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CONCLUSIONS

1. The 2-seleno-2-methyl- and 2-seleno-2-methyl-5,5-dimethyl-1,3,2-dioxaphosphorinanes in the liquid state (melt) and in solution exist as a mixture of two conformers with the structure of a distorted chair, which differ in the orientation of the P=Se bond. The energetically more favorable and quantitatively predominant, and also realized in the crystal, is the less polar form with an axial P=Se bond.

2. The vibrational spectra of the indicated compounds were interpreted on the basis of the experimental data and calculation.

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ACYLATION OF THERMAL ACETYLENES

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Previously it was proposed to run the acylation of terminal acetylenes in the presence of catalytic amounts of $[P(C_6H_5)_3]_2PdCl_2]CuI$ in triethylamine as the medium [1]. We found that terminal acetylenic hydrocarbons react vigorously with the acid chlorides of aromatic and aliphatic acids to give α-acetylenic ketones (50-80% yields) in the presence of catalytic amounts of CuI without using palladium. The reaction was run in an inert gas current in toluene at 60-80°C, and triethylamine was used as the base:

$$C_6H_5C{\equiv}CH + \underset{(I)}{RCOCl} \xrightarrow[\text{Toluene}\;(C_2H_5)_3N]{\text{CuI}} \underset{(II)}{C_6H_5C{\equiv}CC(O)R}$$

$$R = C_6H_5\,(a),\ m\text{-}CH_3C_6H_4\,(b),\ p\text{-}NO_2C_6H_4\,(c),\ (CH_3)_2CH\,(d),\ (CH_3)_3C\,(e).$$

TABLE 1. Characteristics of Acetylenic Ketones (II)

Ketone	Yield, %	T, °C	Time, h	bp, °C (p, mm Hg) mp, °C, n_D (°C)	Found/Calculated, % C	H	N	Empirical formula	Literature reference
(IIa)	82,5	60	6	172(4) 49–50					[1]
(IIb)	70,9	80	12	160(1) 1,6370(25)	87,00 87,24	5,71 5,49		$C_{16}H_{12}O$	
(IIc)	71,7	80	9	162–163 (from acetone)	71,60 71,71	3,87 3,61	5,52 5,58	$C_{15}H_9NO_2$	
(IId)	46,5	80	9	105(1)					[1]
(IIe)	81,0	40	2,5	95–96(2)					[1]

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EXPERIMENTAL

To 100 ml of toluene was added 0.01 mole of CuI, the triethylamine was heated until the CuI dissolved, then 0.1 mole of phenylacetylene and 0.1 mole of acid chloride (Ia-e) were added, and the mixture was stirred at 60-80° in an inert gas current. The reaction course was followed via GLC, based on the disappearance of phenylacetylene. After the usual workup the products were distilled or purified by recrystallization (Table 1).

CONCLUSIONS

A new method was developed for obtaining acetylenic ketones via the reaction of terminal acetylenes with the acid chlorides of aliphatic and aromatic acids in the presence of catalytic amounts of CuI without using Pd compounds.

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QUANTUM-CHEMICAL DISCUSSION OF cis – trans ISOMERIZATION OF NITROSTILBENES DURING ELECTRON TRANSFER AND IN CHARGE-TRANSFER COMPLEXES

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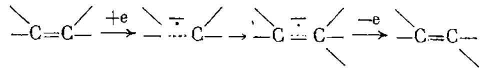
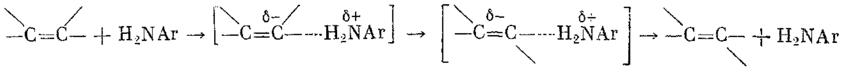
Previously it was shown that nitrostilbenes undergo isomerization at the ethylene bond when changing to the anion-radical form [1] or during bonding in charge-transfer complexes (CTC) to aromatic amines [2]via schemes (1) and (2), respectively:



(1)



(2)

The present paper is devoted to a quantum-chemical discussion of these reactions. In the calculations we used the cis and trans forms of the anion-radicals of the 4- and α-nitrostilbenes (4- and α-NS), and also the 2,4-, 4,4'-, and α,β-dinitrostilbenes (2,4-, 4,4'-, and α,β-DNS, respectively; Table 1).

The SCF MO LCAO method (CNDO/2 approximation) as the Dewar variation [3, 4] was used, taking into account half of the electrons. It was assumed that the stilbene skeleton does not change the interatomic distances and the valence angles when nitro groups are inserted into either the cis or trans isomers; the values of those geometric characteristics were taken from [5]. The results of calculating the one-electron energy levels in the cis and trans isomers of the nitrostilbene anion-radicals are given in Table 2. The meaning of the calculated values, given in Table 1, is as follows. The quantity Δ is the difference between the energies of the upper occupied levels for either the cis or trans form of the corresponding anion-radical, and I is a dimensionless index of the reactivity of the discussed anion-radicals, which reflects their tendency to isomerize, i.e., the degree of saturation of the ethylene bond by the spin density. This index is expressed by the integral of overlapping between the idealized π_g orbital of the nitrostilbene anion-radical, which is completely localized on the ethylene bond, and the higher occupied orbital Ψ_f of this anion-radical: $I = \int \pi_g \Psi_f d\tau$. Apparently, in the case I = 1 the antibonding of the C=C bond should be maximum, i.e., isomerization of the cis–trans type can go easily. In the case I ≈ 0 no antibonding of the bond should occur and the cis–trans conversion cannot be easy. As a result, index I characterizes the degree of double bonding of the inserted C=C fragment in the anion-radical forms of the nitrostilbenes.

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