REACTION OF BENZOYL AND TRICHLOROACETYL ISOCYANATES WITH p-BENZOQUINONE AND α -NAPHTHOQUINONE

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Benzoyl isocyanate readily combines with double and triple bonds of olefines and acetylenes in the 1,2-positions to form a four-membered ring [1, 2]. In addition the many possible electron density distributions can also cause the aroyl and acyl isocyanates to react differently. Thus there are data on 1,4-addition of benzoyl isocyanate to isonitriles [3].

The present report gives the results of an investigation into the reactions of benzoyl and trichloroacetyl isocyanates towards p-benzoquinone and α -naphthoquinone. Benzoyl isocyanate readily combines with p-quinone to form a crystalline product (I), melting at 194-195°C, by the 1,2-addition mechanism:



The IR spectrum of compound (I) contains the following frequencies: C=O group (β -lactam), 1767 cm⁻¹; C=O group (benzoyl), 1678 cm⁻¹; carbonyl group (conjugated with the double bond), 1670 cm⁻¹; and the valency vibrations of the C=C bond, 1609 cm⁻¹.

The IR data were confirmed by a chemical method. When compound (I) is oxidized with an alkaline solution of hydrogen peroxide an epoxide derivative (II) is obtained. The structure of compound (I) is also revealed in its hydrolysis by alkali to 5-aminocyclo-2-hexene-1,4-dione-6-carboxylic acid (III), which (as a β -amino acid and a β -keto acid) loses ammonia and carbon dioxide on heating and is converted into p-quinone. It is well known that p-quinonecarboxylic acid is so unstable that it cannot be isolated [4].



 α -Naphthaquinone also reacts with benzoyl isocyanate to form a crystalline product melting at 226.5°C (IV) by the 1, 2-ring-formation mechanism:



The structure of compound (IV) was proved by the IR spectrum: C=O (β -lactam), 1765 cm⁻¹; C=O (benzoyl), 1675 cm⁻¹; C=O (conjugated), 1670 cm⁻¹; and by its saponification to the aminocarboxylic acid (V), which loses a molecule of ammonia on heating and changes to α -naphthaquinonecarboxylic acid (VI). This acid is fairly stable and can be isolated in the pure form.

The reaction between p-benzoquinone and trichloroacetyl isocyanate (VII) proceeds somewhat differently. The crystalline product melted at 160-161°C; its IR spectrum did not contain the frequency of the

V. I. Ul'yanov Lenin Kazanskii State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2137-2139, September, 1968. Original article submitted March 11, 1968. β -lactam carbonyl, but did contain the frequencies of the C=O group (1728 cm⁻¹), the conjugated C=O group (1670 and 1681 cm⁻¹), and the valency vibrations of the C=C double bond (1604 cm⁻¹), which indicated a different structure for the adduct. Further investigations showed that in this case the reaction proceeds by a diene-synthesis mechanism in the 1,4-position (VIII), where trichloroacetyl isocyanate plays the part of the diene:



On hydrolysis the adduct (VIII) gives 5-hydroxycyclo-2-hexene-1,4-dione-6-carboxylic acid (IX), which as a β -hydroxy and β -keto acid loses the elements of water and carbon dioxide on heating to give p-benzoquinone. An adduct of trichloroacetyl isocyanate with α -naphthoquinone was not obtained.

EXPERIMENTAL

The reactions were carried out with the solvents in sealed glass tubes in an atmosphere of dry CO_2 . The IR spectra were taken in Vaseline oil on a Hilger H800 spectrophotometer.

Reaction of p-Benzoquinone with Benzoyl Isocyanate. Samples of 4.84 g benzoyl isocyanate and 3.55 g p-benzoquinone dissolved in 20 ml anhydrous diethyl ether were heated for 7 h at 70-80°C. The reaction mixture was cooled to 0°C. The crystals which separated were filtered off and washed many times with absolute ether. The pure crystals melted at 194-195°C, and the yield was 3.02 g (45.6% theoretical). Found %: C 65.78; H 3.52. $C_{14}H_9O_4N$. Calculated %: C 65.88; H 3.52.

Reaction of Trichloroacetyl Isocyanate with p-Benzoquinone. A 5.24-g sample of trichloroacetyl isocyanate, obtained by the method described in [5], and 3 g p-benzoquinone dissolved in 30 ml anhydrous dichloroethane were heated for 7 h at 70-80C. The solvent was removed under vacuum, and the crystals which separated were washed with anhydrous diethyl ether. The pure crystals melted at 160-161°C, and the yield was 3.66 g (43.2% theoretical). Found %: C 36.40; H 1.25; Cl 35.87. $C_{3}H_{4}O_{4}NCl_{3}$. Calculated %: C 36.42; H 1.34; Cl 35.91.

<u>Reaction of Benzoyl Isocyanate with α -Naphthoquinone.</u> A 6.19-g sample of benzoyl isocyanate and 6.65 g α -naphthoquinone dissolved in 20 ml pure benzene were heated for 12 h at 80°C. The reaction mixture was cooled to 0°C, and the crystals which separated were recrystallized from absolute ether. They melted at 226.5°C, and the yield was 5.2 g (40.5% theoretical). Found %: C 70.67; H 3.81. C₁₈H₁₁O₄N. Calculated %: C 70.81; H 3.60.

<u>Preparation of the Epoxide (II).</u> Epoxidation was carried out by the method described in [6]. A 1.14-g sample of compound (I) was dissolved in acetone, and while shaking and cooling in iced water 3.42 ml 20% Na_2CO_3 solution followed by 7 ml 30% H_2O_2 solution were mixed. Epoxidation took a few minutes. When the reaction mixture was diluted with three times its volume of water the epoxide separated as a flocculent white product, which after suction was recrystallized from 80% methanol. The epoxide melted at 216°C and gave a yield of 1 g (83% theoretical). Its IR spectrum contained the following lines of the epoxy group: 865, 1165, and 1250 cm⁻¹. Found %: C 61.48; H 3.17. $C_{14}H_9O_5N$. Calculated %: C 61.99; H 3.32.

5-Aminocyclo-2-hexene-1,4-dione-6-carboxylic Acid (III). A 3.25-g sample of compound (I) was saponified with 7 ml 6 N NaOH solution under conditions which we described in [1, 2]. After recrystallization from ethanol the free amino acid melted at 173-175°C. Its yield was 1.08 g (50% theoretical). Found %: C 49.65; H 4.20; N 8.09. $C_7H_7O_4N$. Calculated %: C 49.70; H 4.14; N 8.25.

<u>2-Amino-1,4-dione-1,2,3,4-tetrahydronaphthalene-3-carboxylic Acid (V)</u>. This amino acid was obtained in a similar manner to that in the previous experiment by saponification of 6 g compound (IV) in 17 ml 6 N NaOH solution. It melted at 198-200°C and gave a yield of 1.94 g (45 theoretical). Found %: C 60.53; H 4.08. $C_{11}H_9O_4N$. Calculated %: C 60.27; H 4.19.

 α -Naphthoquinone-2-carboxylic Acid (VI). A 2-g sample of compound (IV) dissolved in alcohol was heated with KOH for 45 min at 40-45°C. On cooling crystals of α -naphthoquinone-2-carboxylic acid separated. It was recrystallized from ether and had a melting point of 178°C. The yield was 0.81 g (44.2% theoretical). Found %: C 65.10; H 3.00. C₁₁H₆O₄. Calculated %: C 65.34; H 2.97.

<u>5-Hydroxycyclo-2-hexene-1,4-dione-6-carboxylic Acid (IX)</u>. A 14-g sample of compound (VIII) was dissolved in 20 ml acetone; a few drops of water and 2-3 drops 2 N HCl were added. The solution was heated at 40°C for 45 min. It was then allowed to stand for 30 min at room temperature, after which it was diluted with an equal volume of water and allowed to stand for another 30 min. The crystals which separated were filtered off and dried. The pure crystals melted at 139-140°C, and the yield was 4.28 g (53.5%). Found %: C 49.28; H 3.17. $C_7H_6O_5$. Calculated %: C 49.41; H 3.52.

CONCLUSIONS

1. Benzoyl isocyanate reacts with p-benzoquinone and α -naphthoquinone by a 1,2-addition with ring formation.

2. Trichloroacetyl isocyanate reacts with p-benzoquinone by a diene-synthesis type of reaction.

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