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SYNTHESIS AND PROPERTIES OF 1,2,3-TRIAZOLES THAT CONTAIN A FERROCENYL RING

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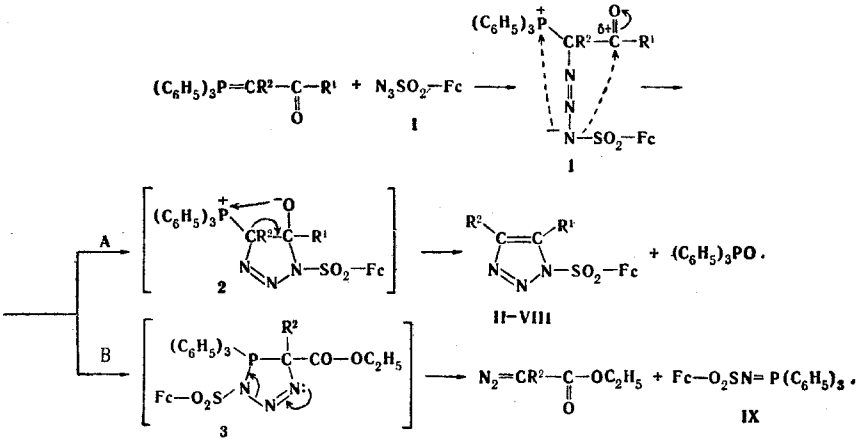
Ferrocenesulfonyl azide reacts with a number of aroylmethylenetriphenylphosphinomethylenes in dry methylene chloride to give 1,4,5-trisubstituted 1,2,3-triazoles (61-77% yields), which are readily converted to 4,5-disubstituted 1,2,3-triazoles and ethyl ferrocenesulfonate when they are refluxed in ethanol. The known triphenylphosphazo ferrocenyl sulfone and ethyl diazoacetate are formed in the case of the reaction of ferrocenesulfonyl azide with carbethoxymethylenetriphenylphosphinomethylene. The structures of the synthesized compounds were proved by the results of elementary analysis and IR, UV, and mass spectroscopy.

No information regarding 1,2,3-triazoles that contain a ferrocenyl ring is available in the literature. In developing our research on sulfur-containing derivatives of ferrocene [1, 2] on the one hand, and continuing our investigation of the reactivities of phosphorus ylids [3] on the other, we studied the reaction of ferrocenesulfonyl azide (I) [4] with phosphorus ylids; it is well known [5] that this reaction may lead to various products, depending on the structure of the phosphorus ylid component. Azide I reacts readily in solution in methylene chloride at room temperature with a number of aroyltriphenylmethylenephosphorus ylids [3] to give 1,4,5-trisubstituted 1,2,3-triazoles (II-VIII) and triphenylphosphine oxide. The formation of triazoles II-VIII can be represented by the following scheme [5]:



Fc = $C_5H_5FeC_5H_4$-ferrocenyl

The direction of cyclization in adduct 1 depends on the nature of substituent R^1 in the starting phosphorus ylid. When R^1 = C_6H_5 or p-substituted phenyl groups that have only a slight effect on the electrophilicity of the carbonyl carbon atom, the partial positive charge on which is higher than on the phosphorus atom, the cyclization proceeds

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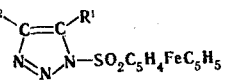
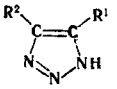
TABLE 1. 1,4,5-Trisubstituted Triazoles II-VIII 

Compound	R^1	R^2	Reaction time, h	mp, °C	IR spectrum, cm^{-1}: ν triazole	ν_{SO_2}	ferrocenyl ring	Found, %: Fe	N	Empirical formula	Calc., %: Fe	N	Yield, %
II	C_6H_5	H	1	134—136[a]	1183	1150, 1350	1408, 1000, 1003, 850	14,61	10,71	$C_{18}H_{15}FeN_3O_2S$	14,20	10,69	61
III	p-$CH_3C_6H_4$	H	3	141—142[a]	1175	1151, 1343	1406, 1113, 1001, 833	13,75	10,44	$C_{19}H_{17}FeN_3O_2S$	13,71	10,31	74
IV	p-$CH_3OC_6H_4$	H	2	129—131[a]	1179	1150, 1355	1410, 1102, 1004, 842	13,08	10,08	$C_{19}H_{17}FeN_3O_3S$	13,21	9,94	66
V	p-ClC_6H_4	H	5	169—171[b]	1183	1158, 1341	1405, 1104, 1000, 850	12,94	9,95	$C_{18}H_{14}ClFeN_3O_2S$[c]	13,05	9,82	60
VI	p-BrC_6H_4	H	6	159—161[b]	1184	1148, 1342	1403, 1106, 998, 838	12,66	9,02	$C_{18}H_{14}BrFeN_3O_2S$[d]	12,43	8,89	57
VII	p-$NO_2C_6H_4$	H	24	155—157[b]	1183	1154, 1352	1415, 1105, 1001, 844	12,79	12,43	$C_{18}H_{14}FeN_4O_4S$	12,74	12,81	77
VIII	C_6H_5	CH_3	10	155—157[a]	1177	1152, 1349	1407, 1111, 1002, 851	13,77	10,26	$C_{19}H_{17}FeN_3O_2S$	13,71	10,31	64

[a]From benzene. [b]From alcohol. [c]Found: Cl 8.51%. Calculated: Cl 8.32%. [d]Found: Br 17.31%. Calculated: Br 16.96%.

TABLE 2. 4,5-Disubstituted 1,2,3-Triazoles 

Compound	R^1	R^2	mp, °C	N found, %	Empirical formula	N calc., %	Yield, %
X	C_6H_5	H	146—147	28,64	$C_8H_7N_3$	28,99	99
XI	p-$CH_3C_6H_4$	H	154—155	26,45	$C_9H_9N_3$	26,42	98
XII	p-$CH_3OC_6H_4$	H	166—167	24,10	$C_9H_9N_3O$	24,02	97
XIII	p-ClC_6H_4	H	157—158	23,48	$C_8H_6ClN_3$[a]	23,41	99
XIV	p-BrC_6H_4	H	184—185[b]	18,68	$C_8H_6BrN_3$[c]	18,76	98
XV	p-$O_2NC_6H_4$	H	198—199[d]	27,42	$C_8H_6N_4O_2$	27,36	96
XVI	C_6H_5	CH_3	165—166	26,45	$C_9H_9N_3$	26,42	97

[a]Found: Cl 19.54%. Calculated: Cl 19.78%. [b]According to the data in [5], this compound has mp 185-187°C. [c]Found: Br 35.18%. Calculated: Br 35.76%. [d]According to the data in [5], this compound has mp 198-199°C.

via pathway A through the formation of a cyclic betaine (2). The latter forms 1,4,5-trisubstituted 1,2,3-triazoles (II-VIII) and triphenylphosphine oxide as a result of redistribution of the electron density (as shown in the scheme presented above).

If $R^1 = OC_2H_5$, the cyclization proceeds via pathway B; this is undoubtedly associated with nucleophilic attack of the azide anion on the more electrophilic (as compared with the carbonyl carbon atom) phosphorus atom. In this case an intermediate ring (3), which as a result of redistribution of the electron density (as shown in the scheme) undergoes decomposition to give triphenylphosphazo ferrocenyl sulfone [2] (IX) and ethyl diazoacetate, is formed.

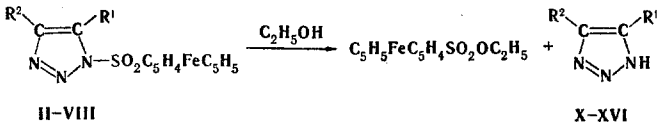
The synthesized triazoles II-VIII are solid well-crystallized substances that melt with decomposition. Their structures are confirmed by the results of elementary analysis and data from the IR and UV spectra (Table 1), as well as by chemical transformations.

In addition to the absorption bands characteristic for the SO_2 group [6] and the ferrocenyl ring [7], the IR spectra of triazoles II-VIII contain bands at 1175-1183 cm^{-1}, which are characteristic for the 1,2,3-triazole ring [5]. The UV spectra of triazoles II-VIII show absorption maxima at 240-250 nm; this is characteristic for this class of compounds [8].

The mass spectrum of triazole III is characterized by a weak-intensity peak of molecular ions M^+, the fragmentation of which leads to the formation of the following fragment

ions: $[M - H]^+$, $[M - p\text{-}CH_3C_6H_4C_2H]^+$, and $[M - SO_2C_5H_4FeC_5H_5]^+$. The most intense peaks in the mass spectrum are the peaks of $[C_5H_5FeC_5H_4 - SO_2N]^+$, $[C_5H_5FeC_5H_4]^+$, and $C_5H_5SO_2$ ions; in addition, peaks of Fe^+ and $C_5H_5^+$ ions, which are due to fragmentation of the ferrocenyl ring [10], are observed.

Triazoles II-VIII readily undergo alcoholysis when they are refluxed briefly in 96% ethanol; ethyl ferrocenesulfonate [1] and 4,5-disubstituted 1,2,3-triazoles (X-XVI) (Table 2) are formed in practically quantitative yields. Some of these products have been previously described [5].



II-VIII X-XVI

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with an IKS-14A spectrometer with NaCl and LiF prisms. The UV spectra of 10^{-4} M solutions of the compounds in alcohol were recorded with an SF-4 spectrophotometer. The mass spectra were obtained with a Varian CH-6 spectrometer at an ionizing-electron energy of 70 eV.

1,4,5-Trisubstituted 1,2,3-Triazoles (II-VIII). A solution of 1.3 g (0.005 mole) of azide I in 10 ml of dry methylene chloride was added to solutions of 0.005 mole of the corresponding triphenylaroylmethylenephosphorus ylid [3] in 30-40 ml of dry methylene chloride, and the mixture was allowed to stand at room temperature in the absence of moisture for the time indicated in Table 1. The solvent was then removed, and the solid residues were washed repeatedly with cold alcohol and crystallized. The alcohol wash solutions were diluted with water and allowed to stand at room temperature for 2 days, during which triphenylphosphine oxide precipitated in the form of characteristic acicular crystals, which were removed by filtration and recrystallized from 70% alcohol. As a result, 70-80% triphenylphosphine oxide, with mp 152-156°C was obtained; this product did not depress the melting point of an authentic sample.

The reaction of azide I with carbethoxymethylenetriphenylphosphorus ylid was carried out by the method in [5]. As a result, sulfone IX, which was identical to the compound synthesized in [2] with respect to its melting point and IR spectrum, and ethyl diazoacetate were obtained.

4,5-Disubstituted 1,2,3-Triazoles (X-XVI). A mixture of 0.5 g of the corresponding 1,4,5-trisubstituted 1,2,3-triazole II-VIII and 5 ml of alcohol was refluxed for 4 h, after which 10 ml of water was added, and the mixture was allowed to stand overnight at 0°C. The precipitate was removed by filtration, dried, and washed repeatedly with hot hexane until the wash solvent was no longer yellow. During this process, the ethyl ferrocenesulfonate, which had mp 61-62°C (mp 61-62°C [1]) after removal of the solvent, dissolved in the hexane. The hexane-insoluble residues — 4,5-disubstituted 1,2,3-triazoles X-XVI — were crystallized from chloroform–hexane (9:1).

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