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THE REACTIONS OF FLAVONE WITH SUBSTITUTED HYDRAZINES

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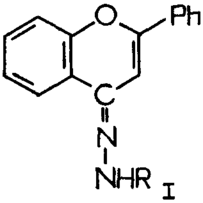
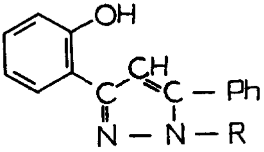
It has been repeatedly stated in the literature that flavone, analogously to γ-pyrones (1), does not react normally with carbonyl reagents (2), but the product is a pyrazole (3). The only example of a normally formed carbonyl derivative, flavone 2,4-dinitrophenylhydrazone (4), has been regarded so far as an exception.

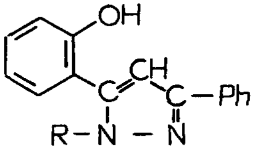
We reported (5) that a tosylhydrazone could be prepared from flavone in 50% yield. Recently we have found that 4-nitrophenylhydrazine, thiosemicarbazide and monoacetylhydrazine also give the normal carbonyl derivatives (I)of flavone. All these reactions take place in the presence of an acid catalyst.



I



II



III

Flavone reacts with phenylhydrazine hydrochloride in pyridine to yield a mixture of I, and the two isomeric pyrazoles II (3) and III (6) (R=Ph) .

Abnormal reactions of flavone take place with hydrazine and semicarbazide. Hydrazine hydrate in ethanol gives 3-(o-hydroxyphenyl)5-phenylpyrazole (II; R = H) prepared (3) formerly from o-hydroxy-dibenzoylmethane; semicarbazide hydrochloride in pyridine suffers decomposition yielding the same pyrazole (II; R = H) and biurea, $H_2NCONHNHCONH_2$.

The yields and m.ps of the products are shown in Table 1.The structures of the true carbonyl derivatives (I) have been proved by acid hydrolysis giving flavone in each case, and by comparison with the compounds obtainable

TABLE I

Reagent	R	I	II	III
4-Nitrophenyl-hydrazine	$-C_6H_4NO_2$	~ 70% 256-257°	-	-
Thiosemi-carbazide	$-CS.NH_2$	~80% 210°(d)	-	-
Monoacetyl-hydrazine	$-CO.CH_3$	~10% 290°	-	-
Phenyl-hydrazine	$-C_6H_5$	~ 28% 155°	~ 20% 117-119°	~ 20% 167-169°
Hydrazine hydrate	-H	-	~ 81% 140-145°	-

from 4-thionflavone or its methiodide (3) . The IR spectra and analyses were consistent with the structures given.

The formation of I is a normal reaction of flavone as long as the carbonyl reagent is not too basic to prevent the use of acid catalysis. The yields of I decrease and the reaction times required become longer with increasing basicity of the substituted hydrazine used.

The details of this research will be published elsewhere.

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