

RADICAL ARYLATION OF DITHIOURETHANES BY ARYLDIAZONIUM TETRAFLUOROBORIDES IN THE PRESENCE OF FERROCENE

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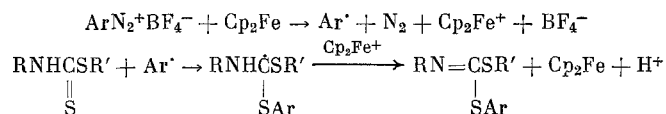
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The radical arylation of phenyl-N-phenyldithiourethane by aryldiazonium tetrafluoroborides (AT) in the presence of ferrocene has given high yields of the aryl esters of N-phenylimidothiocarbonic acid [1].

In a continuation of this study, the radical arylation of dithiourethanes containing alkyl or aralkyl groups at the nitrogen or sulfur atom was investigated in the case of N-phenyl-S-butyl-, N-phenyl-S-benzyl-, and N-allyl-S-phenyldithiourethanes.

The arylation of these compounds by AT in the presence of ferrocene gave high yields of the S-aryl esters of dimidothiocarbonic acid, which are difficult to be obtained by other methods [2].

The reaction scheme was proposed in our previous work [1].



In the N-phenyl-S-butyldithiourethane by p-methoxyphenyldiazonium tetrafluoroboride, the use of CuCl_2 instead of ferrocene as the catalyst for the generation of the aryl radicals does not lead to the desired results. CuCl_2 reacts with dithiourethane to form a complex, $\text{CuCl}(\text{C}_6\text{H}_5\text{NHC(=S)SC}_4\text{H}_9)_2$ (as indicated by elemental analysis), and does not catalyze the decomposition of AT.

The analogous complex was obtained upon the reaction of dithiourethane with CuCl_2 . The structure of this complex was not studied.

EXPERIMENTAL

The reactions were carried out in a nitrogen atmosphere. The PMR spectra were taken on a Bruker WP-200SY spectrometer.

Arylation of N-phenyl-S-butyl-, N-allyl-S-phenyl-, and N-phenyl-S-benzylthiourethanes. A solution of 0.001 moles ferrocene in 5 ml acetone was added dropwise to a solution of 0.01 moles dithiourethane and 0.01 moles AT in 50 ml acetone. A rise in temperature was noted. The reaction mixture was stirred for 4 h at about 20°C. Acetone was removed and the residue was subjected to chromatography on a column packed with silica gel L 100/160 μ with 10:0.5 hexane-ethanol as the eluent. The melting points (from ethanol), yields, and elemental analysis data for the compounds obtained are given in Table 1.

In the case of the arylation of N-phenyl-S-butylthiourethane, the residue obtained after the removal of acetone was recrystallized from ethanol-acetone.

Reaction of N-phenyl-S-butylthiourethane with p-methoxyphenyldiazonium tetrafluoroboride in the presence of CuCl_2 . The reaction was carried out as described above. Upon the addition of aqueous CuCl_2 , the temperature remained unchanged. Gas evolution was not noted. A yellow precipitate formed after some time. Elemental analysis of this precipitate corresponded to a complex $\text{CuCl}(\text{C}_6\text{H}_5\text{NHC(=S)SC}_4\text{H}_9)_2$, mp 123-125°C. Found: C 47.99; H 6.21; N 5.66; S 23.49%. Calculated for $\text{C}_{22}\text{H}_{30}\text{ClCuN}_2\text{S}_4$: C 48.08; H 5.46; N 5.10; S 23.31%.

The analogous complex was obtained upon the reaction of dithiourethane with CuCl_2 . The melting point of a mixed probe was undepressed.

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TABLE 1. Aryl Esters of Imidodithiocarbonic Acids, $RN=C(SR')-SC_6H_4X-4$

R	R'	X	Yield, (%)	Mp, °C	Chemical formula	Found Calculated, %			
						C	H	N	S
Ph	C ₆ H ₉	H	90	51-52	C ₁₇ H ₁₉ NS ₂	67.69	6.29	4.63	21.40
						67.77	6.31	4.65	21.26
Ph	C ₆ H ₉	CH ₃	49	56-57	C ₁₈ H ₂₁ NS ₂	68.25	6.58	4.40	20.44
						68.57	6.66	4.44	20.31
Ph	CH ₂ C ₆ H ₅	H	70	109-110	C ₂₀ H ₁₇ NS ₂	71.39	4.97	4.25	19.15
						71.64	5.04	4.17	19.10
Ph	CH ₂ C ₆ H ₅	NO ₂	88	124-126	C ₂₀ H ₁₆ N ₂ S ₂ O ₂	62.75	4.13	7.23	16.90
						63.15	4.21	7.36	16.84
Ph	CH ₂ C ₆ H ₅	CH ₃	50	123-124	C ₂₁ H ₁₉ NS ₂	72.03	5.34	3.99	18.32
						72.20	5.44	4.01	18.33
CH ₂ =CHCH ₂	Ph	H	41	38-41	C ₁₆ H ₁₅ NS ₂	67.32	5.25	4.41	21.90
						67.32	5.29	4.90	22.46

The signals for the aromatic protons in the PMR spectra of these compounds in CCl₄ (δ , ppm relative to TMS) comprise a complex multiplet at 6.7-7.6 ppm. The signals of the aliphatic hydrogen atoms are characteristic for the different compounds: S-CH₂-CH₂CH₂CH₃) 2.90 t (S-CH₃), 1.58 m (CH₂-CH₂-CH₃), 1.32 m (-CH₂-CH₃), 0.92 t (-CH₃); S-CH₂-Ph) 4.1 s; CH₂=CH-CH₂-N) 4.97 d. d (CH₂=), 5.78 m (=CH-CH₂), 4.04 s (CH₂-N).

CONCLUSIONS

A preparative method was proposed for the synthesis of S-aryl esters of N- and S-alkyl, N- and S-allyl-, and N- and S-arylalkylimidodithiocarbonic acids by the radical arylation of dithiourethane by aryl diazonium tetrafluoroborides in the presence of ferrocene.

LITERATURE CITED

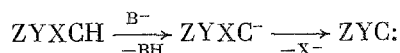
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FORMATION OF ETHYNYLHALO- AND CYANOHALOCARBENES UPON THE SOLVOLYSIS OF ETHYNYL- AND CYANODIHALOMETHANES: QUANTUM CHEMICAL CALCULATION OF THE FEASIBILITY OF THE GENERATION OF HALOANIONS AND HALOCARBENES WITH ETHYNYL AND NITRILE SUBSTITUENTS AT THE REACTION SITE

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One of the most common pathways for the generation of carbenes is found in stepwise solvolytic reactions:



These reactions are carried out, in particular, under phase transfer catalysis (PTC) conditions [1-3]. However, the list of carbenes generated by this method is relatively short including arylhalo-, hetarylhalo-, and (aryltio)halocarbenes in addition to the most well-known dihalocarbenes [2-4]. In the present work the MINDO/3 quantum chemical method used for the interpretation of the carbene decomposition of halomethyl anions [5] was employed for

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