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POLYNUCLEAR HETEROCYCLIC COMPOUNDS

XX. Reduction Products from 2,3 (CO)-Benzoylene-4-phenyl-5-keto-7, 7-dimethyl-5, 6, 7, 8-tetrahydroquinoline*

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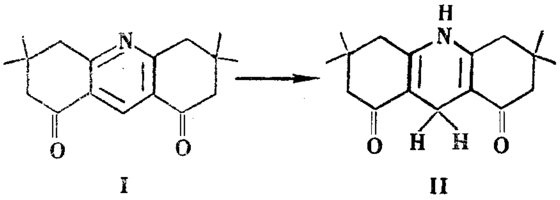
When 2, 3 (CO)-benzoylene-4-phenyl-5-keto-7, 7-dimethyl-5, 6, 7, 8-tetrahydroquinoline is catalytically hydrogenated using Adams catalyst, the five-membered ring carbonyl group is reduced to an alcohol group. The acetate, urethane, monoxime, and hydrochloride of the reduction product are prepared. Their IR spectra are measured. When 2, 3 (CO)-benzoylene-4-phenyl-5-keto-7, 7-dimethyl-5, 6, 7, 8-tetrahydroquinoline is reduced by zinc dust and glacial acetic acid, both carbonyl groups are reduced to CH_2, and 2, 3 (CH_2)-benzylene-4-phenyl-5-keto-7, 7-dimethyl-5, 6, 7, 8-tetrahydroquinoline is formed.

Recently there has been interest in the selective reduction of pyridine systems, with electron-accepting groups in the beta position, to dihydropyridine ones and their reverse oxidation, because similar compounds enter into the composition of redox coenzymes.

In one of our previous papers it was shown that 3, 3, 6, 6-tetramethyloctahydroacridinedione (I) is reduced by sodium borohydride and sodium hydrogen sulfite to the corresponding decahydroacridinedione (II) [1].



Recently the present authors [2] stated that I is very readily reduced (yield 80-90%) to II with hydrogen and Adams catalyst. Under the conditions used, the pyridine ring is selectively converted to a dihydropyridine one, the carbonyl groups remaining unchanged.

It appeared to be of interest to investigate the reduction of a more complex heterocyclic compound, 2, 3 (CO)-benzoylene-4-phenyl-5-keto-7, 7-dimethyl-5, 6, 7, 8-tetrahydroquinoline (III). The synthesis and properties of III have previously been described [3]. It appeared that here too a reverse transformation of the pyridine system of compound III to a dihydropyridine one was possible.

The literature contains information [4] concerning reduction of similar compounds containing the 2, 3-benzo-4-azafluorenone-9 ring. Depending on the reaction conditions, catalytic reduction was found to give different reduction products, the pyridine ring being reduced to tetrahydropyridine, or the dihydropyridine ring and keto group being reduced simultaneously.

Catalytic hydrogenation appeared to be the most convenient method. When III was hydrogenated in alcohol solution using Adams catalyst, 1 mole hydrogen was quickly absorbed, and a hitherto unknown white crystalline substance separated. The latter contained very little in the way of further reduction products as impurities, and they were not identified. Clearly the resultant hydrogenation product was not identical with the previously synthesized [3] 2, 3 (CO)-benzoylene-4-phenyl-5-keto-7, 7-dimethyl-1, 4, 5, 6, 7, 8-hexahydroquinoline (IV). The structure of the catalytic reduction product of III was partly deciphered with the aid of IR spectra. III has ν_{CO} 1680 cm^{-1} (in the six-membered ring) and ν_{CO} 1712 cm^{-1} (in the five-membered ring), and after reduction ν_{CO} 1712 has disappeared, and a ν_{OH} 3384 cm^{-1} band appears in the 3μ region. From that it followed that only the carbonyl group of the five-membered ring was reduced to hydroxyl, and compound V was formed. It was only remarkable why ν_{CO} of the six-membered ring change from ν_{CO} 1680 to ν_{CO} 1655 cm^{-1}.

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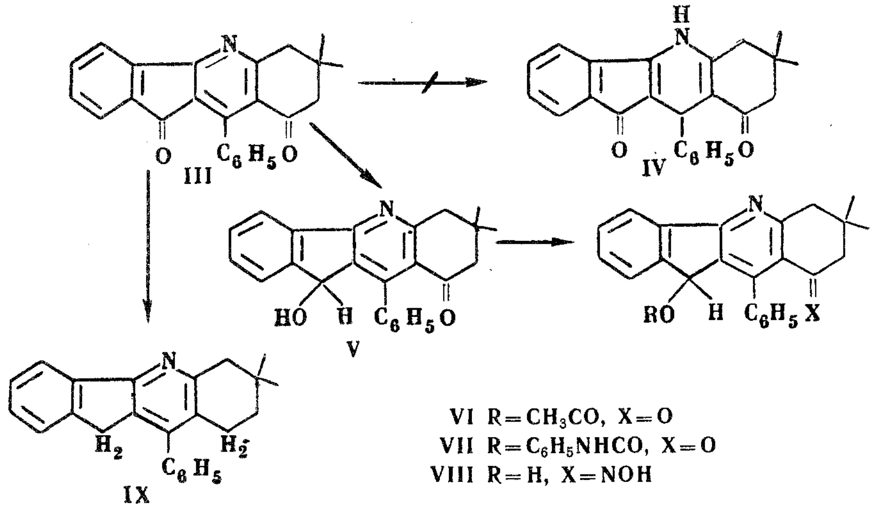
*For Part XIX see [2].



VI $R=CH_3CO$, $X=O$
VII $R=C_6H_5NHCO$, $X=O$
VIII $R=H$, $X=NOH$

Derivatives of 1-phenyl-2, 3-(1'keto-5', 5'-dimethyl-1', 4', 5', 6'-tetrahydrobenzo)-4-azafluorenol-9 (V) were prepared.

The identical compound is formed with acetyl chloride or acetic anhydride. Elementary analysis and IR spectra correspond to structure VI. There is an ester group vibration band at 1729 cm^{-1} and ν_{OH} found with V disappears. A monoxime VIII is obtained. The IR spectrum of the latter lacks ν_{CO} and two bands appear, at 1560 and 1572 cm^{-1}, corresponding to $\nu_{C=C}$ and $\nu_{C=N}$ vibrations. Hydrochloric acid hydrolysis of the ester group of compound VI gave a yellow crystalline substance containing chlorine. After treating this with alkali V was isolated. With hydrochloric acid, and partly on acetylation with acetyl chloride, compound V gave a bright yellow crystalline hydrochloride. Compound V and phenyl isocyanate gave the urethane VII.

Thus only one carbonyl group was reduced by catalytic hydrogenation.

III was also reduced with zinc and glacial acetic acid, when formation of hydroxyl groups was avoided, and both carbonyl groups were reduced to $-CH_2-$. The IR spectrum of IX lacks ν_{CO}, and in the 3 μ region ν_{OH} and ν_{NH} are absent.

The results obtained show that changes in structural symmetry greatly affect the capacity of the pyridine ring to undergo reduction.

Experimental

1-Phenyl-2, 3-(1'-keto-5', 5'-dimethyl-1', 4', 5', 6'-tetrahydrobenzo)-4-azafluorenol-9 (V). 0.05 g PtO_2 in 50 ml ethanol was reduced with hydrogen for 2 hr, about 30 ml hydrogen being consumed in reduction and in absorption on the catalyst surface. Then 0.5 g III in 70 ml ethanol was placed in the pear-shaped flask containing the catalyst, and reduced for 1-1.5 hr, 1-1.25 mole hydrogen being absorbed, after which hydrogenation ceased. The catalyst was filtered off, and part of the ethanol distilled off under reduced pressure. After cooling, the white crystalline precipitate was separated off, yield 0.4 g V, mp 189° (after two recrystallizations from aqueous alcohol.). It was readily soluble in polar solvents. IR spectrum in vaseline: 1492, 1556, 1655 (CO), 3384 cm^{-1} (NH). Found: C 81.28, 81.25; H 5.82, 5.54; N 3.84%. Calculated for $C_{24}H_{21}NO_2$: C 81.14; H 5.95; N 3.94%.

Acetyl derivative. a) Acetylation with acetic anhydride. 0.2 g V was dissolved in 15 ml acetic anhydride, 0.1 g AcONa added, and the mixture heated for 2 hr. After cooling the products were poured into 10 times their own volume of water. Next day a white flocculent precipitate of compound VI had formed. It was separated, and washed well with water. Mp 171° (after three recrystallizations from ethanol). IR spectrum in vaseline: 1500, 1580, 1693 (CO), 1740 (COOR) cm^{-1}. Found: C 78.50; H 5.44; N 3.49%. Calculated for $C_{26}H_{23}O_3N$: C 78.57; H 5.83; N 3.52%.

b) Acetylation with acetyl chloride. 0.2 g was suspended in 10 ml acetyl chloride and heated for 2 hr on a water bath, temperature 60-70°. The white precipitate obtained after cooling was filtered off, and the filtrate carefully poured into a large volume of water, when, after some hours, a white crystalline precipitate of VI formed. Mp 171° (after two crystallizations from ethanol.) Undepressed mixed mp with the compound prepared by method (a).

Monoxime (VIII). 0.2 g V was dissolved in 10 ml pyridine, 0.15 g $NH_2OH \cdot HCl$ added, and the mixture heated for 3 hr on a water bath. The white precipitate obtained on pouring into dilute hydrochloric acid was washed well with water, mp 261° (after two recrystallizations from dioxane). IR spectrum in vaseline: 1560, 1572 cm^{-1}. Found: C 77.78;

H 5.96; N 7.30%. Calculated for $C_{24}H_{22}N_2O_2$: C 77.50; H 5.98; N 7.56%.

Urethane (VII). 0.3 g V was dissolved in 5 g phenyl isocyanate, the mixture refluxed for 1 hr, then placed in a refrigerator. The white precipitate formed was filtered off, and washed with benzene. After three recrystallizations from benzene mp 179°. Found: C 78.80; H 5.79; N 6.30%. Calculated for $C_{31}H_{26}N_2O_3$: C 78.43; H 5.52; N 5.91%.

Hydrochloride of (V). 0.2 g V was dissolved in HCl (1 : 1), and refluxed for 1 hr. The yellow crystals which separated were filtered off. MP 242-243° (after recrystallizing from a mixture of dry methanol and dry ether). A similar substance was obtained by hydrolyzing VI with hydrochloric acid, and in part by acetylating V with acetyl chloride. Found: C 73.11; H 5.81; N 3.60; Cl 8.68%. Calculated for $C_{24}H_{21}NO_2 \cdot HCl$: C 73.38; H 5.90; N 3.57; Cl 9.02%.

2,3 (CH_2)-benzylene-4-phenyl-7,7-dimethyl-5,6,7,8-tetrahydroquinoline (IX). 0.5 g III was dissolved in 20 ml glacial acetic acid, and over a period of 4 hr reduced with zinc dust. The hot solution was filtered to remove zinc dust, neutralized with sodium carbonate, and the white precipitate which formed filtered off and recrystallized three times from aqueous ethanol, mp 142°. IR spectrum in vaseline: 1494, 1548 cm^{-1}. Found: C 88.98; H 7.00; N 4.40%. Calculated for $C_{24}H_{23}N$: C 88.61; H 7.13; N 4.30%.

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