

because of disproportionation reaction (5). Monopyridylphosphine and dipyridylphosphine were not detected during the experiment, since they participate in similar transformations more rapidly than  $\text{PH}_3$ .

Dimeric  $\text{Cu(II)}\text{--Cu(I)}$  complexes of mixed valence bring about reaction (1). The fact is that  $\text{Cu(I)}$  ions, in contrast to  $\text{Cu(II)}$  ions, form complexes with  $\text{PH}_3$ . The optimum conditions for coordination of the  $\text{PH}_3$  and  $\text{C}_5\text{H}_5\text{N}$  reactants and their interaction in the coordination sphere are created in a complex with mixed valence.

The  $\text{PH}_3$  was obtained by the acidic hydrolysis of  $\text{Zn}_3\text{P}_2$ . The  $\text{CuX}_2$  was rendered anhydrous at  $100\text{--}200^\circ\text{C}$ . The  $\text{PH}_3\text{--Ar}$  and  $\text{PH}_3\text{--O}_2$  gas mixtures were dried with granulated  $\text{NaOH}$ . The pyridine was purified by fractional distillation over sodium. The synthesis was carried out in a stirred thermostatted flow reactor. The  $(2\text{-C}_5\text{H}_4\text{N})_3\text{P}$  accumulated with repetition of the number of cycles of  $\text{PH}_3$  and  $\text{O}_2$  absorption in the  $\text{Py--CuX}_2$  solution (0.5 mole/liter). The  $^{31}\text{P}$  NMR spectrum of the solution after precipitation of the  $\text{Cu(I)}$  ions by means of potassium iodide contained only one intense signal at 3.6–3.8 ppm, which is characteristic for tripyridylphosphine. The IR spectrum of the precipitate after removal of the pyridine contains absorption bands at 430, 500, and  $620\text{ cm}^{-1}$  ( $\text{P--C}$ ) and at  $1640\text{ cm}^{-1}$  ( $\text{C=C}$ ).

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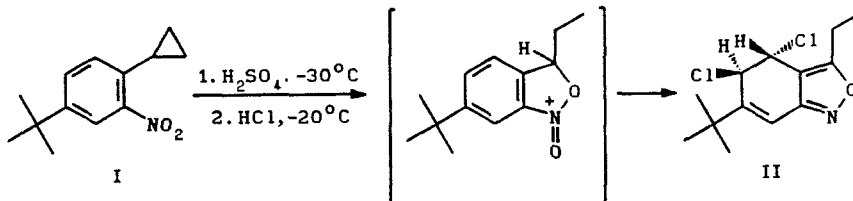
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## SYNTHESIS OF 3,6-DIALKYL-4,5-DIHYDRO-4,5-DICHLORO-2,1-BENZISOXAZOLES FROM o-NITROPHENYLCYCLOPROPANES

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Acid-catalyzed reactions of o-nitrophenylcyclopropanes that make it possible to transform them directly to o-nitroalkenylbenzenes [1] and o-nitrosopropiophenones [2, 3] or to substituted 2,1-benzisoxazoles [4] are known. These reactions are realized through intermediates of a common type — N-oxo-2,1-benzisoxazolinium ions, which are formed as a result of intramolecular interaction of the o-nitro group with the carbonium ion that develops upon opening of the protonated cyclopropane ring of the starting nitro compound.

We have found that, in contrast to the previously studied transformations, the 2,1-benzisoxazolinium ion formed when (4-tert-butyl-2-nitrophenyl)cyclopropane (I) is dissolved in concentrated sulfuric acid is converted by the action of hydrochloric acid not to the corresponding halo-substituted 2,1-benzisoxazole (taking into account the data in [4]) but rather to 6-tert-butyl-4,5-dihydro-4,5-dichloro-3-ethyl-2,1-benzisoxazole (II).



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The structure of II was confirmed by the PMR spectral data and the results of x-ray diffraction analysis. The vicinal chlorine atoms in II are trans-oriented. The mechanism and possibilities of the use of this unusual transformation are under investigation.

**trans-6-tert-Butyl-4,5-dihydro-4,5-dichloro-3-ethyl-2,1-benzisoxazole (II, C<sub>13</sub>H<sub>17</sub>Cl<sub>2</sub>NO).** A 2.2-g (0.01 mole) sample of (4-tert-butyl-2-nitrophenyl)cyclopropane (I) was added slowly at  $-35^{\circ}\text{C}$  to 8 ml of concentrated H<sub>2</sub>SO<sub>4</sub>, after which the reaction mixture was stirred for 1 h at the same temperature. It was then poured into 50 ml of concentrated HCl cooled to  $-20^{\circ}\text{C}$  to  $-25^{\circ}\text{C}$ , and the reaction products were extracted with CHCl<sub>3</sub>. The extract was washed successively with water and sodium carbonate solution and dried with MgSO<sub>4</sub>. The solvent was evaporated, and the residue was recrystallized from alcohol to give 1.79 g (65%) of II with mp  $101-103^{\circ}\text{C}$ . PMR spectrum (in CDCl<sub>3</sub>):  $\delta$  1.21 (s, 9H), 1.32 (t, 3H), 2.92 (q, 2H), 4.92 (d, 1H, J = 3.0 Hz), 5.31 (d, 1H, J = 3.0 Hz), 6.82 ppm (s, 1H).

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## ANOMALOUS REACTION OF PHOSGENE TOSYLIMINE WITH ETHYLENE GLYCOL

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It is known that arylsulfonyliminocarbonic acid esters are formed in the reaction of phosgene arylsulfonylimines with sodium alkoxides [1, 2].

We have established that the reaction of phosgene tosylimine in the presence of triethylamine in acetonitrile unexpectedly leads to 3-tosyl-2-oxazolidinone (I). Its formation cannot be due to rearrangement of the hypothetical tosyliminocarbonate, since such processes are possible under considerably more severe conditions [1]. Oxazolidinone I is evidently formed through the intermediate 2-chloroethyl N-tosylcarbamate (II), the intramolecular alkylation of which leads to the formation of the oxazolidine ring:

