

SHORT
COMMUNICATIONS

Synthesis of Diethyl 3,4-Dicyano-5-hydroxy-2-oxo-7-phenyl-1,2,4a,7-tetrahydroquinoline-6,8-dicarboxylate and Its Reaction with Piperidine

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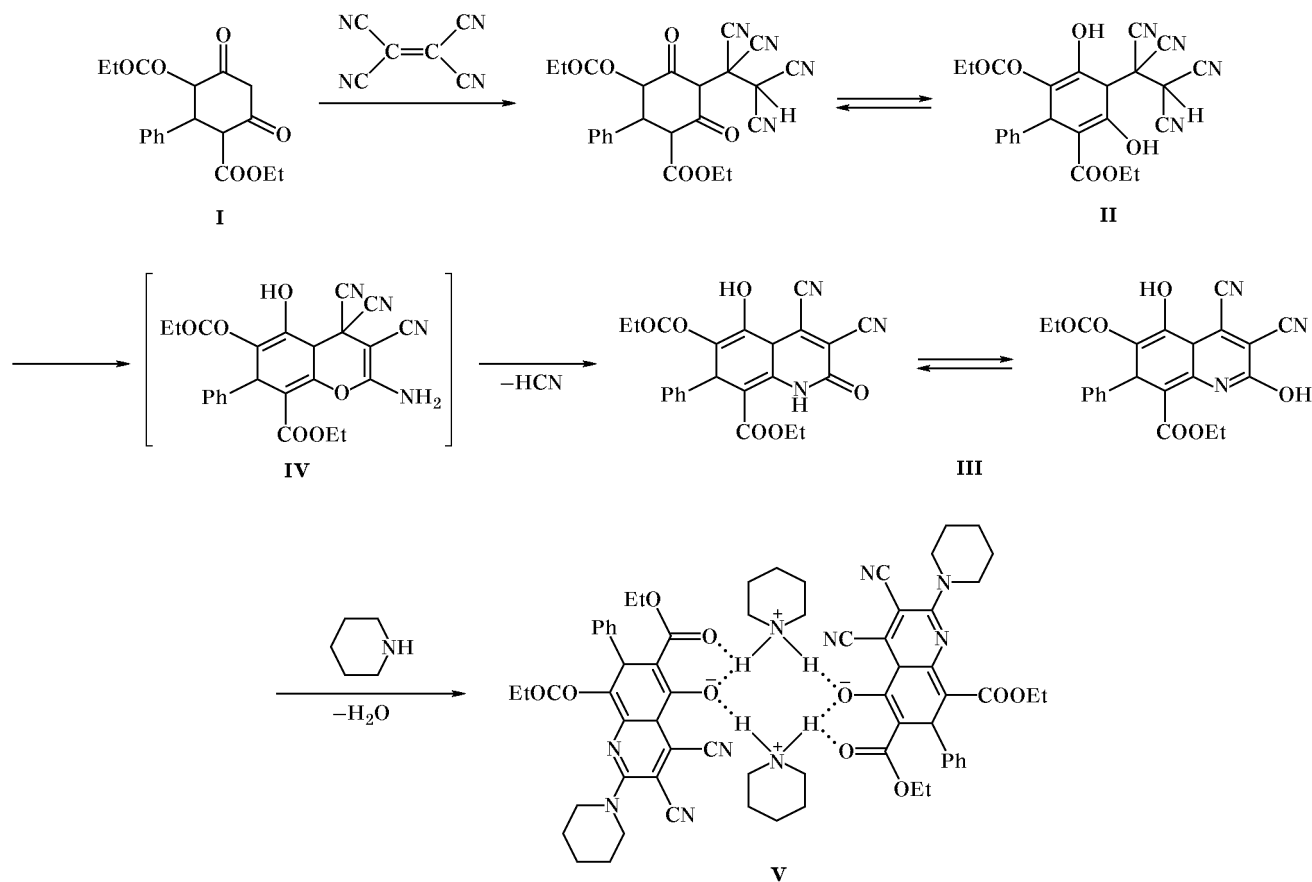
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It is known that 1,3-cyclohexanedione, dimedone, barbituric acid derivatives, pyrazolones, and *N*-aryl-acetoacetamides react with tetracyanoethylene to form cyano-substituted pyrans [1, 2]. We have found that the reaction of diethyl 2-phenyl-4,6-dioxocyclohexane-

1,3-dicarboxylate (**I**) with tetracyanoethylene yields tetracyano derivative **II**. The reaction takes 1–2 h at room temperature. When the reaction mixture was kept for 24 h at room temperature, substituted quinoline **III** was obtained (Scheme 1).

Scheme 1.



As in the reaction of tetracyanoethylene with 1,3-cyclohexanedione [1, 2], the formation of quinoline **III** is likely to be preceded by cyclization of **II** to substituted benzopyran **IV**. Insofar as the formation of pyran ring by intramolecular interaction of hydroxy and cyano groups is a reversible process [3], recyclization to the corresponding quinolines or quinolinones is possible [4]. Presumably, an analogous recyclization of **IV** yields quinoline **III**. By treatment of compound **III** in ethanol with piperidine in 24 h we isolated crystalline complex **V** whose structure was established by X-ray analysis.

Diethyl 4,6-dihydroxy-2-phenyl-5-(1,1,2,2-tetracyanoethyl)-3,6-cyclohexadiene-1,3-dicarboxylate (II). To a solution of 1.28 g of tetracyanoethylene in 20 ml of dioxane we added 1.12 g of diketone **I** and 3–4 drops of concentrated hydrochloric acid. When the reaction was complete, the mixture was diluted with 100 ml of water, and the precipitate was filtered off and washed with 2-propanol and diethyl ether. Yield 53%, mp 139–140°C. IR spectrum, ν , cm^{-1} : 1670, 1700, 2260. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 12.92 s (1H, OH), 12.78 s (1H, OH), 7.20–7.10 m (5H, H_{arom}), 5.93 s [1H, $\text{C}(\text{OH})\text{CHC}(\text{CN})_2$], 5.72 s (1H, CHPh), 4.11 q (2H, OCH_2 , $J = 6.5$ Hz), 4.03 q (2H, OCH_2 , $J = 6.5$ Hz), 0.98 t (6H, CH_3 , $J = 6.5$ Hz). Found, %: C 62.78; H 4.37; N 12.23. $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_6$. Calculated, %: C 62.61; H 4.38; N 12.17.

Diethyl 3,4-dicyano-5-hydroxy-2-oxo-7-phenyl-1,2,4a,7-tetrahydroquinoline-6,8-dicarboxylate (III). To a solution of 1.28 g of tetracyanoethylene in 20 ml of dioxane we added 1.12 g of diketone **I** and 6–7 drops of concentrated hydrochloric acid. When the reaction was complete, the mixture was kept for 24 h at room temperature and diluted with 100 ml of water. The precipitate was filtered off and washed with acetic acid and diethyl ether. Yield 81%, mp 139–140°C. IR spectrum, ν , cm^{-1} : 1670, 1700, 2220, 3200, 3390. ^1H NMR spectrum ($\text{DMSO}-d_6$), δ , ppm: 12.62 s (1H, OH), 9.08 s (1H, NH), 7.21–7.13 m

(5H, H_{arom}), 6.21 s (1H, $\text{CHC}=\text{C}$), 5.95 s (1H, CHPh), 4.12 q (2H, OCH_2 , $J = 6.5$ Hz), 4.03 q (2H, OCH_2 , $J = 6.5$ Hz), 1.09 t (6H, Me, $J = 6.5$ Hz). Found, %: C 63.62; H 4.31; N 9.83. $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_6$. Calculated, %: C 63.74; H 4.42; N 9.70.

Complex of ester III with piperidine. To a solution of 2.65 g of compound **III** in 5 ml of anhydrous ethanol we added 2 ml of piperidine in 5 ml of anhydrous ethanol. The mixture was stirred until it became homogeneous and was left to stand for 24 h. The precipitate was filtered off and washed with ethanol. Yield of complex **V** 48%, mp 162–164°C. IR spectrum, ν , cm^{-1} : 1665, 1710, 2220, 3205–3310. X-Ray diffraction data: space group *P*-1; unit cell parameters (20°C): $a = 10.333(2)$, $b = 12.14(3)$, $c = 14.256(3)$ Å; $\alpha = 90.75(2)$, $\beta = 106.27(2)$, $\gamma = 109.64(2)^\circ$; $V = 1605.4(6)$ Å³; $Z = 2$, $R = 0.0784$.

The progress of reactions was monitored, and the purity of products was checked, by TLC on Silufol UV-254 plates. The IR spectra were taken on a UR-20 spectrometer from samples dispersed in mineral oil. The ^1H NMR spectra were obtained on a Bruker AM-300 instrument in $\text{DMSO}-d_6$. The unit cell parameters and intensities of reflections were measured on a Siemens P3/PC four-circle diffractometer ($\lambda\text{MoK}\alpha$, graphite monochromator, $\theta/2\theta$ -scanning).

REFERENCES

1. Rappoport, Z. and Ladkani, D., *J. Chem. Soc., Perkin Trans. 1*, 1974, pp. 2595–2601.
2. Junek, H. and Aigner, H., *Z. Naturforsch., Teil B*, 1970, vol. 25, no. 2, pp. 1423–1426.
3. Babichev, F.S., Sharanin, Yu.A., Litvinov, V.P., Promonenkov, V.K., and Volovenko, Yu.M., *Vnutrimolekulyarnoe vzaimodeistvie nitril'noi i CH-, OH- i SH-grupp* (Intramolecular Interactions between the Cyano and CH, OH, and SH Groups), Kiev: Naukova Dumka, 1985.
4. Elnadgi, M.H., Fatma, A.M.A.A., and Youssef, M.Y., *J. Prakt. Chem.*, 1989, vol. 331, no. 6, pp. 971–974.