Am Löwentor.

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

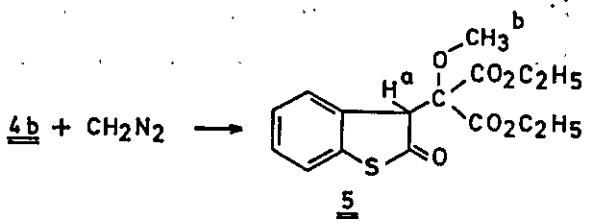
Within the scope of our studies on the condensation of lactones, thiolactones and lactams with ortho-esters[1,2] and activated carbonyl compounds, we have also tried the condensation with diethyl mesoxalate (2). Analogous to the reaction with aldehyde or ketones[3,4], we expected in connection with the 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.



	X
1, 4a	O
b	S
c	NH

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}H-NMR spectrum the proton H^b appears as a sharp singlet at τ=5.9 and disappears when D_2O is added. The positions of both diastereoisomeric ethyl-ester groups vary slightly but distinctly ($\Delta\tau(CH_3)$=0.05 ppm; $\Delta\tau$ (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	Analysis H
4a	180	40	84	$C_{15}H_{16}O_7$	calc.	58.44	5.23
				(308.3)	found	58.63	5.13
4b	150	45	57	$C_{15}H_{16}O_6S$		55.55	4.97
				(324.3)		55.41	4.97
4c	120	35	113	$C_{15}H_{17}NO_6$		58.63	5.58
				(307.3)		58.43	5.58
5	10	95	98	$C_{16}H_{18}O_6S$		56.80	5.36
				(338.3)		57.02	5.45

Characteristic ^{1}HNMR- and IR-Data of the Compounds 4a-c and 5

	NMR ($CDCl_3$; τ-values) H^a	NMR ($CDCl_3$; τ-values) H^b	IR ($CHCl_3$; cm^{-1}) ν_{OH}	IR ($CHCl_3$; cm^{-1}) $\nu_{C=O(Ester)}$	IR ($CHCl_3$; cm^{-1}) $\nu_{C=O(Ring)}$
4a	5.30	5.85	3460	1740	1805
4b	5.24	5.95	3460	1730	1700
4c	5.53	5.65	3420	1740	1720
5	5.83	6.09	-	1720	1750

REFERENCES

1 H. Wolfers, U. Kraatz and F. Korte, Chem. Ber., 106, 874 (1973).

2 H. Wolfers, U. Kraatz and F. Korte, in preparation.

3 H. Zimmer, D. Gracian and J. Rothe, J. Org. Chem. 25. 838 (1960).

4 R. Walter and H. Zimmer, J. Heterocycl. Chem. 1, 205 (1964).

5 K. Wastl, T. F. Lemke and M. Mosher, Synthesis 1974, 570.

Received, 21st April, 1975