REACTION OF 2,6-DI-tert-BUTYLCYCLOHEXADIENONE CARBENE WITH THIOPHENES

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The reaction of carbenes with the simpler heterocyclic compounds has been studied inadequately [1-3]. In the present paper we studied the reaction of cyclohexadienone carbene (II), which is formed in the thermolysts of quinone diazide (I) [4-6], with thiophene and its derivatives. From the reaction products with thiophene were isolated diphenoquinone (III) (which is formed by the recombination of the phenoxyl radicals and subsequent dehydrogenation of the formed bisphenol by the carbene), 2,6-di-tert-butylphenol (IV) and the quinoid derivatives (V) and (VI):



According to the composition of the reaction products, the process proceeds stepwise by a radical path via the intermediate formation of biradical (VII). The possibility of resonance stabilization for this biradical (due to the delocalization of the unpaired electrons along the system of conjugated bonds of the phenyl and thiophene rings) assures its adequate stability, which facilitates progress of the reaction by the proposed mechanism.

The structure of the compounds obtained as a reaction result was confirmed by the spectra analysis data (UV, IR, NMR and mass spectroscopy) and by chemical methods. Thus, an absorption band, corresponding to the hydroxyl group, is absent in the IR spectra of compounds (V) and (VI), while a number of bands is present in the 1550-1650 cm⁻¹ region, which correspond to the absorption of the conjugated carbonyl group and the conjugated double bonds. The NMR spectra of compounds (V) and (VI) contain signals

Institute of Chemical Physics, Academy of Sciences of the USSR, N. D. Zelinskii Institute of Organic Chemistry Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 846-850, April, 1973. Original article submitted June 12, 1972.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00. from the protons of the tert-butyl groups (respectively δ 1.21 and 1.28 ppm), two doublets each from the protons of the cyclohexadienone rings [6.75 and 7.21 ppm for (V), and 6.89 and 7.42 for (VI)], and multiplet signals from the olefinic protons in the 6.4-6.9 ppm region. The molecular ions of compounds (V) and (VI) (m/e respectively 458 and 510) and the character of the fragmentation under electron impact also corroborate their structure.

The reduction of (V) with Zn in CH_3COOH , $LiAlH_4$, and catalytically with hydrogen (over Pd black), led to the corresponding phenol compounds (VIII)-(X), the structure of which was confirmed by the spectral data and elemental analysis. The UV spectra (λ 275 and 282 nm) reflect the aromatic character of bisphenols (VIII)-(X). The IR spectra contain the absorption band of an unassociated hydroxyl group (3540 cm⁻¹), while the NMR spectrum contains signals from the protons of the hydroxyl groups in the 4.90-4.75 ppm region.



Compound (VI) was successively reduced with $LiAlH_4$ and catalytically with hydrogen over Pd black, initially to bisphenol (XI) and then to phenol (XII). The UV, IR and NMR spectra of these compounds correspond to their structure:



An alternate mechanism for the reaction of cyclohexadienone carbene (II) with thiophene postulates the initial addition of the singlet carbene to the double bond of thiophene with the formation of the bicyclic derivative. The latter, after opening of the thiophene ring, is converted to (V) via the addition of a second molecule of the carbene and the elimination of sulfur. However, the absence in the reaction mixture of the monoaddition product of the carbene to the multiple bond of thiophene and the presence of compounds (III), (IV) and (VI) make this mechanism improbable.

The thermolysis of quinone diazide (I) in the α , α -dichloro- and α , α -dibromothiophenes led to other reaction products, namely to the substituted 2,5-dihydrothiophene (XIII) and diphenoquinone (III). The total yield of these compounds is 90-95%, in which connection in the case of the thermolysis of (I) in α , α -dibromothiophene the yield of the diphenoquinone increases approximately two-fold. It is obvious that the presence of halogen atoms in the thiophene leads to the situation that the ylid derivative (XIV) is formed initially, which then under goes rearrangement to the geminal product (XV). The latter loses a halogen molecule and is converted to the dihydrothiophene derivative (XIII): Scheme 1.

The structure of (XIII) was confirmed by the spectral analysis data and by chemical methods. Thus, an absorption band is present in the IR spectrum of (XIII) that corresponds to the stretching vibrations of a conjugated carbonyl group (1600 cm⁻¹), while the NMR spectrum contains signals from the protons of the tert-butyl groups (1.32 and 1.34 ppm), two doublet signals from the protons of the cyclohexadienone rings (7.18 and 7.32 ppm), and a singlet signal from the protons of the dihydrothiophene ring (7.58 ppm). Dihydrothiophene (XIII) was reduced by LiAlH₄ and by hydrogen over Pd to α , α -di-(4-hydroxy-3, 5-di-tert-butylphenyl)thiophene (XVI), the UV spectrum of which has an absorption maximum that is characteristic for the



thiophene ring (230 nm), the IR spectrum contains the absorption bands of the hydroxyl group (3630 cm⁻¹) and the thiophene ring (850 cm⁻¹), while the NMR spectrum contains signals from the protons of the tertbutyl groups (1.43 ppm), the protons of the hydroxyl groups (4.47 ppm), the phenyl m-protons (6.39 ppm), and the protons of the thiophene ring (6.73 ppm).

EXPERIMENTAL METHOD

Thermolysis of Quinone Diazide (I) in Thiophene. A solution of 0.5 g of (I) in 25 ml of thiophene was refluxed for 8 h. After removal of the excess thiophene in vacuo the residue was chromatographed on a thin layer of Al_2O_3 in the system: hexane-benzene. Here we obtained: a) 1,4-di-(3',5'-di-tert-butyl-2',5'-cyclohexadien-4'-onylidene)-2-butene (V), 0.28 g (56%), as red crystals with mp 280° (from CCl₄). C 83.61; H 9.60%; mol. wt. 460.672; b) 1,8-di-(3',5'-di-tert-butyl-2',5'-cyclohexadien-4'-onylidene)-2,4, 6-octatriene (VI), 0.15 g (25%), as violet crystals with mp 260° (from ethyl acetate). C 84.09; H 9.40%; mol. wt. 512 (mass spectrometery). $C_{36}H_{48}O_2$; C 84.32; H 9.43%; mol. wt. 512.744; and c) 3,3',5',5'-tetra-tert-butyl-diphenoquinone (III), 0.09 g (20%), mp 246° [7].

Reduction of Compound (V). To a suspension of 0.25 g of LiAlH₄ in 30 ml of absolute ether was added in drops a solution of 0.6 g of (V) in 20 ml of absolute ether. The reaction mixture was heated for 2 h, and then it was decomposed with dilute H₂SO₄ solution (1:25). We obtained 0.55 g (92%) of 1,4-di-(4'-hydroxy-3',5'-di-tert-butylphenyl)-2-butene (VIII), mp 136.5-137.5° (from hexane). Found: C 82.70; H 10.41%. $C_{32}H_{48}O_{2}$. Calculated: C 82.55; H 10.61%.

To a suspension of 0.5 g of (V) in 50 ml of CH_3COOH was added 2 g of Zn in portions, after which the mixture was brought up to the boil, the excess zinc was removed, and the residual solution was diluted with 10 volumes of water. The obtained crystals were filtered. We obtained 0.45 g (95%) of 1,4-di-(4'-hydroxy-3',5-di-tert-butylphenyl)-1,3-butadiene (IX), mp 230-231° (from hexane). Found: C 82.91; H 9.95%. $C_{32}H_{46}O_2$. Calculated: C 38.06; H 10.02%.

A solution of 0.5 g of (V) in CH_3COOH was hydrogenated over Pd. The catalyst was separated, the mixture was diluted with 10 volumes of water, and the obtained crystals were filtered. We obtained 0.48 g of 1,4-di-(4'-hydroxy-3',5'-di-tert-butylphenyl) butane (X), mp 126-127° (from hexane). Found: C 82.40; H 10.83%. $C_{32}H_{50}O_2$. Calculated: C 82.34; H 10.79%.

<u>Reduction of Compound (VI)</u>. A solution of 0.5 g of (VI) in 50 ml of absolute ether was added to a suspension of 0.25 g of LiAlH₄ in 30 ml of absolute ether, after which the mixture was heated for 2 h and then decomposed with dilute H₂SO₄ solution (1:25). The ether was vacuum-distilled, and the residue was recrystallized from a hexane-benzene mixture. We obtained 0.45 g (90%) of 1,8-di-(3',5'-di-tert-butyl-4'-hydroxyphenyl)-2,4,6-octatriene (XI), mp 203-204.5°. Found: C 83.46; H 10.20%. C₃₆H₅₂O₂. Calculated: C 83.60; H 10.14%.

A solution of 0.3 g of (XI) in CH₃COOH was hydrogenated over Pd black (see above). We obtained 0.28 g of 1, 8-di-(4'-hydroxy-3', 5'-di-tert-butylphenyl) octane (XII), mp 141-143.5° (from hexane). Found: C 82.41; H 11.35%. C₃₈H₅₈O₂. Calculated: C 82.69; H 11.18%.

 $\frac{\text{Thermolysis of (I) in the } \alpha, \alpha - \text{Dichloro- and } \alpha, \alpha - \text{Dibromothiophenes.}}{\text{manner as the thermolysis of (I) in thiophene.}} We obtained: a) 35\% of 2, 5-di-(3, 5'-di-tert-butyl-2', 5'-cyclohexadien-4'-onylidene)-2,5-dihydrothiophene (XIII), mp 144-145° (from hexane). Found: C 78.15; H 8.68; S 6.59\%. C_{32}H_{42}O_2S. Calculated: C 78.32; H 8.62; S 6.53\%; and b) 45\% of diphenoquinone (III), mp 246° [7].$

<u>Reduction of Compound (XIII) with Aluminum Lithium Hydride</u>. The reaction was run in the same manner as the reduction of (V). We obtained 2, 5-di-(4^t-hydroxy-3^t, 5^t-di-tert-butylphenyl)thiophene (XVI), mp 199-200°. Found C 77.62; H 8.98; S 6.76%. C₃₂H₄₄O₂S. Calculated C 77.99; H 9.00; S 6.50%.

CONCLUSIONS

The reaction of 2,6-di-tert-butylcyclohexadienone carbene with thiophene leads to an opening of the thiophene ring, and to the formation of the substituted 2,5-dihydrothiophene in the case of the halo deriva-tives of thiophene.

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