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HETEROCYCLIC ANALOGS OF PLEIADIENE. XXIV*. UNEXPECTED PRODUCTS OF THE REACTION OF 1-METHYLPERIMIDINE WITH PHENYLMETALLIC COMPOUNDS IN THE PRESENCE OF BENZOPHENONE

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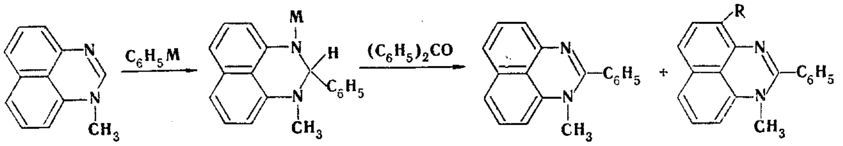
UDC 547.856.7'559

1-Methylperimidine adds phenylsodium and phenyllithium to the $C \doteq N$ bond to give 1-methyl-2-phenyl-2,3-dihydroperimidines. However, if benzophenone is present in the reaction mixture, a mixture of 1-methyl-2-phenylperimidine and 1-methyl-2,4-diphenylperimidine (when phenylsodium is used) or 1-methyl-2-phenyl-4-(α-hydroxybenzhydryl)perimidine (when phenyllithium is used) is formed. It is assumed that the formation of products involving substitution in the naphthalene ring is associated with the participation of $C_6H_5^{\bullet}$ and $(C_6H_5)_2C^{\bullet}-O^-$ radical particles that are formed on reaction of the phenylmetallic compound with benzophenone.

We have previously shown that organomagnesium and organolithium compounds react with 1-methylperimidine (I) to give almost exclusively products of addition to the $C=N$ bond [2]. We have now established that phenylsodium also reacts similarly with I and that the character of the final product depends on the reagents used in the last step. 1-Methyl-2-phenyl-2,3-dihydroperimidine is formed in 90% yield in the case of carbonization with dry ice (to ascertain the possible metallation products). However, completely different compounds — the known 1-methyl-2-phenylperimidine (III, in 54% yield) and the previously undescribed 1-methyl-2,4-diphenylperimidine (IVa, in 14-17% yield) — are obtained on attempts to establish the reaction products by reaction with benzophenone.



I II a,b III IV a,b

II a M=Na; b M=Li; IV a $R=C_6H_5$; b $R=\underset{OH}{C}(C_6H_5)_2$

The structure of IVa is confirmed by the results of elementary analysis, the mass spectrum (molecular weight 334), the absence of bands at 3100-3600 cm^{-1} in the IR spectrum, the yellow-orange color characteristic for 2-arylperimidines [3], and the following features of its PMR spectrum: a) the absence of a quartet at δ 6.87 ppm (Fig. 1) related to the proton attached to the C_4 atom in the spectrum of I [3] and III (Fig. 1); b) the ratio of the signals of the aromatic protons to the protons of the CH_3 group (5:1). In addition, IVa does not form even traces of a methiodide on prolonged heating with excess methyl iodide. The

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[*] See [1] for communication XXIII.

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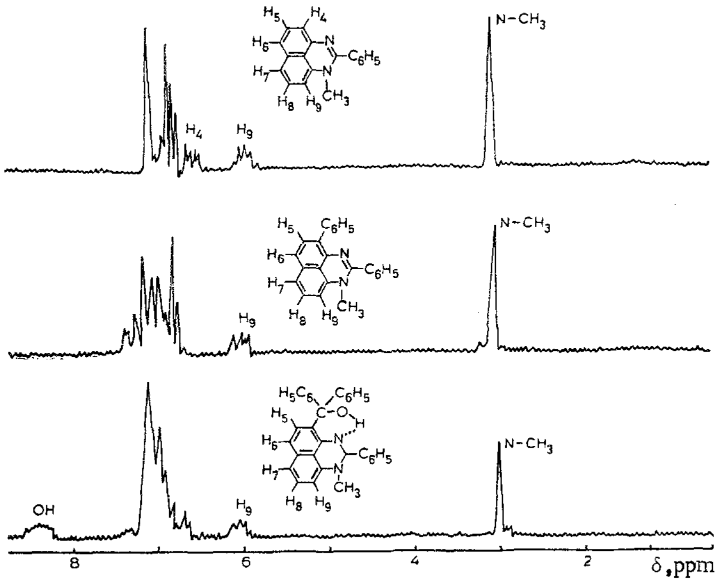
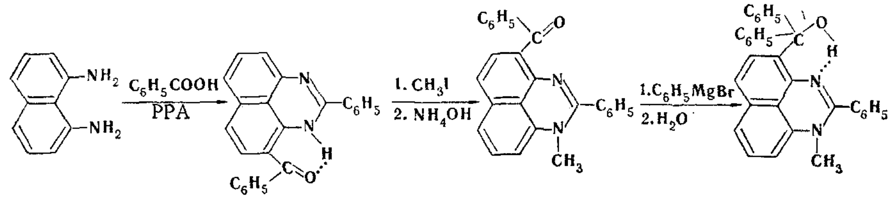


Fig. 1. PMR spectra of $CDCl_3$ solutions of 1-methyl-2-phenylperimidine, 1-methyl-2-4-diphenylperimidine, and 1-methyl-2-phenyl-4-(α-hydroxybenzhydryl)perimidine.

reason for this may be the steric hindrance caused by the substituents found only in the 4 position of the perimidine system.

It might have been expected that similar results would be obtained when phenylsodium was replaced by phenyllithium, but this was not so. The yield of 1-methyl-2-phenylperimidine in this case was reduced to 14-20%, and the chief product (in 33% yield) was a new substance, which, according to the results of elementary analysis, is the 3-hydroxybenzhydryl derivative of 1-methyl-2-phenylperimidine. According to the IR spectroscopic data, this substance contains an OH group tied up in an intramolecular hydrogen bond (a broad ν_{OH} band at 3100-3500 cm^{-1} that does not change on dilution). The proton of the hydroxyl group appears in its PMR spectrum as a broad singlet at δ 8.45 ppm and vanishes after deuteration; the quartet of the H_4 proton is not found in the spectrum (Fig. 1). In addition, this substance did not undergo quaternization. On the basis of these data we assigned the 1-methyl-2-phenyl-4-(α-hydroxybenzhydryl)perimidine structure (IVb) to it. The definitive confirmation of structure IVb was obtained by alternative synthesis of this compound via the following scheme (transformations of the V→VI→VII type are discussed in [4]):



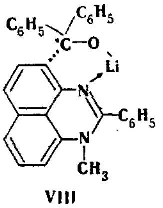
V VI VII IVb

Compound III is evidently formed by the splitting out of a metal hydride from N-metallated derivative II under the influence of benzophenone, which, as is well known, is a good hydride-ion acceptor. We established that 1-methyl-2-phenyl-2,3-dihydroperimidine itself is not aromatized by benzophenone.

The incorporation of α-hydroxybenzhydryl and, particularly, phenyl groups in the 4 position can be explained by a radical mechanism. In fact, metallation of I in the 4 position is unlikely, inasmuch as the addition of carbon dioxide or benzaldehyde to the reaction mixture instead of benzophenone does not result in the isolation of 1-methyl-2-phenylperimidine-4-carboxylic acid or the corresponding alcohol. It is most likely that benzophenone reacts with excess organometallic compound to give phenyl radicals and benzophenone anion radicals [5-7]:

$$C_6H_5{:}M + (C_6H_5)_2C{=}O \longrightarrow C_6H_5^{\bullet} + (C_6H_5)_2\dot{C}{-}O^- + M^+$$

Because of the extremely high capacity of the Li^+ cation for coordination with the unshared electron pairs, the primary formation of IVb when phenyllithium is used can be explained by reaction through stabilized cyclic transition complex VIII:



VIII

When phenylsodium is used, the significance of this sort of coordination naturally decreases, and the phenyl radicals play a more active role, and this leads to the formation of IVa.

The reactions that we studied in this research represent the first instance of C-radical substitution in the naphthalene ring of perimidines.

EXPERIMENTAL

The IR spectra were obtained with a UR-20 spectrometer. The UV spectra were recorded with an SF-4A spectrophotometer. The PMR spectra of $CDCl_3$ solutions of the compounds were obtained with a Tesla spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The mass spectrum was obtained with an MKh-1303 spectrometer with direct introduction of the sample into the inlet system at an ionizing-electron energy of 70 eV and an ion-source temperature of 250° (the ion detector was a secondary electron multiplier). Chromatography was carried out on Brockmann activity V aluminum oxide (the R_f values in a thin layer of absorbent are presented for an Al_2O_3—benzene system).

Reaction of 1-Methylperimidine with Phenylsodium in the Presence of Benzophenone. A 1.8-g (0.08 g-atom) sample of sodium was finely granulated under melted paraffin, after which the paraffin was washed away successively with 30-40 ml of absolute toluene and absolute benzene. The sodium was then suspended in 10-13 ml of benzene, and the suspension was transferred to a flask filled with nitrogen. The sodium was activated with drops of isoamyl alcohol, after which a solution of 4.4 ml (0.04 mole) of freshly distilled chlorobenzene in 5 ml of benzene was added in portion at such a rate that the temperature of the mixture did not exceed 35°. The resulting phenylsodium was cooled to room temperature, and a solution of 1.8 g (0.01 mole) of 1-methylperimidine in 15-20 ml of benzene was added all at once. The mixture was then stirred at 45-50° for 1 h, after which a solution of 7.2 g (0.04 mole) of benzophenone in 15 ml of benzene was added. After 1 h, 2-3 ml of alcohol was added to destroy the sodium residues after which 20 ml of 15% hydrochloric acid was added. The resulting yellow precipitate was removed by filtration and washed with benzene. The benzene layer of the filtrate was treated several times with 15% HCl solution (a total of 50-60 ml). The hydrochloric acid extract was washed with benzene and combined with the precipitate, and the mixture was neutralized with ammonia and extracted with chloroform. The extract was washed with water until the wash waters were neutral, after which it was dried, and a portion of the solvent was removed by distillation. The residual solution was passed through a column filled with 500 g of aluminum oxide with elution by benzene. The first fraction yielded 0.35 g (14%) of orange crystals of 1-methyl-2,4-diphenylperimidine with R_f 0.75 and mp 179° (from hexane). UV spectrum, λ_{max}, nm (log ε): 360 (4.20) and 433 (3.24). Mass spectrum, m/e: 334 (M^+), 319 ($M^+ - 15$), and 257 ($M^+ - 77$). Found: C 86.1; H 5.5; N 8.8%. $C_{24}H_{18}N_2$. Calculated: C 86.2; H 5.4; N 8.4%. The second fraction yielded 1.4 g (54%) of 1-methyl-2-phenylperimidine with R_f 0.3.

Reaction of 1-Methylperimidine with Phenyllithium in the Presence of Benzophenone. A few drops of a solution of 4.7 g (0.03 mole) of bromobenzene in 10 ml of ether were added at

20-25° in a nitrogen atmosphere to a stirred suspension of 0.42 g (0.06 g-atom) of finely cut lithium in 10 ml of absolute ether. The reaction mixture warmed up spontaneously, and the surface of the lithium metal became clean. The rest of the bromobenzene solution was added at such a rate that the mixture refluxed gently. After all of the bromobenzene solution had been added, the mixture was stirred for 15-20 min, after which a solution of 1.8 g (0.01 mole) of 1-methylperimidine in 25-30 ml of absolute toluene was added all at once, and the mixture was stirred at 55-60° for 1 h. A solution of 5.5 g (0.03 mole) of benzophenone in 10 ml of toluene was added, and the mixture was allowed to stand for 2 h. A total of 20 ml of 15% hydrochloric acid was then added, and the liberated oil was crystallized easily by trituration with petroleum ether. The crystals were treated carefully with ammonium hydroxide in portions, after which they were removed by filtration and washed with water until the wash waters were neutral. Separation by means of thin-layer chromatography (TLC) (elution with benzene) yielded two principal products: 0.5 g (20%) of 1-methyl-2-phenylperimidine and 1.5 g (33%) of yellow crystals of 1-methyl-2-phenyl-4-α-hydroxybenzhydryl)perimidine with R_f 0.77 and mp 229° (from acetone). UV spectrum, λ_{max}, nm (log ε): 344 (4.11) and 405 (3.22). Found: C 84.5; H 5.8; N 6.4%. $C_{31}H_{24}N_2O$. Calculated: C 84.5; H 5.4; N 6.3%.

2-Phenyl-4(9)benzoylperimidine (VI). A 5.5-g (0.035 mole) sample of 1.8-naphthalenediamine and 12.2 g (0.1 mole) of benzoic acid were added successively with vigorous stirring to 70 g of polyphosphoric acid (PPA) heated to 100°. All of the solid material dissolved gradually to give a dark-red mixture. The mixture was heated to 135-140° and stirred at this temperature for 4 h. The viscous solution was poured in a fine stream into 700-800 ml of cold water with vigorous stirring. The aqueous mixture was made alkaline to pH 8-9 with ammonia, and the brown precipitate was removed by filtration, washed to neutrality with water, and dried. The dry product was dissolved by heating in 80-90 ml of benzene, and the solution was filtered. The filtrate was chromatographed with a column filled with 500 g of Al_2O_3 with elution by benzene. The first fraction was collected and worked up to give 2.4 g (20%) of orange-red crystals of VI with mp 202° (from benzene—petroleum ether). IR spectrum (chloroform), cm^{-1}: ν_{N-H} 3180 and $\nu_{C=O}$ 1620. Found: C 82.5; H 4.7; N 8.3%. $C_{24}H_{16}N_2O$. Calculated: C 82.7; H 4.6; N 8.0%.

1-Methyl-2-phenyl-4-benzoylperimidine (VII). A 1.2-ml (0.02 mole) sample of methyl iodide was added to a suspension of 1.8 g (0.005 mole) of VI in 15 ml of DMF, and the mixture was heated to 115-120° and stirred at this temperature for 4 h. All of the solid material gradually dissolved to give a red solution. At the end of the indicated time, the mixture was cooled and filtered to give 0.6 g (33%) of unchanged VI. The filtrate was diluted with ether to give a 50-luminous yellow precipitate. The precipitate was removed by filtration, washed with water, suspended in 25 ml of 10% ammonium hydroxide, and refluxed for 2-3 min. The solid material was separated by filtration, washed to neutrality with water, and dried to give 1.25 g (65%) of shiny yellow plates of VII with mp 166-167° (from aqueous alcohol). IR spectrum (chloroform), cm^{-1}: $\nu_{C=O}$ 1620. Found: C 82.72; H 4.75; N 7.90%. $C_{25}H_{18}N_2O$. Calculated: C 82.87; H 4.97; N 7.73%.

1-Methyl-2-phenyl-4-(α-hydroxybenzhydryl)perimidine (IVb). Ether (3 ml) was added to 0.2 g (0.0075 g-atom) of magnesium powder activated with an iodine crystal, after which a solution of 1.57 g (0.01 mole) of bromobenzene in 3 ml of ether was added dropwise at such a rate that the mixture refluxed gently. After all of the bromobenzene solution had been added, the mixture was refluxed until all of the magnesium had dissolved. A suspension of 0.9 g (2.5 mmole) of VII in 15 ml of absolute toluene was added, whereupon all of the solid material dissolved immediately to give a genuinely red solution. After 15 min, 20 ml of water was added, and the layers were separated. The solvent was evaporated from the organic layer to give 1 g (91%) of IVb. No melting-point depression was observed for a mixture of this product with a genuine sample, and the IR spectra were identical.

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1,4-CYCLOADDITION OF 4-PHENYL-1,2,4-TRIAZOLINE-3,5-DIONE TO 2-VINYLPYRIDINES

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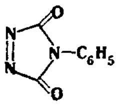
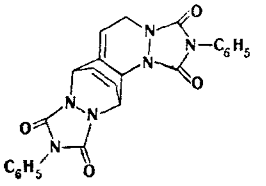
The addition of 4-phenyl-1,2,4-triazoline-3,5-dione (I) to the pseudodienic system of 2-vinylpyridines leads to a new heterocyclic system – triazolo[1,2-*a*]-5-azacinnoline. A second molecule of I undergoes further reaction of the substitutive addition type.

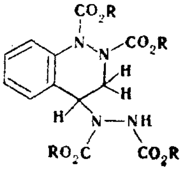
It is well known that styrene, because of its pseudodienic system, which is formed by the vinyl group and the aromatic ring double bond conjugated with it, is capable of reacting with active dienophiles via a 1,4-cycloaddition scheme [1,2]. In the reaction of styrene and its analogs with 4-phenyl-1,2,4-triazoline-3,5-dione (I), two molecules of the latter undergo reaction, and the product has structure II. Styrene reacts differently with azodicarboxylic acid esters, and adduct III is formed [2].



I



II



III

We have investigated the behavior of 2-vinylpyridine and its derivatives in the reaction with dienophile I. The bright color of 4-phenyl-1,2,4-triazoline-3,5-dione vanishes after a few minutes in ether at room temperature, and colorless amorphous adducts with compositions corresponding to the addition of two molecules of dienophile I to one molecule of vinyl pyridine are formed in 60-80% yields.

In contrast to styrene, 2-vinylpyridines react with I with retention of the aromatic character of the pyridine ring. Compounds with structure IV are formed in this case, as is shown in the scheme at the top of the next page.

Evidence in favor of this structure is offered by the presence of an intense absorption band of an NH group at 3180-3190 cm^{-1}, which cannot be present in the spectrum in the case of structure II. In addition, the chemical shifts of the signals of the protons in the aromatic region (in addition to the signals of the two C_6H_5 groups), their multiplicities, and the J constant are characteristic for the protons of the pyridine ring [3](see Table 2). For example, quartets of 9-H protons at δ 9.4 ppm ($J_{98} = 9$ Hz, $J_{97} = 1.5$ Hz), 7-H at δ 8.57 ppm ($J_{78} = 4.5$ Hz, $J_{79} = 1.5$ Hz), and 8-H at δ 8.03 ppm ($J_{87} = 4.5$ Hz, $J_{89} = 9$ Hz) are observed for IVa. In the case of structure II one should have expected the presence of signals of olefinic protons at stronger field. It is characteristic that, in contrast to compounds of the

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