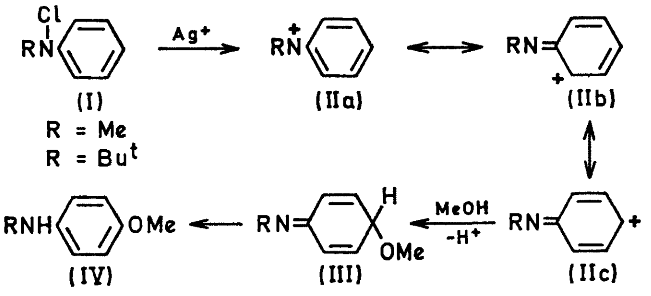
Conversion of Anilines into Derivatives of Cyclohexa-2,5-dienones

By PAUL G. GASSMAN* and GERALD A. CAMPBELL

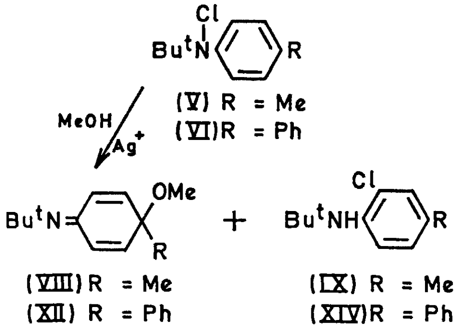
(*Department of Chemistry, The Ohio State University, Columbus, Ohio* 43210)

Summary The reaction of *p*-substituted *N*-chloro-anilines with silver ion in the presence of methanol gives good yields of derivatives of cyclohexa-2,5-dienone, and provides added evidence for the intermediacy of anilenium ions.

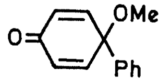
WE recently demonstrated that *N*-alkyl-*N*-chloro-anilines could be methoxylated in the *p*-position *via* silver-ion-assisted ionization in methanol,[1] and suggested that the silver-ion-assisted solvolysis of (I) may have produced (II) (with resonance contributors a—c). Reaction of (II) with solvent (MeOH) could then have given (III), which would be expected to isomerize rapidly under the reaction conditions to give the observed product (IV).



In order to demonstrate the transient existence of intermediates such as (III), we have studied the silver-ion-assisted solvolysis of (V) and (VI).† Treatment of *N*-(t-butyl)-*p*-toluidine (VII) in carbon tetrachloride at 0—5° for 1 hr. with *ca.* 10 equiv. of solid calcium hypochlorite gave, after filtration, a clear solution of (V) which was added to a methanolic solution of silver trifluoroacetate at 0—5°. Precipitation of silver chloride started immediately and the reaction mixture was stirred for 3 hr. at 0—5°. Removal of the silver chloride, followed by neutralization of the solution and isolation of the product, gave 70% of (VIII) and 17% of (IX) [yields based on (VII)]. The structures of the products were established by a combination of n.m.r., u.v., and i.r. spectroscopy. In addition, an authentic sample of (VIII) was prepared from 4-methoxy-4-methylcyclohexa-2,5-dienone[2] (X) through the initial addition of lithio-t-butylamine in ether to (X) followed by the addition of 1 equiv. of methyl-lithium and 12 hr. at reflux.[3]

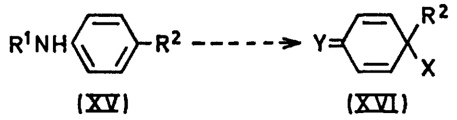


Treatment of 4-t-butylaminobiphenyl (XI) with calcium hypochlorite, as described above, gave an 85% yield of (VI). Silver-ion-assisted methanolysis of (VI) gave (XII), which was hydrolysed without isolation to (XIII), m.p. 91—93°. In addition to a 62% yield of (XIII), (VI) gave a 5% yield of 3-chloro-4-t-butylaminobiphenyl (XIV; R = Ph). The structure of (XIII) was firmly established by its n.m.r., u.v., and i.r. spectra.



(XIII)

The isolation of (VIII) and (XIII) from the silver-ion-assisted solvolyses of (V) and (VI), respectively, provides ample evidence for the existence of an intermediate such as (III) in the solvolytic path from (I) to (IV). In addition to establishing the validity of this hypothesis, the isolation of (VIII) and (XIII) illustrates a simple new method for the synthesis of derivatives of cyclohexa-2,5-dienone. In general our findings suggest that anilines of the general formula (XV; R^1 = alkyl, R^2 = carbonium ion stabilizing group) should be capable of being converted in high yield into compounds of the general formula (XVI), where Y is either R^1N or O, R^2 is a carbonium ion stabilizing group, and X is derived from a nucleophilic solvent or nucleophile present in solution. As recently pointed out by Corey and his co-workers, cyclohexa-2,5-dienone derivatives are valuable intermediates for the synthesis of a variety of organic compounds.[4]



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† Satisfactory elemental analyses were obtained on all new compounds except (V) and (VI), which were not purified on account of their instability.

[1] P. G. Gassman, G. Campbell, and R. Frederick, *J. Amer. Chem. Soc.*, 1968, **90**, 7377.
[2] E. Hecker and R. Lattrell, *Annalen*, 1963, **662**, 48.
[3] We thank Dr. R. Steppel for suggesting this synthetic approach.
[4] E. J. Corey, S. Barcza, and G. Klotmann, *J. Amer. Chem. Soc.*, 1969, **91**, 4782.