first time. A monomercurial, a dimercurial and a double compound have been prepared. The structures have been elucidated.

Several new halogen derivatives of benzothienone have been synthesized in the course of this investigation.

The arsenicals of benzothienone have been prepared from 2-chloromercuri-5-benzothienone and some of their properties studied.

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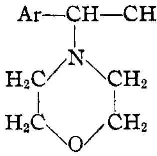
[CONTRIBUTION FROM THE ORGANIC CHEMICAL LABORATORY OF THE UNIVERSITY OF FLORIDA]

Derivatives of Morpholine. I. Addition to Conjugate Systems. I.

BY VINCENT E. STEWART AND C. B. POLLARD

α,β-Unsaturated ketones with addition compounds of piperazine have been described by us in previous papers.[1] Similar addition compounds with morpholine instead of piperazine have now been prepared, of the type



Procedure.—The α,β-unsaturated ketone (0.2 mole), prepared as previously described,[1a] was dissolved in a minimum amount of boiling, commercial heptane under reflux. As soon as solution was complete, anhydrous morpholine (0.3 mole = 0.1 mole excess) was added and the solution refluxed for ten hours. In the case of dibenzalacetone the amount of morpholine was doubled (0.6 mole), forming the bisymmetrical compound, no mono-addition product being isolated. The use of an excess of morpholine tended to make the addition more complete and obviated much difficulty in the recrystallization process. The addition compound separated out after standing in the ice-box for several hours. It was filtered, washed with a small amount of alcohol and then with a large amount of water to remove unreacted morpholine, air dried, and recrystallized from commercial heptane three times before being subjected to analysis. The yield of crude product was almost quantitative, although considerable loss was incurred in recrystallization.

The resulting addition compounds are listed in Table I.

TABLE I

Morpholine	M. p. (corr.), °C.	Formula	Analyses, % N Found	Calcd.
4-Chalcone	80.5- 81.0	$C_{19}H_{21}O_2N$	4.81	4.75
4-(4-Methylchalcone)	90.0- 90.5	$C_{20}H_{23}O_2N$	4.70	4.53
4-(4-Chlorochalcone)	89.5- 90.0	$C_{19}H_{20}O_2NCl$	4.28	4.25
4-(4'-Bromochalcone)	90.0- 90.5	$C_{19}H_{20}O_2NBr$	3.76	3.74
4-(4'-Methylchalcone)	90.0- 90.5	$C_{20}H_{23}O_2N$	4.50	4.53
4,4'-(Dibenzalacetone)-*bis*	99.6-100.2	$C_{25}H_{32}O_3N_2$	6.82	6.86

They are insoluble in cold water, soluble in alcohol and readily soluble in ether, acetone, toluene and halogenated solvents. They are all stable under ordinary conditions. Unlike the piperazine addition compounds, but like the piperidine addition compound reported by Georgi and Schwyzer,[2] they are decomposed by heating with water, yielding morpholine and the α,β-unsaturated ketone. Similarly, dilute hydrochloric acid decomposes them into the hydrochloride of morpholine and the unsaturated ketone.

The following α,β-unsaturated ketones failed to give addition compounds with morpholine under the above conditions: 4-methoxy-4-bromochalcone, 4-methoxy-4'-chlorochalcone, 4-methyl-4'-bromochalcone, 4,4'-dimethylchalcone, cinnamalacetophenone. As was pointed out in a previous paper,[1a] this apparent inertia of certain ketones is probably due to the instability of the addition compounds which prevented their isolation, rather than their failure to add. Thus, in the case of 4,4-dimethylchalcone the crude product was almost pure white, indicating that addition had occurred; yet, upon recrystallization from a variety of solvents, complete decomposition into the reactants took place.

Summary

1. Addition compounds of morpholine with α,β-unsaturated ketones have been prepared and studied.

2. The apparent lack of addition observed with certain ketones is believed to be due to the instability of the addition compounds.

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[1] (a) Stewart and Pollard, THIS JOURNAL **58**, 1980 (1936); (b) **59**, 2006 (1937).

[2] Georgi and Schwyzer *J. prakt. Chem.* **86**, 273-276 (1912).