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ACETOXYLATION OF ARYLACETONITRILES USING (DIACETOXYIODO)BENZENE

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<u>Abstract</u>: The direct α -acetoxylation of some arylacetonitriles using (diacetoxyiodo)benzene in the presence of dibenzoyl peroxide provides O-acetylated mandelonitriles in good yields.

Cyanohydrins are well-known starting materials for the preparation of several important classes of compounds. When their hydroxyl function is protected by acylation, alkylation, tosylation or silylation they are stabilised and can undergo further interesting reactions, in addition to those of the cyano-group. Their most prominent feature is their ability to serve as acyl anion equivalents in a variety of Michael additions and also in reactions with several electrophiles¹, including aldehydes² with which they afford products of benzoin type condensation. In the presence of a Lewis acid they behave as carbo- cations and yield with benzene phenylated nitriles³. Several O-acyl cyanohydrins are biologically active^{4,5}.

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Most methods for the preparation of cyanohydrins or their O-protected derivatives use carbonyl compounds as starting materials. The direct introduction of an oxygen substituent α to a nitrile is not a widely used reaction⁶, the most successful being those⁷ using lithium isopropylamide and molecular oxygen or MoO₅. The synthesis of racemic O-acetylated cyanohydrins of the general formula <u>3</u> is reported presently from arylacetonitriles, <u>1</u>, which undergo α -acetoxylation by reaction with (diacetoxylodo)benzene, <u>2</u>, in boiling acetonitrile. Best results were obtained in the presence of a radical initiator, e.g. <u>1a</u> after 3 h gave a 58% yield of <u>3a</u> which was increased to 85% when some dibenzoyl peroxide was added. By contrast, the use of a radical inhibitor such as tetrachloro-p-benzoquinone gave only 19% of <u>3a</u>.

 $\frac{MeCN, \Delta \quad OAc}{ArCH_2CN + PhI(OAc)_2} \xrightarrow{MeCN, \Delta} ArCHCN + PhI + AcOH$ $(PhCO)_2O_2$ $\underline{1a-d} \quad \underline{2} \qquad \underline{3a-d}$

(a: $Ar=C_6H_5$; b: $Ar=p-MeOC_6H_4$; c: $Ar=p-ClC_6H_4$; d: $Ar=p-O_2NC_6H_4$)

Acetonitrile reacts also with <u>2</u> but more slowly than <u>1</u>, since after 100 h reflux only 29% of acetoxyacetonitrile was formed, without peroxide. The reaction has an analogy to the α -acetoxylation⁸ and α -sulfonyloxylation⁹ of ketones, effected with <u>2</u> or iodine (III) reagents of the general formula PhI(OH)(OSO₂R). However, in contrast to ketones, nitriles appear to follow a homolytic rather than a heterolytic pathway. Homolysis occurs also in the reaction of <u>2</u> with some complex nitriles which undergo oxidative

dimerisation¹⁰. A similar pathway is likely to occur in acetonitrile itself, since during a polarographic study¹¹ it was found that two equivalents of acetic acid were slowly produced from <u>2</u> in this solvent at room temperature. This observation implies that after the abstraction of a H atom by <u>2</u>, the lack of the aryl group permits the dimerisation of $^{\circ}CH_2CN$, while at elevated temperature this reacts preferentially with PhI OAc to give the acetoxylated product. It should be mentioned that a third reaction mode has also been detected : when a concentrated solution of <u>2</u> in acetonitrile was briefly heated at 75 °C, a precipitate of an iodine(III) compound of unknown constitution was formed¹².

In conclusion, it appears that the direct α -acetoxylation of simple nitriles by (diacetoxylodo)benzene is a general reaction; work underway will show its scope.

Experimental

<u>General Procedure</u> : Equal quantities (0.05 mol each) of arylacetonitriles <u>la-d</u> and (diacetoxylodo)benzene 2 in acetonitrile (40 ml) containing dibenzoyl peroxide (0.0025 mol) were refluxed for 3 h. After removal of the solvent and volatiles in a rotary evaporator, the residue was chromatographed in a silica gel column using petroleum etherdichloromethane (3:1) as eluant. Compounds <u>3a-d</u> were eluted after some iodobenzene and unreacted nitrile as follows:

(±)<u>-O-acetyl-mandelonitrile</u> (or α -acetoxy-phenylacetonitrile), <u>3a</u>, in 85% yield; mp 30-31 °C (in the old literature¹³ it is described as an oil).

(±)<u>-O-acetyl-p-methoxymandelonitrile</u>, <u>3b</u>, in 80% yield; mp 37-38 °C (lit.¹⁴ mp 38-39).

(±)-<u>O-acetyl-p-chloromandelonitrile</u>, <u>3c</u>, in 79% yield; mp 30-32 °C (lit.¹⁵ mp 31-32).

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(±)<u>-O-acetyl-p-nitromandelonitrile</u>, <u>3d</u>, in 87% yield; mp 110-12 °C (from benzene-petroleum ether); IR: $\bar{\nu}$ =2150,1730,1500 cm⁻¹; ¹H NMR (CDCl₃): δ = 2.44 (s,3H),7.20-8.10 (m,5H); MS(70eV) :m/z (%) 220(M⁺,31), 205 (100), 194 (26), 177 (53), 161 (46). (Found: C,54.75;H, 3.44; N,12.67. C₁₀H₈N₂O₄ requires C,54.56; H,3.66; N,12.72.)

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