parative gas-liquid chromatography, bp 139°C [11]. ¹⁹F NMR spectrum: -14.5 br. s (CF₃). Mass spectrum: 296 (M)⁺, 277 (M - F)⁺, 227 (M - CF₃)⁺, 207 (M - F - CF₃ - H)⁺, 127 (C₆H₅-CF₂)⁺, 77 (C₆H₅)⁺, and 69 (CF₃)⁺.

Analogously, 1.5 g CsF, 20 g perfluoroisobutylene, 15 ml tetraglyme, and 3.2 g diphenylbromonium tetrafluoroboride in 5 ml tetraglyme gave 1.7 g of a mixture containing 5% C_6H_5F , 59% C_6H_5Br , and 35% (IV) (20% yield) as indicated by gas-liquid chromatography.

CONCLUSIONS

The phenylation of fluorinated C-, O-, and N-anions by diphenylhalonium tetrafluoroborides was reported.

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SULFURATION OF 2,2,4-TRIMETHYL-1,2,3,4-TETRAHYDROQUINOLINES

Kh. S. Shikhaliev, O. T. Kasaikina, and Zh. V. Shmyreva

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Heating 1-R-6-R'-2,2,4-trimethyl-1,2-dihydroquinolines (Ia)-(Ie) at reflux with a 3-5fold excess of sulfur in DMF gives the corresponding 5-R-8-R'-4,5-dihydro-4,4-dimethyl-2,3dithiolo[3,4-c]quinoline-1-thiones (IIa)-(IIe) in 15-50% yield. These products are effective antioxidants for rubbers and have bactericidal properties [1].



Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Lenin Komsomol Voronezh State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 191-192, January, 1989. Original article submitted May 26, 1988.

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In the present work, we have established that 1-R-6-R'-2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines (IIIa)-(IIIe) under the conditions described, independently of the nature and structure of the substituents, give the corresponding dithiolthiones (IIa)-(IIe) when a sixfold amount of sulfur is used, but with yields of only 5-8%. However, the yields of the desired products are considerably enhanced (to 45-55%) upon an increase in the temperature, specifically, upon fusing tetrahydroquinolines (IIIa)-(IIIe) with sulfur at 210-220°C or upon heating the reagents at reflux in high-boiling inert solvents such as trichlorobenzenes.

Analogously, the reaction of 7-methyl-, 8-methyl, and 8-methoxy-2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines with sulfur gave previously undescribed 4,5-dihydro-4,4,7-trimethyl-2,3-dithiolo[3,4-c]quinoline-1-thione (IV), 4,5-dihydro-4,4,6-trimethyl-2,3-dithiolo[3,4-c]quino-1ine-1-thione (V), and 4,5-dihydro-4,4-dimethyl-6-methoxy-2,3-dithiolo[3,4-c]quinoline-1-thione (VI).



Various sulfur-containing compounds used in such reactions as catalysts such as mercaptobenzothiazole, 8-mercaptoquinoline, and thiourea [3], virtually do not affect the yields of the desired products. This is apparently related to the circumstance that tetrahydroquinolines themselves are efficient catalysts for this reaction.

A mass spectral study of (IIa)-(IIe) and (IV)-(VI) showed the presence of molecular ion peaks. The major type of fragmentation upon electron impact is the loss of one of the geminal methyl groups as a radical and formation of maximum-intensity ions of the corresponding 4-methyl-2,3-dithiolo[3,4-c]quinoline-1-thiones, $[M - CH_3]^+$. Peaks for ions $[M - CH_3-CS]^+$ and $[M - CH_3-S]^+$ were also recorded.

The case of this reaction and its satisfactory yields permit us to recommend it as an alternative method for the synthesis of substituted 4,5-dihydro-4,4-dimethyl-2,3-dithiolo[3, 4-c]quinoline-1-thiones.

EXPERIMENTAL

The reaction course and product purity were monitored by thin-layer chromatography on Silufol UV-254 plates using 4:1 benzene-CCl₄ as the eluent. The IR spectra were taken on a UR-20 spectrometer for vaseline mulls. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz in CDCl₃ with TMS as the internal standard. The mass spectra were taken on a Ribermag R10-20C chromato-mass spectrometer with direct sample inlet into the ion source. The ionizing radiation was 70 eV.

Typical Procedure for the Sulfurization of Substituted 2,2,4-Trimethyl-1,2,3,4-tetrahydroquinolines. a. A mixture of 0.01 mole of the corresponding tetrahydroquinoline and 1.92 g (0.06 mole) sulfur was heated at 210-220°C for 40-60 min. After cooling, the reaction product was extracted with ethyl acetate and concentrated. The crystalline precipitate was filtered off and recrystallized from benzene.

b. A mixture of 0.02 mole tetrahydroquinoline and 3.84 g (0.12 mole) sulfur in 50 ml 1,2,4-trichlorobenzene was heated at reflux for 6-10 h. The solvent was distilled off at reduced pressure and the product was isolated as described above.

Products (IIa)-(IIe) obtained by methods a and b were shown to be completely identical to previously obtained samples obtained by the sulfuration of the corresponding dihydroquinolines by IR and PMR spectroscopy and mass spectrometry [1, 2].

<u>4,5-Dihydro-4,4,7-trimethyl-2,3-dithiolo[3,4-c]quinoline-1-thione (IV)</u> was obtained by method a from 1.9 g (0.01 mole) 2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline and 1.92 g (0.06 mole) sulfur over 40 min as orange crystals. The yield of (IV) was 1.3 g (47%), mp 152-153°C. Found, %: C 55.49, H 4.78, N 5.19; M⁺ 279. $C_{13}H_{13}NS_3$. Calculated, %: C 55.88,

H 4.69, N 5.01; M 279.45. IR spectrum (ν, cm⁻¹): 1230 (C=S), 3400 (NH). PMR spectrum (δ, ppm): 1.56 s (CMe₂), 2.28 s (7-Me), 3.64 s (NH), 6.5-7.0 m (arom.), 9.16 m (9-CH).

CONCLUSIONS

Substituted 2,2,4-trimethyl-1,2,3,4-tetrahydroquinolines upon reaction with a six-fold amount of sulfur at 210-220°C, similarly to dihydroquinolines, give the corresponding 4,5-dihydro-4,4-dimethyl-2,3-dithiolo[3,4-c]quinoline-1-thiones.

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