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# SYNTHESIS OF 1,2-DIPHENYL-1,2,3,4-TETRAHYDROCINNOLINES FROM ALKENES AND THE CATION OF TRIPHENYLDIAZENE

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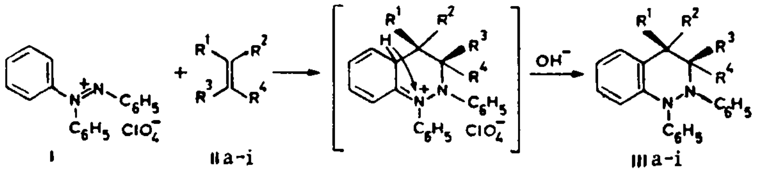
It is well-known that [1] the cation of triphenyldiazene, obtained by the electrochemical oxidation of triphenylhydrazine, reacts with ethyl vinyl ether, with closing of the tetrahydrocinnoline cycle. It would be timely to investigate the preparational possibilities of this reaction, since methods for the synthesis of cinnoline derivatives, including tetrahydrocinnolines, are extremely limited [2, 3], and to obtain information on the stereochemical special characteristics of this process, which is important for an understanding of its mechanism. To these ends, we have examined the interaction of triphenyldiazene perchlorate (I) with alkenes of different types: vinyl ethers IIa-d, enamines IIe, and styrenes IIf-i, as well as with acrylonitrile and methyl acrylate.



II, III a $R^1=OCH_3$; b $R^1=OC_2H_5$; c $R^1=OC_2H_5$, $R^4=D$; d $R^1=OCH_3$, $R^3=R^4=CH_3$; e $R^1=N(CH_2)_5$, $R^3=R^4=CH_3$; f $R^1=C_6H_5$; g $R^1=C_6H_5$, $R^3=D$; h $R^1=C_6H_5$, $R^4=D$; i $R^1=C_6H_5$, $R^2=CH_3$ (unindicated R=H)[3]

It was found that, from vinyl ethers and enamine, the corresponding 1,2-diphenyl-1,2,3,4-tetrahydrocinnolines (IIIa-e) are formed with a high yield even cold, while from styrenes they are formed only with prolonged heating. The latter was found possible due to the fact that salt I, in contrast to other diazene salts [1, 4, 5], remains practically unchanged with long-term boiling of an acetonitrile solution of it. Under these same conditions, there was no kind of reaction between the cation of I with acrylonitrile or methyl acrylate. Thus, the cation of triphenyldiazene reacts only with olefins with a nucleophilic character, and this reaction can serve as a method for the synthesis of 1,2-diphenyl-1,2,3,4-tetrahydrocinnolines (IIIa-i, Tables 1 and 2), having an electron-donor substituent $R^1$.

In the IR spectra of compounds III there are no characteristic frequencies of any kind of short bonds or functional groups, except for the usual frequencies of the aromatic rings, and their UV spectra are similar to the spectra of triphenylhydrazine. The PMR spectra of the derivatives III (Table 1) have a corresponding set of signals, reflecting the structure ascribed to them.

A conclusion with respect to the position of the substituent $R^1$ in the ring can be drawn from the mass spectroscopy of typical representatives of the compounds III: derivatives IIIa and IIIf with a methoxy or phenyl group, respectively.* In the mass spectra of these compounds (Table 3) there are intense peaks of molecular ions (m/e 316 for IIIa and 362 for IIIf), which attests to their stability with respect to electron impact. A lowering of the

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*The mass spectrum of the compound IIIe could not be obtained due to the thermal destruction of the substance under the conditions of the recording of the spectrum.

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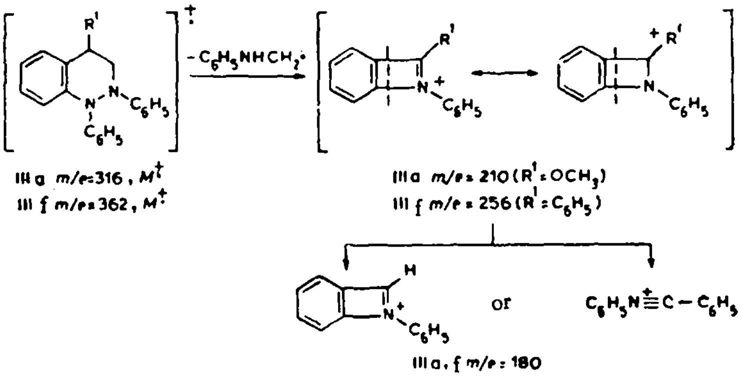
TABLE 1. PMR Spectra of Compounds IIIa-i

| Compounds | $R^1$ | $R^2$ | $R^3$ | $R^4$ | Solvent | PMR spectra, δ ppm (J, Hz) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
| IIIa | $OCH_3$ | H | H | H | $C_6H_5NO_2$ | 3,39s | 4,46dd (6,0, 7,0) | 3,73dd (7,0, 14,5) | 4,00dd (6,0, 14,5) |
| IIIb | $OC_2H_5$ | H | H | H | $CDCl_3$ | 3,71m[a], 1,26t (7,0) | 4,59dd (5,5, 8,0) | 3,80dd (8,0, 14,0) | 4,14dd (5,5, 14,0) |
| IIIc | $OC_2H_5$ | H | H | D | $CDCl_3$ | 3,57m[a], 1,15t (7,0) | 4,60d (8,0) | 3,79d (8,0) | — |
| IIId | $OCH_3$ | H | $CH_3$ | $CH_3$ | DMSO-$d_6$ | 3,48, 3,38s | 3,97, 3,88s | 1,25, 0,95s | 1,35, 1,18s |
| IIIe | $N(CH_2)_5$ | H | $CH_3$ | $CH_3$ | $CCl_4$ | 2,74—1,94m, 1,41m | 3,62s | 1,03s | 1,24s |
| IIIf | $C_6H_5$ | H | H | H | $CCl_4$ | —b | 4,08dd (6,5, 12,0) | 3,43dd (12,0, 14,0) | 3,83dd (6,5, 14,0) |
| IIIg | $C_6H_5$ | H | D | H | $CCl_4$ | —b | 4,08d (6,5) | — | 3,82d (6,5) |
| IIIh | $C_6H_5$ | H | H | D | $CCl_4$ | —b | 4,09d (12,0) | 3,42d (12,0) | — |
| IIIi | $C_6H_5$ | $CH_3$ | H | H | $CD_3CN$ | —b | 1,48s | 3,85s[c] | 3,90s[c] |

[a] $ABX_3$ system. [b] The signal coincides with the multiplet resonance of other aromatic protons at 6.4-7.4 ppm. [c] In $CDCl_3$, protons at 3-H are magnetically equivalent.

energy of the ionizing electrons from 70 to 15 eV makes the peaks of the molecular ions in the spectra more intense. The main primary process of their fragmentation is the formation of ions with m/e of 210 and 256, respectively, which points to their decomposition with the evolution of exactly the same particle $C_6H_5NHCH_2^{\cdot}$. This is confirmed also by the mass spectrum of the deuterated compound IIIg, in which as in the case of the compound IIIf, there is the peak of an ion with m/e 256. The structure of ions with m/e 210 and 256 is demonstrated by their further decomposition into ions with m/e 180, whose multistage formation from $M^{+\cdot}$ is confirmed by the dependence of the intensity on the energy of the ionizing electrons (Table 3). Thus, the electron-donor substituent is located in position 4 of the cycle, i.e., in the para position with respect to the nitrogen atom, carrying a formal positive charge.



An idea of the spatial characteristics of the closing of the cycle in the reaction being studied can be obtained from a comparison of the PMR spectra of the compounds IIIb and IIIf with the spectra of their deuterated analogs IIIc and IIIg, h.

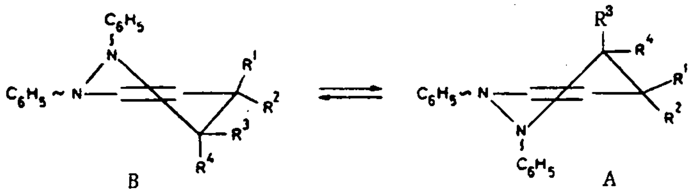
In the spectrum of the compound IIIf the signals of the protons in positions 3 and 4 correspond to the AMX system. If it is assumed that 1,2,3,4-tetrahydrocinnolines, like a majority of other six-membered unsaturated heterocycles [6] with one double bond, exist in the form of a half-chair, then, starting from the value of the spin-spin coupling constant (SSCC) between the strong-field proton in position 3 and the proton 4-H, it can be concluded that the molecules of the substance IIIf are in conformation A, with an equatorial orientation of the phenyl substituent in position 4. With a transition to the compounds IIIg and IIIh, synthesized from the cis- and trans-deuterostyrenes IIg and IIh, respectively, changes are

TABLE 2. Compounds IIIa-i

| Compound | mp, °C (from ethanol) | $R_f$ | UV spectrum in $CH_3CN$[a] |  | Found, % |  |  | Empirical formula | Calculated, % |  |  | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | $\lambda_{max}$, нм | lg ε | C | H | N |  | C | H | N |  |
| IIIa | 151 | 0,28 | 282<br>248 | 4,38<br>4,45 | 79,8 | 6,3 | 8,7 | $C_{21}H_{20}N_2O$ | 79,7 | 6,4 | 8,8 | 96 |
| IIIb[b] | 130 | 0,30 | 280<br>245 | 4,11<br>4,23 | 80,2 | 6,6 | 8,4 | $C_{22}H_{22}N_2O$ | 80,0 | 6,7 | 8,5 | 95 |
| IIId | 96 | 0,40 | 299<br>267<br>240 | 4,13<br>4,14<br>4,06 | 80,1 | 6,9 | 8,2 | $C_{23}H_{24}N_2O$ | 80,2 | 7,0 | 8,1 | 97 |
| IIIe | 129 | 0,65 | 298<br>267<br>240 | 4,02<br>4,20<br>4,05 | 81,3 | 8,0 | 10,4 | $C_{27}H_{31}N_3$ | 81,6 | 7,9 | 10,6 | 96 |
| IIIf[c] | 184 | 0,80 | 286<br>247 | 4,32<br>4,50 | 86,3 | 6,0 | 7,6 | $C_{26}H_{22}N_2$ | 86,2 | 6,1 | 7,7 | 48 |
| III i | 60 | 0,81 | 282<br>255 | 4,20<br>4,37 | 86,3 | 6,4 | 7,3 | $C_{27}H_{24}N_2$ | 86,1 | 6,4 | 7,4 | 46 |

[a] UV spectrum of triphenylhydrazine in acetonitrile — $\lambda_{max}$, nm (log ε): 248 (4.52), 288 (4.38). [b] Analogous properties are possessed by the deutero derivative IIIc. [c] Analogous characteristics are possessed by the deutero derivatives IIIg, h.

observed in their PMR spectra (Table 1), which indicate unambiguously that the configuration of the starting alkenes is retained in the cyclic products.



B

A

In the case of the compounds IIIa-c, the lowered value of the SSCC between the strong-field proton 3-H and the protons at $C_4$ (Table 1) points to the existence of a conformational equilibrium A ⇄ B. It is possible that this is also argued by the doubling, at room temperature, of all the singlet signals of the substituents $R^1$-$R^4$ in the PMR spectrum of the compound IIId, with a ratio of the intensities close to 1:1. With heating, there is a pairwise coalescence of the signals. The presence of an equilibrium is due to the lower, in comparison with the compounds IIIf-i, values of the 1,3-diaxial interactions in conformation B between the substituents $R^1$ and the inverting* phenyl group in position 2. In the PMR spectrum of the tetrahydrocinnoline IIIc, in contrast to the spectrum of the undeuterated compound IIIb, the signal of the equatorial proton 3-H is absent (Table 1), which points to a trans configuration of the substance.

Consequently, in the examples under study here there is complete retention of the configuration of the olefins in the cycloaddition products, i.e., the cis principle is satisfied, as in the case of the reactions, already discussed by the present authors, of several other salts of aryldiazene with cis- and trans-β-deuterostyrenes [8, 9]. This serves as a strong basis for relating the present conversions to the class of reactions of polar 1,4-cycloaddition, which, in turn, is regarded [10] as a partial case of diene synthesis. This is borne out by other noted regularities (the nucleophilic character of the reacting alkene, the sharply expressed regioselectivity), characteristic of a 1,4-cycloaddition as a whole.

By analogy [11], it can be postulated that in the present reaction there is a joint interaction between the LUMO of the diazene salt and the HOMO of the alkene, as a result of which the cis principle is observed. The strong asymmetry of the reacting components leads to the formation of a sole structure of the isomer; as in all known cases of 1,4-cycloaddition with the participation of an ionic diene component, there is a para-orienting effect

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*The rapid inversion of the substituents at the nitrogen atom is a characteristic feature of hydrazine derivatives of this type [7].

TABLE 3. Mass Spectra of 1,2,3,4-Tetrahydrocinnolines IIIa and IIIf with an Energy of the Polarizing Electrons of 70 and 15 eV

| Energy of polarizing electrons, eV | m/e (relative intensity, %)* |
|---|---|
| | 1,2-Diphenyl-4-methoxy-1,2,3,4-tetrahydrocinnoline IIIa |
| 70 | 317 (23), 316 (90), 285 (3), 280 (2), 279 (9), 239 (2), 224 (4), 223 (3), 216 (2), 211 (10), 210 (29), 209 (5), 207 (5), 196 (37), 183 (6), 182 (9), 181 (9), 180 (60), 179 (35), 177 (4), 170 (4), 169 (28), 167 (56), 165 (6), 150 (9), 149 (100), 147 (4), 139 (6), 124 (6), 120 (5), 77 (37), 76 (12), 71 (8), 70 (6), 69 (8), 57 (13), 55 (17), 51 (21), 43 (28), 39 (9) |
| 15 | 317 (27), 316 (100), 212 (3), 211 (13), 210 (9), 181 (13), 180 (11), 170 (4), 169 (35), 168 (4), 167 (4), 147 (7), 106 (7), 104 (8) |
| | 1,2,4-Triphenyl-1,2,3,4-tetrahydrocinnoline IIIf |
| 70 | 362 (24), 361 (32), 285 (4), 271 (4), 270 (8), 269 (5), 258 (3), 257 (21), 256 (100), 255 (6), 182 (3), 181 (3), 180 (9), 179 (4), 178 (3), 169 (8), 168 (4), 167 (5), 166 (3), 165 (6), 153 (3), 152 (5), 151 (3), 150 (2), 149 (12), 139 (2), 128 (2), 127 (3), 126 (2), 125 (3), 123 (3), 121 (2), 113 (2), 111 (4), 109 (4), 105 (5), 104 (5), 102 (3), 97 (7), 96 (3), 95 (6), 93 (5), 92 (3), 91 (8), 85 (5), 84 (3), 83 (7), 82 (4), 81 (7), 80 (2), 79 (6), 78 (67), 77 (29), 76 (5), 74 (4), 71 (8), 70 (4), 69 (10), 68 (3), 67 (5), 66 (2), 65 (4), 63 (2), 57 (14), 56 (6), 55 (11), 54 (3), 52 (11), 51 (18), 50 (9), 45 (2), 44 (10), 43 (13), 42 (3), 41 (14), 39 (10), 38 (3), 34 (10). |
| 15 | 363 (63), 362 (100), 332 (3), 279 (4), 270 (4), 257 (5), 256 (22), 182 (3), 170 (5), 169 (38), 168 (5), 167 (6), 148 (8), 104 (3), 97 (3), 79 (18), 77 (8), 71 (3), 57 (3), 52 (5) |

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*Peaks with an intensity less than 2% and with m/e less than 29 are not given.

for the electron-donor substituent of the alkene with respect to the positively charged atom of nitrogen. The subsequent stages of the process, after the appearance of a six-membered cycle, consist in a 1,3-proton shift and a further deuteration under the action of the base.

## EXPERIMENTAL

The IR spectra were obtained in a UR-20 spectrophotometer for suspensions in Vaseline oil or for 1% solution in $CCl_4$. The UV spectra were recorded in an SF-8 instrument for $10^{-4}$-$10^{-5}$ M solutions in acetonitrile. The PMR spectra were obtained in Brücker HX-270 (270 MHz) and Varian HA-100 (100 MHz) instruments for 10% solutions; the internal standard was ethanol—TMS. The mass spectra were recorded in an MKh-1303 mass spectrometer with energies of the ionizing electrons of 15 and 70 eV, using the system of direct introduction into an ionizing chamber having a temperature of 150°C. The electrochemical oxidation of triphenylhydrazine was carried out using a P-5827M potentiostat with the regulated potential of a platinum anode (Ag/$Ag^+$ $10^{-2}$ M) in an atmosphere of argon.

E-1-Deutero-2-ethoxyethylene (IIc) was obtained by the method of [12]; Z- and E-1-deutero-2-phenylethylene (IIg, h) were synthesized by the methods of [13, 14]. Admixtures of undeuterated analogs and synthesized deutero derivatives, judging by the PMR spectra, are not observed (accuracy ~5%). 1-(Piperidino)-2-methyl-1-propene (IIe) was synthesized by the procedure of [15].

1,2-Diphenyl-1,2,3,4-tetrahydrocinnolines (III). One gram (4 mmole) of triphenylhydrazine [16] in 250 ml of an acetonitrile solution of lithium perchlorate (0.1 M) is oxidized in the presence of 1.25 ml of 2,6-lutidine and 3 g of anhydrous sodium carbonate according to the method of [1]. The yield of cation I, determined using UV spectrometry and coulometry, was not less than 95%. A fivefold excess of the corresponding alkene II was then introduced. With the synthesis of the compounds IIIa-e, the mixture is held for 8 h at room temperature and, to obtain the derivatives IIIf-i, for the same period of time at 80°C. Then ~90% of the solvent is removed in a vacuum; the residue is mixed with 50 ml of water, dried with potash, and extracted with ether (3 × 50 ml). The extract is dried with potash, the ether is removed, and the residue is chromatographed in a column with $Al_2O_3$ with a II degree of activity; the eluent is hexane—benzene, 4:1. The purification is monitored by thin-layer chromatography (Table 2). The sorbed pure fractions are dried with potash, the solvent is removed in a vacuum, and the residue is recrystallized (Table 2).

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# 1,2,4-TRIAZOLE AND ITS DERIVATIVES IN THE REACTION OF ADDITION TO α-ACETYLENE KETONES

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It is well-known that 1,2,4-triazole is capable of being added to acetylacetylene with the formation of (1-(1-buten-3-one)-1,2,4-triazole [1]. The present article is devoted to an investigation of the reaction of the nucleophilic addition of 1,2,4-triazole (Ia, b) to α-acetylene ketones. In distinction from primary and secondary amines [2], symmetrical triazoles react with ethynyl ketones (II) only in the presence of triethylamine; the reaction stops at the stage of the formation of monoadducts, i.e., triazolylvinyl ketones (III). Addition to an unsubstituted ketone with a triple bond (IIb) is possible with the course of a reaction under rigid conditions in an excess of triethylamine. In the PMR spectra of triazolylvinyl ketone (IIIa) there are recorded nonequivalent signals of the protons of the triazole ring (8.42 and 7.98 ppm), which points to the addition of triazole to a vicinal atom of nitrogen. There are observed also the signals of the protons of the ketovinyl grouping (8.17 and 7.72 ppm), characteristic for the trans isomer [1]. In the IR spectra of these adducts there are noted absorption bands in the regions 1640-1675 and 1620-1610 $cm^{-1}$. The first band must be ascribed to vibrations of the α,β-unsaturated carbonyl group, and the second to a polarized double bond. The structure of triazolylvinyl ketones (III) is confirmed by their hydrolysis in 1-phenylpropanedione (IV), which was obtained by the hydration of benzoylacetylene (IIa) [3]. (See Scheme 1.)

With an attempt to add a molecule of piperidine to the multiple bond of 1-(3-phenyl-1-propen-3-one)-1,2,4-triazole (IIIa), there was a substitution of the triazole radical by an amine residue with the formation of the compound V.

The interaction of functionally substituted derivatives of triazole, i.e., 1,2,4-triazole-3-thiones (VIa, b) and 3-amino-1,2,4-triazole (VII) is somewhat more complex. The presence of several reaction centers offers the possibility of obtaining different isomeric adducts, whose structure is determined by the direction of the addition of an electrophile

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