

A PHTHALANYLIDENEAMMONIUM SALT AND ITS TRANSFORMATIONS

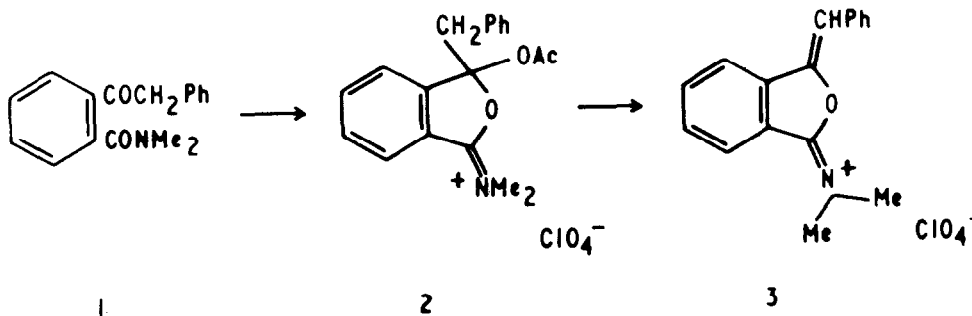
G.V. Boyd

Department of Chemistry, Chelsea College, London SW3 6LX

(Received in UK 18 May 1972; accepted for publication 25 May 1972)

In the course of our studies¹ of the cyclisation of compounds with the general formula $-OC.X.Y.CO-$ in the presence of acetic anhydride - perchloric acid, we investigated the action of the reagent on *N*-substituted *o*-phenylacetylbenzamides and obtained novel heterocyclic cations. This Letter concerns the synthesis and reactions of a representative example.

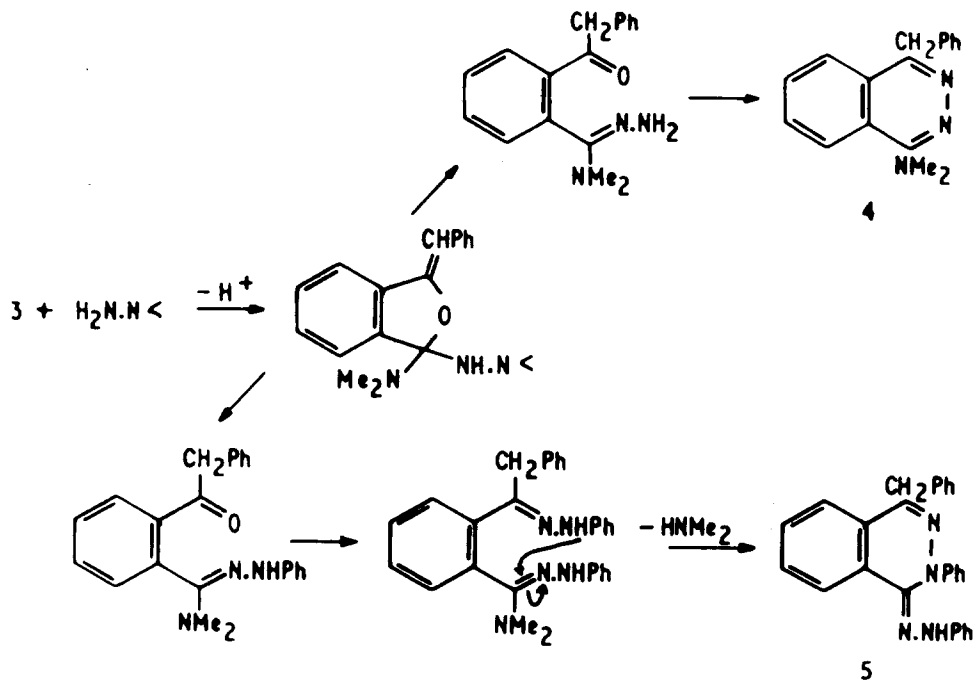
Treatment of the keto-amide (1)² with acetic anhydride and 70 % perchloric acid gave an unstable hygroscopic perchlorate, whose i.r. spectrum was consistent with the presence of the bicyclic compound (2). Brief heating with acetic acid produced the pale-yellow *N*-(3-benzylidenephthalan-1-ylidene)dimethylammonium perchlorate (3) (81 %),* m.p. 249 - 250.5°, i.r. (Nujol) 1685, 1600 and 1080 cm^{-1} , n.m.r. ($CF_3.CO_2H$) τ 1.7 - 2.62 (m, Ar), 3.03 (s, $-CH$), 6.02 (s, *N*-Me) and 6.15 (s, *N*-Me). The salt is unaffected by cold water; hot dilute hydrochloric acid hydrolyses it to benzylidenephthalide, a reaction that confirms the proposed constitution.

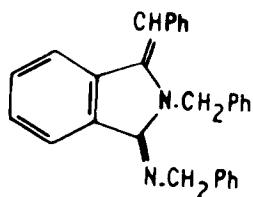


* Satisfactory analytical data were obtained for all new compounds.

The iminium salt (3) is highly susceptible to attack by nucleophilic reagents to yield a variety of products formed by ring-opening and recyclisation.

Brief treatment with hydrazine produced 1-benzyl-4-dimethylaminophthalazine (4) (91 %), m.p. 129.5 - 130.5°, $\bar{\nu}_{\max}$ 1610 cm^{-1} , τ (CDCl_3) 1.87 - 2.92 (m, Ar), 5.42 (s, CH_2) and 6.84 (s, 2 N-Me); but the reaction with phenylhydrazine was more complex, giving the orange phenylhydrazonodihydrophthalazine (5) (74 %), m.p. 156.5 - 157.5°, $\bar{\nu}_{\max}$ 3360w and 1600 cm^{-1} , τ (CDCl_3) 1.78 - 3.27 (m, Ar), 3.64 br (s, NH) and 5.83 (s, CH_2), with displacement of the dimethylamino group. Dimethylamine was also eliminated when the iminium perchlorate was boiled with benzylamine in acetic acid, the cream hydroperechlorate of 1-benzylidene-3-benzyliminoisoindoline (6), m.p. 248° (decomp.), $\bar{\nu}_{\max}$ 3210, 3130, 1650 and 1100 cm^{-1} , being formed in 89 % yield. The corresponding yellow base (6), m.p. 113 - 114°, i.r. 1640 and 1630 cm^{-1} , n.m.r. (CDCl_3) τ 2.0 - 2.9 (m, Ar), 3.95 (s, =CH) and 4.76 (s, 2 N- CH_2), was obtained by deprotonating the hydroperechlorate with aqueous sodium carbonate.

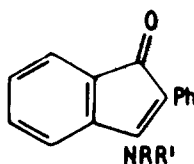




6

These transformations presumably occur by initial nucleophilic attack at C-1 of the iminium cation, followed by ring-fission. The hydrazine intermediate then cyclises to the dimethylaminophthalazine; but in the reaction with phenylhydrazine the intermediate condenses with a second molecule of the nucleophile and the ring-closure proceeds with the expulsion of dimethylamine. An analogous mechanism can be written for the benzylamine - acetic acid reaction.

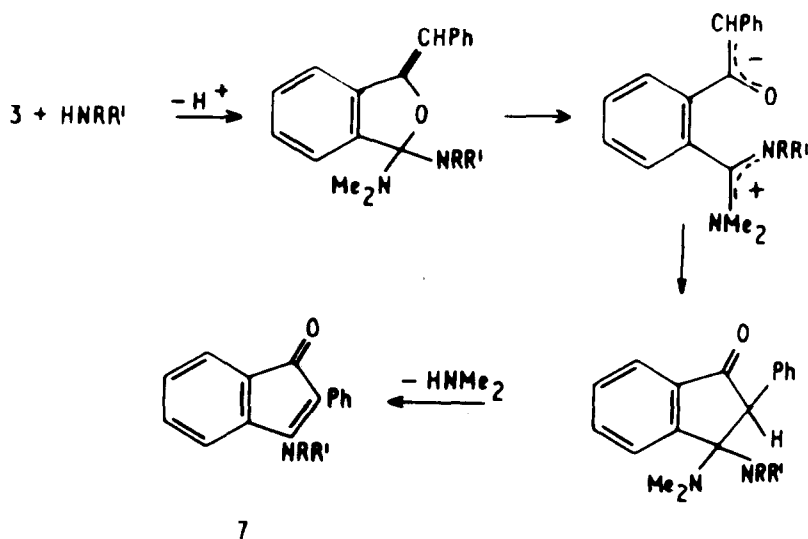
The action of hot ethanolic benzylamine on the perchlorate (3) followed a radically different course: the salt rapidly dissolved to a red solution, from which the known³ benzylaminophenylindenone (7a) was isolated in almost quantitative yield. Aqueous - alcoholic ammonia similarly gave 3-amino-2-phenylinden-1-one (7b)⁴ (36 %), ethanolic aniline the anilino-analogue (7c)⁴ (41 %) and dimethylamine yielded the red tertiary enamine (7d) (83 %), m.p. 101 - 102°.



7

- a: R = PhCH₂, R' = H
 b: R = R' = H
 c: R = Ph, R' = H
 d: R = R' = Me

It is suggested that these rearrangements occur by way of cross-conjugated 1,5-dipolar intermediates, as shown:



References

- ¹ G.V. Boyd and K. Heatherington, Chem. Comm., 1971, 348 and references cited there.
- ² M. Sekiya and Y. Terao, Yakugaku Zasshi, 1968, 88, 1085.
- ³ J. Freimanis and G. Vanags, Latvijas P.S.R. Zinatnu Akad. Vestis, Khim. Ser., 1961, 205 (Chem. Abs., 1963, 58, 4481).
- ⁴ G. Vanags, J. Freimanis and G. Zakis, Zhur. Obshchei Khim., 1957, 27, 2509.