

FORMATION OF 6,6-DIMETHYL-2,4-CYCLOHEXADIENYLIDENE-1-IMINES
 FROM PRIMARY AMINES AND 2,6-DIISOPROPYLPYRYLIUM SALTS

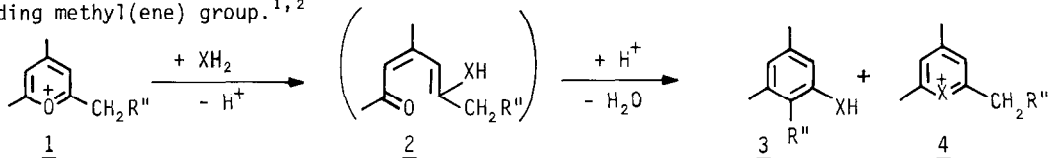
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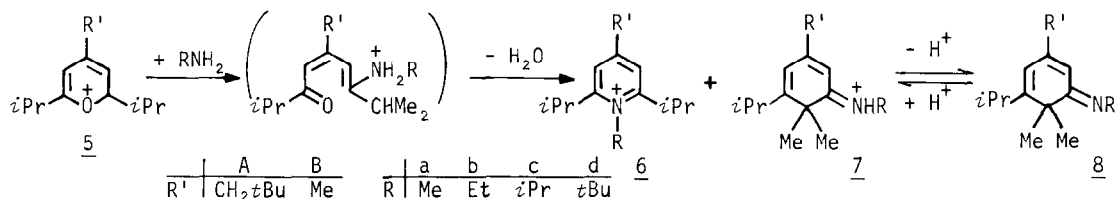
Abstract. 2,6-Diisopropyl-substituted pyrylium salts 5 react with primary amines RNH₂ yielding pyridinium salts, 6, and 6,6-dimethyl-2,4-cyclohexadienylidene-1-iminium salts, 7, in relative amounts depending on the group R (100/0 for R = Me, 93/7 for R = Et, 20/80 for R = *i*Pr, and 0/100 for R = *t*Bu) proving that steric factors are as important as aromatic delocalization in ANRORC reactions of pyrylium salts.

It is generally assumed that a more pronounced aromatic delocalization is the driving force in the conversion of pyrylium rings 1 into benzenic rings 3 (phenol, X = O, or aniline derivatives, X = NR) by incorporation of a methyl or methylene side-chain carbon atom from position 2 or 6 in the pyrylium salt on nucleophilic attack of alkali hydroxides or of primary amines, respectively. With primary amines RNH₂ as nucleophiles, a pyridinium salt 4 is the main cyclization product of the acyclic unstable intermediate 2 if the amino group is bonded to a primary carbon atom, but aniline derivatives result preferentially if the primary amine group is attached to a secondary or tertiary carbon atom and if the pyrylium salt has a 2- or 6- standing methyl(ene) group.^{1,2}



We show in the present communication that another type of product may result which, unlike benzene or pyridinium derivatives 3 and 4, is non-aromatic; this finding indicates that steric factors are as important as electronic delocalization in governing the ANRORC reactions of pyrylium salts.³

On treating 2,6-diisopropyl-substituted pyrylium perchlorates 5A or 5B⁴ with primary amines RNH₂ (R = Et, *i*Pr) we obtained in 95-99% total yield two perchlorates 6 and 7. These were separated by converting one of them (7) into the free base (8) under the action of aqueous ammonia, while the pyridinium perchlorate 6 remained unchanged; the bases 8 can be reconverted into their perchlorates 7.



The perchlorates 7Ac (m.p. 184-5°) and 7Bc (m.p. 157-8°) are stereochemically pure, but 7Ab contains comparable amounts of *syn-anti* diastereomers which have not been separated. No evidence for stereoisomerism of the configurationally labile bases 8 was apparent at room temperature. From elemental analysis, IR, ^1H - and ^{13}C -NMR spectral evidence, the structure of 8Ac is N,5-diisopropyl-3-neopentyl-6,6-dimethyl-2,4-cyclohexadienylidene-1-imine, and the other products 7 and 8 have analogous structures. The ^{13}C - and ^1H -NMR chemical shifts of 8Ac in CDCl_3 are shown in Fig. 1 together with the ^1H -NMR molar induced shifts (MIS) by $\text{Eu}(\text{fod})_3$ in CDCl_3 ; the complexation site is the sterically shielded nitrogen atom.

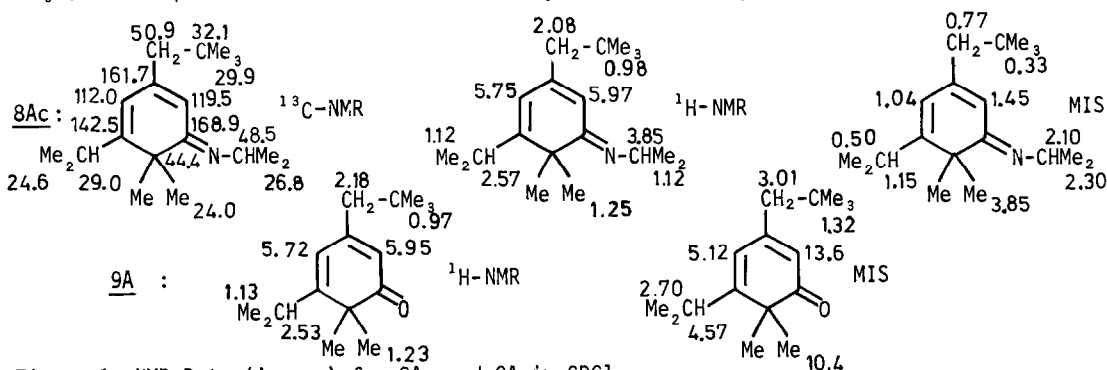


Figure 1. NMR Data (in ppm) for 8Ac and 9A in CDCl_3 .

Hydrolysis of 7Ac with refluxing aqueous sodium acetate yields 6,6-dimethyl-2,4-cyclohexadienone 9A, whose 2,4-dinitrophenylhydrazone has m.p. 147-8°. The ^1H -NMR chemical shifts (in CDCl_3) and the ^1H -NMR molar induced shifts by $\text{Eu}(\text{fod})_3$ in CDCl_3 , for 9A, are also given in Fig. 1.

The relative amounts pyridinium / iminium salt, i.e. 6/7, are for ethylamine 93/7 but for isopropylamine 20/80 %. The analogous reaction between methylamine and pyrylium perchlorate 5A yielded exclusively the pyridinium salt 6Aa; under the same experimental conditions, no reaction between *t*-butylamine and 5A was observed.

In conclusion, we demonstrated that when three contiguous isopropyl groups would lead to an overcrowded pyridinium cation (6Ac formed in low yield), the main product in ANRORC reactions of pyrylium salts is a non-aromatic intramolecular cyclization product 7 or 8 where the steric congestion is relieved.

References and Notes

1. A.T. Balaban, A. Dinculescu, G.N. Dorofeenko, G.W. Fischer, A.V. Koblik, V.V. Mezheritskii and W. Schroth, "Pyrylium Salts. Syntheses, Reactions and Physical Properties", *Adv.Heterocyclic Chem. Suppl.* Vol. 2, Editor A.R. Katritzky, Academic Press, New York, 1982.
2. C. Toma and A.T. Balaban, *Tetrahedron*, Suppl. 7, 9 (1966).
3. H.C. Van der Plas, *Acc.Chem.Res.*, 11, 462 (1978).
4. Pyrylium perchlorate 5B [m.p. 117°; ^1H -NMR (CDCl_3), δ (ppm) : 1.05 (s, 9H; 4- CH_2CMe_3), 1.47 (d, J=7 Hz, 12H; 2,6- CHMe_2), 2.93 (s, 2H; 4- CH_2), 3.55 (septet, J=7 Hz, 2H; 2,6- CHMe_2), 7.75 (s, 2H; 3,5- H_2)] and perchlorate 5A (m.p. 175°) were prepared by diacylating with isobutyric anhydride and 70% HClO_4 , diisobutene and *t*-butanol, respectively; A.T. Balaban and A. Bota, *Org.Prep.Proc.Int.*, 14, 31 (1982).

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