

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

Derivatives of Piperazine. XI. Addition to Conjugate Systems. II

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Several addition compounds of piperazine with α,β -unsaturated ketones have been reported by us in a previous paper.¹ By the same experimental procedures, we have prepared other members of this series, as indicated in Table I, using ketones containing the "katio-enoid type of conjugate system."² The properties of these compounds are entirely analogous to those of the compounds previously reported.

compound. The reaction with 2-nitrochalcone yielded a dark viscous oil which repulsed further investigation. The addition of 3,4-methylenedioxy-4'-bromochalcone is surprising, in view of the fact that piperonalacetophenone (3,4-methylenedioxychalcone) did not undergo addition.

In a forthcoming publication we shall report addition reactions of morpholine with α,β -unsaturated ketones. This work may suffice to show

TABLE I

Piperazine	M. p. (corr.), °C.	Formula	Analyses, % N	
			calcd.	Found
1,4-Bis-(3-methylchalcone)	116.0-116.5	C ₃₈ H ₃₈ O ₂ N ₂	5.28	5.33
1,4-Bis-(3,4-methylenedioxy-4'-bromochalcone)	154.5-155.2	C ₃₆ H ₃₀ O ₆ N ₂ Br ₂	3.75	3.80
1,4-Bis-(4-methyl-4'-chlorochalcone)	149.2-149.6	C ₃₈ H ₃₆ O ₂ N ₂ Cl ₂	4.68	4.73
1,4-Bis-(3-methyl-4'-bromochalcone)	128.8-129.2	C ₃₆ H ₃₆ O ₂ N ₂ Br ₂	4.07	4.37
1,4-Bis-(3-methyl-4'-chlorochalcone)	125.6-126.0	C ₃₆ H ₃₆ O ₂ N ₂ Cl ₂	4.68	4.69
1,4-Bis-(4-methoxy-4'-chlorochalcone)	152.0-152.5	C ₃₆ H ₃₆ O ₄ N ₂ Cl ₂	4.44	4.52
1,4-Bis-(4-methyl-4'-bromochalcone)	153.0-153.5	C ₃₆ H ₃₆ O ₂ N ₂ Br ₂	4.07	4.29
1,4-Bis-(4-methoxy-4'-bromochalcone)	154.8-155.2	C ₃₆ H ₃₆ O ₄ N ₂ Br ₂	3.89	3.85
1,4-Bis-(3,4'-dimethylchalcone)	165.5-166.0	C ₃₈ H ₄₂ O ₂ N ₂	5.02	5.05

It was stated¹ that certain α,β -unsaturated ketones apparently do not yield addition compounds with piperazine. Cinnamalacetophenone, piperonalacetophenone, mesityl oxide, and 2-nitrochalcone, were treated successfully with piperazine under conditions which were successful with the foregoing compounds. Since cinnamalacetophenone undergoes chelate formation, it would scarcely be expected to form an addition

that the apparent lack of addition with certain ketones is probably due to the instability of the addition compounds. This would indicate a failure in isolating the compounds, rather than a lack of addition.

Summary

1. Other addition compounds of piperazine with α,β -unsaturated ketones have been studied. Ketones which did not add successfully to piperazine are reported.

(1) Stewart and Pollard, *THIS JOURNAL*, **58**, 1980 (1936).

(2) Robinson, "Solvay Reports," 1931.

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