REACTIONS OF 3-CYANO-1-METHYLQUINOLINIUM METHYL SULPHATE WITH SOME C-ACIDS AND WITH *p*-NITROANILINE*

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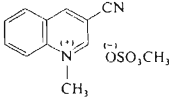
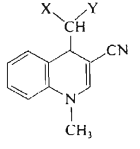
The action of malononitrile, ethyl cyanoacetate, dibenzoylmethane and/or *p*-nitroaniline on compound *I* in the presence of sodium methoxide gives rise to derivatives of 3-cyano-1-methyl-1,4-dihydroquinoline, *II* and *III*.

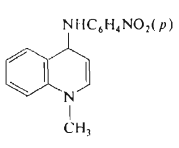
The positions 2 and 4 of 1-alkylquinolinium salts are electrophilic centres for nucleophilic additions. The possible nucleophilic agents are also anions of some C-acids, such as nitromethane[1], malononitrile[2] and ethyl cyanoacetate[2]. The formed derivatives of 1,4-dihydroquinoline have substituents at position 4. Attachment of



I



IIa, X, Y = CN
IIb, X = CN, Y = $COOC_2H_5$
IIc, X, Y = COC_6H_5



III

* Part IX of the series Quinoline and Isoquinoline Derivatives; Part VIII: This Journal *46*, 262 (1981).

a nitro group to position 3 increases the reactivity of the quinolinium salts and stability of the arising products[3].

We were interested in the behaviour of 3-cyano-1-methylquinolinium methyl sulphate toward compounds with an active methylene group, *viz.* malononitrile, ethyl cyanoacetate and dibenzoylmethane on the one hand, and *p*-nitroaniline on the other. The products, formed in the presence of sodium methoxide, were identified by IR and ^{1}H-NMR spectra as derivatives of 3-cyano-1-methyl-1,4-dihydroquinoline, *II* and *III*. The results show that in the studied reactions the 3-cyanoquinoline derivative *I* behaves in the same way as methiodide of 3-nitroquinoline[3].

EXPERIMENTAL

The temperature data are not corrected. The IR spectra were measured with a spectrophotometer Perkin–Elmer 325, ^{1}H-NMR spectra with an apparatus Varian XL-100-15 (100 MHz), tetramethylsilane being used as internal standard.

Reaction of Compound *I* with C-Acids and/or *p*-Nitroaniline

To a stirred suspension of *I* (1·5 g, 5·4 mmol) and the equivalent amount of a C-acid or *p*-nitroaniline in methanol (70 ml) was added dropwise a solution of sodium methoxide in methanol (5·4 mmol, 15 ml) at room temperature. The mixture was stirred for 1 h and the methanol was distilled off *in vacuo*. The residue was diluted with water and extracted into dichloromethane. The extract was washed with water and dried with $MgSO_4$. The solvent was removed by distillation and the residue was purified by crystallization.

2-(3-*Cyano*-1-*methyl*-1,4-*dihydro*-4-*quinolyl*)*malononitrile* (IIa), m.p. 146—147°C (ethanol–acetone), yield 80%. For $C_{14}H_{10}N_4$ (234·3) calculated: 71·78% C, 4·30% H, 23·92% N; found: 71·68% C, 4·60% H, 24·08% N. IR spectrum (KBr pellet, cm^{-1}): 2200*v* (CN), 1640*v* (C=C). ^{1}H-NMR spectrum (hexadeuterodimethyl sulphoxide–$CDCl_3$ 1 : 1, δ ppm): 3·36 (s, 3 H) NCH_3; 4·52—4·88 (m, 2 H), at 60°C 4·62 (bs, 2 H) C<u>H</u>$(CN)_2$ and CH(4); 7·02—7·68 (m, 5 H) benzene ring and CH(2).

Ethyl cyano(3-*cyano*-1-*methyl*-1,4-*dihydro*-4-*quinolyl*)*acetate* (IIb), m.p. 151—152°C (ethyl acetate–ethanol), yield 74%. For $C_{16}H_{15}N_3O_2$ (281·3) calculated: 68·31% C, 5·37% H, 14·94% N; found: 68·34% C, 5·43% H, 14·89% N. IR spectrum ($CHCl_3$, cm^{-1}): 2200*v* (CN), 1745*v* (C=O). ^{1}H-NMR spectrum ($CDCl_3$, δ ppm): 1·29 (t, 3 H, J = 7 Hz) CH_2<u>CH_3</u>; 3·33 (s, 3 H) NCH_3; 4·55 (d, 1 H, J = 5 Hz) C<u>H</u>$CNCO_2C_2H_5$; 6·93—7·45 (m, 5 H) benzene ring and CH(2).

1,3-*Diphenyl*-2-(3-*cyano*-1-*methyl*-1,4-*dihydro*-4-*quinolyl*)-1,3-*propanedione* (IIc), m.p. 174 to 175°C (ethanol–acetone), yield 81%. For $C_{26}H_{20}N_2O_2$ (392·5) calculated: 79·57% C, 5·14% H 7·14% N; found: 79·61% C, 5·34% H, 6·96% N. IR spectrum ($CHCl_3$, cm^{-1}): 2210*v* (CN), 1700 and 1670*v* (C=O), 1640*v* (C=C). ^{1}H-NMR spectrum ($CDCl_3$, δ ppm): 3·00 (s, 3 H) NCH_3; 5·02 (d, 1 H, J = 5 Hz) CH (4); 5·48 (d, 1 H, J = 5 Hz) C<u>H</u>$(COC_6H_5)_2$; 6·62—7·90 (m, 15 H) benzene rings and CH(2).

1-*Methyl*-4-(4-*nitroanilino*)-1,4-*dihydro*-3-*quinolinecarbonitrile* (III), m.p. 179—180°C (ethanol–ethyl acetate), yield 73%. For $C_{17}H_{14}N_4O_2$ (306·3) calculated: 66·66% C, 4·61% H, 18·29% N, found: 66·49% C, 4·84% H, 18·41% N. IR spectrum (KBr pellet, cm^{-1}): 3300*v* (NH), 2190*v* (CN); 1645*v* (C=C), 1595*v* (NO_2). ^{1}H-NMR spectrum (trideuteroacetonitrile, δ ppm): 3·28 (s, 3 H)

NCH_3; 5·20 (s, 1 H) CH(4); 6·64 (d, 2 H, $J = 8$ Hz) CH *meta* in respect to NO_2; 6·76—7·52 (m, 6 H) benzene ring, CH(2) and NH; 7·98 (d, 2 H, $J = 8$ Hz) CH *ortho* in respect to NO_2.

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