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OXIDATION OF N-AROYLHYDRAZONES OF o-HYDROXYARYL KETONES WITH LEAD(IV)ACETATE : A FACILE ROUTE TO AROMATIC o-DIKETONES

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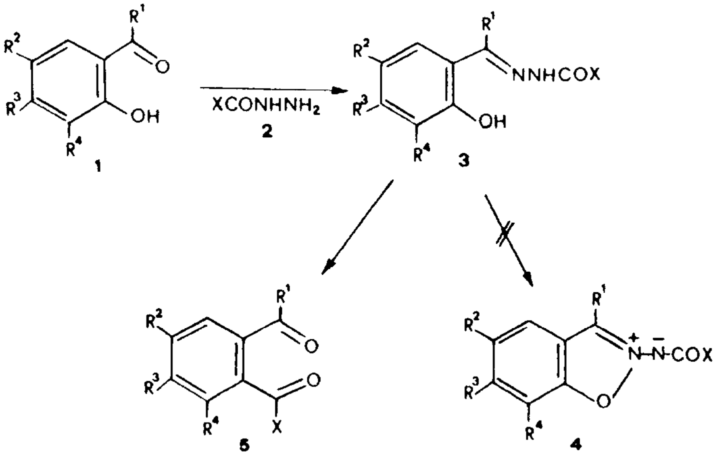
Abstract : N-Aroylhydrazones of o-hydroxyaryl ketones are oxidized with lead(IV)acetate to aromatic o-diketones in a synthetically useful reaction.

The reactions of nitrogen-containing derivatives of carbonyl compounds with lead(IV)acetate (LTA) and other metallic acetates, have been the subject of extensive research[1]. Hydrazones , unsubstituted or N-substituted, have been among those that have attracted considerable attention in this context.

In the course of our work on the synthesis of 1,2-benzisoxazole N-imine **4**, the oxidation of the N-aroylhydrazones **3** with LTA, was investigated as a possible route to the novel mesomeric betaine **4** (Scheme 1). However, the reaction of the previously unreported hydrazones **3** with the reagent did not give **4** and the diketone **5** was isolated instead.

SCHEME 1



The reaction sequence represents a simple and efficient route to the synthesis of the o-diketones 5, most of them unreported before, which may serve as useful synthetic intermediates in general and to various heterocycles in particular. The method is of wide scope (Table 1) and in many respects (readily accessible starting materials, simple experimental procedures and high yields of 5) superior to earlier literature ones, such as isolated cases of the oxidation of o-ethylacetophenone[2], indanes[3] or benzo[*c*]furans[4] with various oxidizing agents. A single case of a Friedel-Crafts acylation of benzene with o-acetylbenzoylchloride is also reported[5].

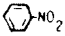
In a typical oxidation procedure, the hydrazone 3 (1 mol) in either dichloromethane or tetrahydrofuran (a much cleaner reaction is obtained in the latter solvent) was stirred with a slight excess of LTA (1.2 mol), at room temperature, for 2 h. A mild effervescence (evolution of N_2) was generally observed, upon addition of the oxidant. The reaction mixture was filtered, the filtrate was concentrated *in vacuo* and the oily residue was dissolved in the minimum ammount of chloroform and triturated with petroleum ether to give **5** as a crystalline product in high yield (Table 1).

Two discernible intense absorptions in the range of 1650-1680 cm^{-1} due to $\nu_{max}CO$ appear in the ir spectra of the diketones 5. In their mass spectra prominent peaks, corresponding to the molecular ions, were observed, while fragments $[M-X]^+$, $[M-R]^+$, $[M-CO]^+$, $[M-COX]^+$ and $[M-COR]^+$ were characteristic of the proposed structures.

Further confirmation of the stucture of **5** was obtained by a) independent synthesis of **5b** via acylation of benzene with o-acetylbenzoylchloride in the presence of $AlCl_3$[5]; b) condensation of **5a**, **5b** and **5i** with hydrazine to their corresponding phthalazines[9,10] in accord with published methods.

The mechanism of the reaction is currently under investigation.

TABLE 1

						Hydrazones 3[a,b,d]		o-Diketones 5[c,d]	
Compound	R^1	R^2	R^3	R^4	X	mp /°C	Yield %	mp /°C (lit.)	Yield %
a[e]	Me	H	H	H	Me	176-7	71	39-40 (38[illegible])	75
b	Me	H	H	H	Ph	164-5	81	96-7 (99[5])	80
c	Me	Me	H	H	Ph	190-2	80	118-20	68
d	Me	H	OMe	H	Ph	218-9	73	viscous oil	75
e	Me	Br	H	Br	Ph	246-7	89	175-6	87
f	Me	H	H	H		259-61	91	151-3	79
g	Me	H	H	H		240-2	75	115-6	93
h	Ph	H	H	H		220-1	78	138-9	78
i	Ph	H	H	H	Ph	158-60	65	145-6 (145-6[4])	95
j	Ph	H	OMe	H	Ph	203-5	75	viscous oil[f]	70

[a] Ketones 1 and hydrazines 2 used for the condensation to 3 (in either propan-1-ol or xylene at reflux temperature) were commercially available except for 1e[illegible], 2a[7] and 2f[8], which were prepared by published methods.

[b] Recrystallized from ethanol/chloroform mixture.

[c] Recrystallized from either ethanol or chloroform/petroleum ether mixture.

[d] Spectroscopic and analytical data were consistent with the proposed structures.

[e] Included to demonstrate the general applicability of the reaction.

[f] Solidifies upon long standing.

REFERENCES

1. a) R.N.Butler, F.L.Scott and T.A.F.O'Mahoney, Chem.Rev., 1975, 73, 93 and references therein; b) R.N.Butler, ibid., 1984, 84, 249 and references therein.
2. F.Weygand, H.Weber, E.Maekawa and G.Eberhardt, Chem.Ber., 1956, 89, 1994.
3. A.Dierichs and E.Preu, Chem.Ber., 1957, 90, 1208.
4. M.S.Newman, J.Org.Chem., 1961, 26, 2630 ; Beilstein, Handbuch der Organische Chemie, 7, 828.
5. R.Riemschneider, H.G.Kaahn and L.Hörner, Monatsh.Chem., 1960, 91, 1034.
6. A.J.Boulton, P.G.Tsoungas and C.Tsiamis, J.Chem.Soc. Perkin Trans. 1, 1986, 1665.
7. Beilstein, Handbuch der Organische Chemie, 2, 191.
8. R.Kahl, Chem.Zentr., 1904, 1493.
9. I.S.Walker, J.Chem.Soc., 1954, 3151.
10. M.A.Shah and G.A.Taylor, J.Chem.Soc., 1970, C, 1651.

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