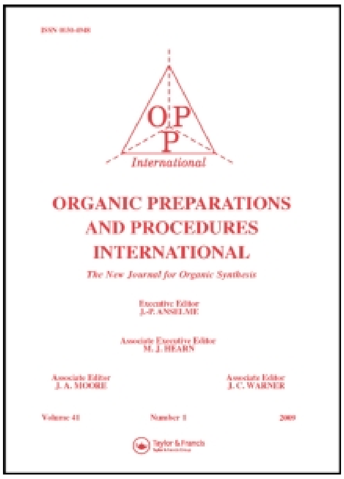

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AN IMPROVEMENT IN THE SYNTHESIS OF 1,2,4,9-TETRAHYDROCARBAZOL-3-ONE

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AN IMPROVEMENT IN THE SYNTHESIS OF 1, 2, 4, 9-TETRAHYDROCARBAZOL-3-ONE

Subnitted by
(07/06/93)

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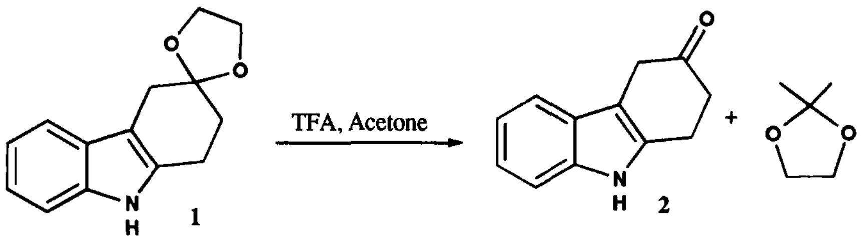
We recently needed to prepare a substantial quantity of ketone **2**, but found the published method[1,2] to be difficult and low-yielding on a large scale. Although the formation of the phenylhydrazone and the indole synthesis gave satisfactory results, freeing the ketal using *p*-toluenesulfonic acid and acetone resulted in poor yields and substantial amounts of colored impurities. This situation was exacerbated by attempts to purify the crude product by chromatography, particularly when using silica gel.



It appears that the free ketone is readily enolized and air-oxidized to highly-colored phenolic products. Removal of the *p*-toluenesulfonic acid with even a mild base like bicarbonate contributes to this process. To avoid this problem, the ketal was exchanged with acetone using trifluoroacetic acid. The acetone ketal produced is volatile (bp 92°) as is the catalyst trifluoroacetic acid, and they can be removed during evaporation of the solvent. This approach yielded ketone **2** in high yield.[3,4] TFA has been used for aqueous deketalizations in acetone.[3,4]

EXPERIMENTAL SECTION

Melting points are corrected. NMR spectra were run on a Hitachi 60 Mhz NMR. IR spectra were run on a MIDAC FT-IR. Commercial solvents and reagents were used without further purification.

3H-1,2,4,9-Tetrahydrocarbazol-3-one.- Recrystallized ketal **1**[2] (139.3 g, 0.608 mol) in a solution of 8 L acetone and 100 mL trifluoroacetic acid was refluxed under nitrogen. The reaction was complete in 2 hrs, as judged by TLC (hexane-ethyl acetate 4:1; silica gel; visualized by UV light). The solvent was distilled using a rotoevaporator under reduced pressure. The residue solidified and was recrystallized from methanol-water. The resultant crystals were essentially pure and were dried in a vacuum desiccator to yield 110.1 g (98%) of ketone **1** in two clean crops, mp 158.5-159.5° (corr.) ^{1}H NMR δ 2.8 (dd, 2H), 3.1 (dd, 2H), 3.6 (s, 2 H), 6.9-7.5 (m, 4 H), 8.0 (br. s, 1H). IR: 3472 (N-H) 1713 (C=O)

cm^{-1}. MS: m/z 185.

Anal. Calcd for $C_{12}H_{11}NO$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.48; H, 5.97; N, 7.48

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A SIMPLE PREPARATION OF 4-AMINO-5-ARYL-2H-IMIDAZOL-2-ONES

Submitted by (7/30/92)

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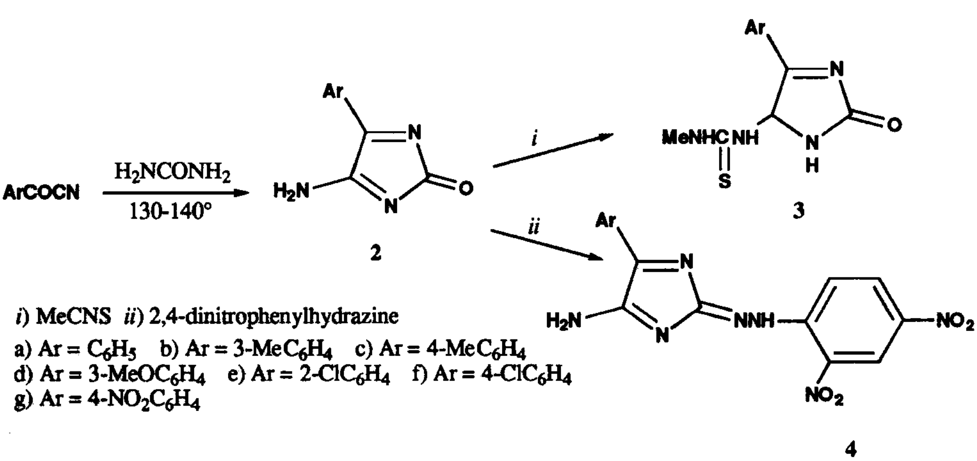
In continuation of our earlier work[1] on the utilization of α-oxonitriles **1** in heterocyclic syntheses and of our interest in imidazole chemistry, we now report a simple preparation of 4-amino-5-aryl-2H-imidazole-2-ones (**2**) by heating a mixture of **1** and urea at 130-140° for 2-6 hrs. The present synthesis affords the 4-amino-5-aryl-2H-imidazol-2-ones (**2a-g**) in 40-75% yields from **1a-g** as the only isolable products.



i) MeCNS *ii*) 2,4-dinitrophenylhydrazine
a) Ar = C_6H_5 b) Ar = 3-MeC_6H_4 c) Ar = 4-MeC_6H_4
d) Ar = 3-$MeOC_6H_4$ e) Ar = 2-ClC_6H_4 f) Ar = 4-ClC_6H_4
g) Ar = 4-$NO_2C_6H_4$