CONCLUSIONS

1. The reaction of 3,4-dibromo-4-methyltetrahydropyran with primary and secondary amines in triethylamine leads to 4-methyl-5-amino-5,6-dihydropyrans.

2. When 4-methyl-5-(R)-anilino-5,6-dihydropyrans are heated in the presence of zinc chloride, an amino-Claisen rearrangement takes place with the formation of ortho-substituted anilines.

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REACTION OF ETHYL DIAZOACETATE WITH N-2,7-OCTADIENYLANILINES CATALYZED BY COMPOUNDS OF COPPER

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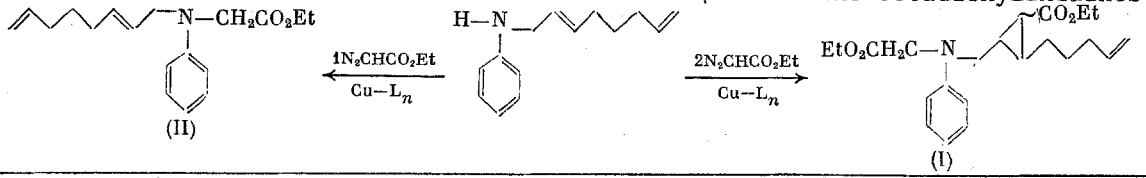
We recently established that the reaction of aliphatic allylamines with ethyl diazoacetate (EDA) in the presence of a copper compound is accomplished by the isomerization of the allyl substituent of the initial amine and the introduction of ethoxycarbonylcarbene (ECC) at the active C–H bond [1].

Continuing these investigations, we studied the reaction of EDA with the N-2,7-octadienyl derivatives of anilines of different structure in the presence of copper bis[N-(R,S)-α-phenylethylsalicylaldiminate], which is characterized by high activity and solubility in organic solvents [2].

Under these conditions, the reaction of N-2,7-octadienylaniline with excess EDA (molar ratio of 1:2) leads to the formation of N-carbethoxymethylanilino-N-methyl-2-(4-pentenyl)-3-carbethoxycyclopropane (I) – the product of the introduction of ECC at the active N–H bond and its addition to the disubstituted allyl double bond of octadienylaniline. By carrying out the reaction with the utilization of equimolar amounts of the unsaturated amine and EDA, N-carbethoxymethyl-N-2,7-octadienylaniline (II) is formed exclusively. The results obtained indicate that ECC is initially introduced at the N–H bond with the formation of (II); and the next molecule of ECC adds to the allylic disubstituted double bond with the formation of the cyclopropane derivative (I). The terminal vinyl group is not subjected to the cyclopropanation under the conditions of our experiments independently of the concentration of EDA. In connection with this, we performed all the subsequent experiments with the application of a twofold excess of EDA with respect to the octadienylanilines.



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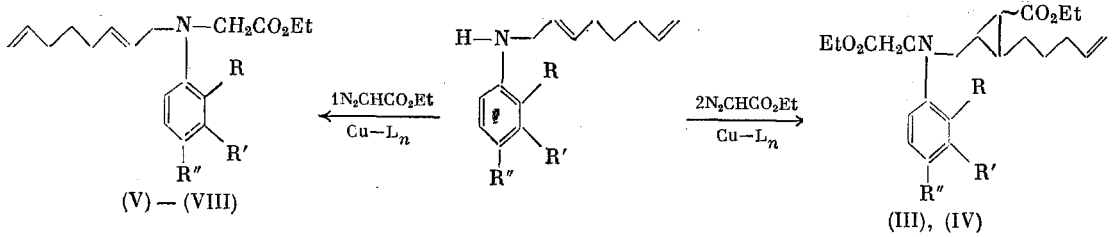
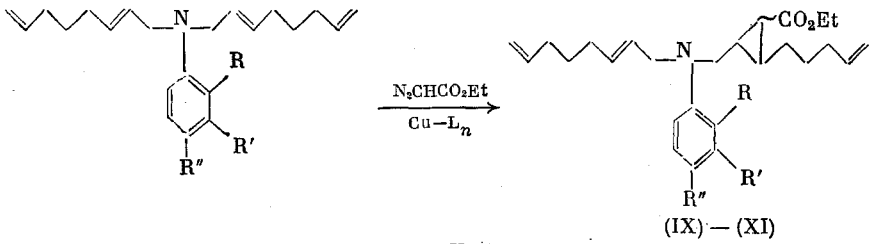
Analogous results were obtained in the experiments with N-2,7-octadienyl-m-,p-toluidines. In all cases, the yields of the corresponding functionally substituted cyclopropanes [N-carbethoxymethyl-p-toluidino-N-methyl-2-(4-pentyl)-3-carbethoxycyclopropane (III) and N-carbethoxymethyl-m-toluidino-N-methyl-2-(4-pentyl)-3-carbethoxycyclopropane (IV)] comprise ∿65%. All attempts to involve N-2,7-octadienyl-o-toluidine and N-2,7-octadienylxylidine in the given reaction were unsuccessful; and only the products [N-carbethoxymethyl-N-2,7-octadienyl-o-toluidine (VII) and N-carbethoxymethyl-N-2,7-octadienyl-o, p-xylidine (VIII)] of the introduction of ECC at the N–H bond were obtained.



(V) — (VIII) (III), (IV)

R = R′ = H; R″ = CH_3 (III), (V); R′ = CH_3, R = R″ = H (IV), (VI); R = CH_3, R′ = R″ = H (VII); R = R″ = CH_3, R′ = H (VIII).

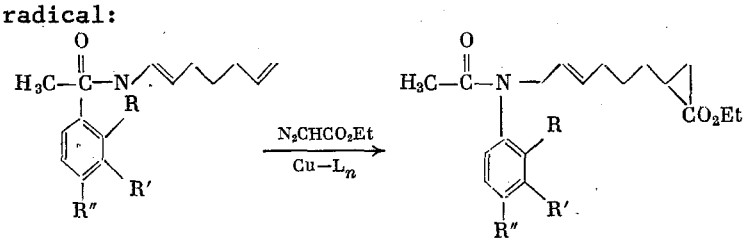
The bis-N-2,7-octadienyl derivatives of aniline, m- and p-toluidines, and xylidine react similarly with EDA, forming the adducts of the monoaddition of ECC to the allylic double bond. The cyclopropanation of the second allylic double bond was not rendered possible by the alteration of the ratio of the initial reagents, the concentration of the catalyst, and the conditions. The bulky substituents at the N atom of (IX) evidently induce steric hindrance to the approach of the active catalyst molecules, as well as of the second molecule of ECC, to the free allylic double bond in the octadienyl residue. The possibility that compound (IX) forms sufficiently stable coordination-saturated complexes with the central atom of the catalyst is not excluded. These complexes have low activity in the cyclopropanation reaction:



(IX) — (XI)

R = R′ = R″ = H (IX); R = R′ = H, R = CH_3 (X); R = R″ = H, R′ = CH_3 (XI).

In contrast to the mono- and bisoctadienylanilines, the N-acetyl-N-2,7-octadienylanilines participate in the reaction with EDA giving the mixture of disubstituted esters of cyclopropanecarboxylic acids, containing the cis and trans isomers in equal amounts, with high selectivity. As is apparent, the addition of ECC proceeds exclusively at the terminal vinyl group when the electron-acceptor acetyl grouping is present on the N atom together with the 2,7-octadienyl radical:



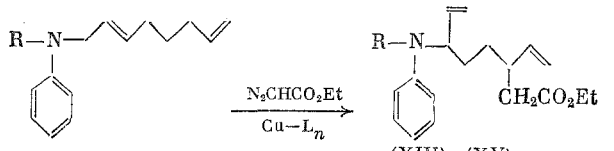
(XII), (XIII)

R=R′=R″=H (XII); R=R″=H; R=CH_3 (XIII).

The ratios of the cis and trans isomers were determined by the method of PMR from the intensity of the signals of the methylene protons in the ester grouping.

When the acetyl grouping in N-acetyl-N-2,7-octadienylanilines is replaced by an alkyl radical, the action of EDA leads to the skeletal isomerization of the initial amine to the 1,7 isomer with the simultaneous introduction of carbethoxycarbene at the allylic C–H bond. For example, the esters of amino acids (XIV) and (XV) are formed in high yields from the N-methyl- or N-ethyl-N-2,7-octadienylanilines and EDA, in the presence of the complex of

copper referred to, in the solution of benzene (80°C, 6 h):



(XIV), (XV)

R=CH_3 (XIV), C_2H_5 (XV).

Therefore, the investigations carried out permitted the development of a simple method for the isolation of the arylaminocarboxylic acids in good yields. It was established that, as dependent on the structure and the nature of the substituents at the N atom, the reaction of N-2,7-octadientylanilines with EDA proceeds strictly selectively with the formation of the products of the addition of ECC at the disubstituted trans or the terminal double bond, or of the introduction at the allylic C–H bond accompanied by an allylic rearrangement.

EXPERIMENTAL

We utilized N-2,7-octadienylanilines and EDA of ∿99% purity, obtained according to [3, 4]. The PMR spectra were recorded on a Tesla BS-487B instrument with $CDCl_3$ and the internal standard of TMS. The ^{13}C NMR spectra were recorded on a Jeol FX-90 (22, 63 MHz) radiospectrometer with broad-band suppression for protons and in the regime of monoresonance. We employed CCl_4 as the internal standard (96.00 ppm). The chemical shifts are presented in parts per million relative to TMS. The IR spectra were taken on a UR-20 spectrometer in a thin layer. The mass spectra were taken on an MX-13-06 instrument with an ionizing-electron energy of 70 eV and an ionization chamber temperature of 200°C. We analyzed the reaction mixtures on a Khrom-41 chromatograph with a flame-ionization detector, using a column 2.4 mm × 3 mm, SE-30 5% on Chromaton, and He as the carrier gas.

General Method for Arylaminocarboxylic Acids

To a solution of 20 mmoles of the corresponding N-2,7-octadienylaniline and 0.5 mmole of copper bis[N-(R, S)-α-phenylethylsalicylaldiminate] in 50 ml of benzene was added a solution of 40 mmoles of EDA in 40 ml of abs. benzene in a current of AR at 80°C, dropwise with intensive stirring. The mixture was thermostated for 6 h. Then the reaction mass was cooled and filtered through 10-15 g of Al_2O_3 (II grade of activity). After the removal of the solvent, the residue was analyzed with the aid of GLC and fractionated on a Widmer column under a vacuum. The isolated arylaminocarboxylic acids had the following constants.

N-Carbethoxymethylanilino-N-methyl-2-(4-pentyl)-3-carbethoxycyclopropane (I). The yield was 5.07 g (68%), np 187°C (2 mm), n_D^{20} 1.5042. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH{=}CH_2$), 1730, and 1750 (CO_2Et). PMR spectrum (δ, ppm): 0.93-1.5 (13H, CH_3, CH_2, CH in cyclopropane), 1.98 multiplet (2H, $C{=}CCH_2$), 4.03 multiplet (8H, NCH_2, CO_3CH_2), 5.03 multiplet (2H, $C{=}CH_2$), 5.03 multiplet (2H, $C{=}CH_2$), 5.3 multiplet (1H, CH=C), and 6.8 multiplet (5H, C_6H_5). M+ 373.

N-Carbethoxymethyl-N-2,7-octadientylaniline (II). The yield was 5.28 g (92%), bp 133°C (1 mm), n_D^{20} 1.5015. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH{=}CH_2$), 980, 1620 (trans CH=CH), and 1750 (CO_2). PMR spectrum (δ, ppm): 1.07 triplet (3H, CH_3), 1.42 multiplet (2H, CH_2), 1.85 multiplet (4H, $CH_2C{=}C$), 3.8 singlet (4H, NCH_2), 4.0 quartet (2H, CO_2CH_2, J = 7 Hz), 4.89 multiplet (2H, $C{=}CH_2$), 5.45 multiplet (3H, CH=CH), and 6.42-7.18 (5H, C_6H_5). M+ 287.

N-Carbethoxymethyl-p-toluidino-N-methyl-2-(4-pentenyl)-3-carbethoxycyclopropane (III). The yield was 5.18 g (67%), bp 205°C (2 mm), n_D^{20} 1.5035. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH{=}CH_2$), 1730, and 1750 (CO_2Et). PMR spectrum (δ, ppm): 0.93-1.5 (13H, CH_3, CH_2, CH in cyclopropane), 1.98 multiplet (2H, $CH_2C{=}C$), 2.13 singlet (3H, CH_3–A), 4.03 multiplet (8H, NCH_2, CO_2CH_2), 5.03 multiplet (2H, $C{=}CH_2$), 5.3 multiplet (1H, CH=C), and 6.7 multiplet (4H, C_6H_4). M+ 387.

N-Carbethoxymethyl-m-toluidino-N-methyl-2-(4-pentenyl)-3-carbethoxycyclopropane (IV). The yield was 5.03 g (65%), bp 195°C (2 mm), n_D^{20} 1.5090. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH{=}CH_2$), 1730, and 1750 (CO_2Et). PMR spectrum (δ, ppm): 1.2 multiplet (13H, CH_3, CH_2, CH in cyclopropane), 2.0 multiplet (2H, $CH_2C{=}C$), 2.20 singlet (3H, CH_3Ph), 3.34 multiplet (2H, NCH_2C), 4.05 multiplet (6H, CO_2CH_2, NCH_2CO_2), 4.98 multiplet (2H, $C{=}CH_2$), 5.4 multiplet

(1H, CH=C), and 6.5-6.94 (4H, C_6H_4). M+ 387.

N-Carbethoxymethyl-N-2,7-octadienyl-p-toluidine (V). The yield was 3.71 g (95%), bp 171°C (2 mm), n_D^{20} 1.5025. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH=CH_2$), 980, 1640 (trans CH=CH), and 1750 (CO=Et). PMR spectrum (σ, ppm): 1.08 triplet (3H, CH_3), 1.45 multiplet (2H , CH_2), 1.89 multiplet (4 H, $CH_2C=C$), 2.13 singlet (3H, CH_3Ph), 4.10 multiplet (6H, CO_2CH_2, NHC_2), 5.03 multiplet (2H, $C=CH_2$), 5.51 multiplet (3H, CH=CH), and 6.7 multiplet (4H, C_6H_4). M+ 301.

N-Carbethoxymethyl-N-2,7-octadienyl-m-toluidine (VI). The yield was 5.77 g (96%), bp 168°C (2 mm), n_D^{20} 1.5023. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH=CH_2$) 980, 1640(trans CH=CH), and 1750 (CO_2Et). PMR spectrum (δ, ppm): 1.12 triplet (3H, CH_3), 1.50 multiplet (2H, CH_2), 1.92 multiplet (4H, $CH_2C=C$), 2,21 singlet (3H, CH_3Ph), 4.05 multiplet (6H, CO_2CH_2, NCH_2), 4.98 multiplet (2H, $C=CH_2$), 5.4 multiplet (3H, CH=CH), and 6.5-6.95 (4H, C_6H_4). M+ 301.

N-Carbethoxymethyl-N-2,7-octadienyl-o-toluidine (VII). The yield was 5.65 g (94%), bp 146°C (1 mm), n_D^{20} 1.5022. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH=CH_2$), 975, 1635 (trans CH=CH), and 1750 (CO_2Et). PMR spectrum (δ, ppm): 1.08 triplet (3H, CH_3), 1.45 multiplet (2H, CH_2), 1.98 multiplet (4H, $CH_2C=C$), 2.18 singlet (3H, CH_3Ph), 5.15 multiplet (6H, CO_2CH_2, NCH_2), 4.89 multiplet (2H, $C=CH_2$), 5.51 multiplet (3 H, CH=CH), and 6.6-70.1 (4H, C_6H_4). M+ 301.

N-Carbethoxymethyl-N-2,7-octadienyl-o,p-xylidine (VIII). The yield was 6.02 g (95%), bp 178°C (2 mm), n_D^{20} 1.5021. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH=CH_2$), 980, 1640 (trans CH=CH), and 1730 (CO_2Et). PMR spectrum (δ, ppm): 1.13 singlet (3H, CH_3), 1.4 multiplet (2H, CH_2), 2.0 multiplet (4H, $CH_2C=C$), 2.20 singlet, 2.22 singlet (6H, CH_3Ph), 3.61 singlet (4H, NCH_2CO_2), 4.00 quartet (2H, CO_2CH_2, J = 7 Hz), 4.9 multiplet (2H, $C=CH_2$), 5.46 multiplet (3H, CH=CH), and 6.94 multiplet (3H, C_6H_3). M+ 317.

N-2,7-Octadienylanilino-N-methyl-2-(4-pentenyl)-3-carbethoxycyclopropane (IX). The yield was 5.45 g (69%), bp 151°C (1 mm), n_D^{20} 1.5210. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH=CH_2$), 975, 1640 (trans CH=CH), and 1740 (CO_2Et). PMR spectrum (δ, ppm): 1.16 triplet (3H, CH_3, J = 7 Hz), 1.38 multiplet (9H, CH_2, CH in cyclopropane), 1.98 multiplet (6H, $CH_2C=C$), 3.42 mutliplet (2H, NCH_2), 3.88 multiplet (2H, $NCH_2C=C$), 4.04 quartet (2H, CO_2CH_2, J = 7 Hz), 4.9 multiplet (4H, $C=CH_2$), 5.5 multiplet (4H, CH=CH), and 6.7-7.1 (5H, C_6H_5). M+ 395.

N-2,7-Octadienyl-p-toluidino-N-methyl-2-(4-pentenyl)-3-carbethoxycyclopropane (X). The yield was 6.31 g (77%), bp 204°C (3 mm), n_D^{20} 1.5110. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH=CH_2$), 980, 1640 (trans CH=CH), and 1740 (CO_2Et). The PMR spectrum (δ, ppm): 1.32 multiplet (12H, CH_3, CH_2, CH in cyclopropane), 2.06 multiplet (6H, $CH_2C=C$), 2.29 singlet (3H, CH_3Ph), 3.5 (2H, NHC_2), 3.93 (multiplet (2H, $NCH_2C=C$), 4.16 quartet (2H, CO_2CH_2, J = 7 Hz), 5.0 multiplet (4H, $C=CH_2$), 5.5 multiplet (4H, CH=CH), and 6.82-7.0 (4H, C_6H_4). M+ 410.

N-2,7-Octadienyl-m-toluidino-N-methyl-2-(4-pentenyl)-3-carbethoxycyclopropane (XI). The yield was 5.08 g (62%), bp 210°C (2 mm), n_D^{20} 1.5135. IR spectrum (ν, cm^{-1}): 920, 1000 ($CH=CH_2$), 980, 1640 (trans CH=CH), and 1740 (CO_2Et). PMR spectrum (δ, ppm): 1.2 multiplet (12H, CH_3, CH_2, CH in cyclopropane), 2.0 multiplet (6H, $CH_2C=C$), 2.26 singlet (3H, CH_3Ph), 3.9 multiplet (4H, NCH_2), 4.1 quartet (2H, CO_2CH_2, J = 7 Hz), 4.98 multiplet (4H, $C=CH_2$), 5.4 multiplet (4H, CH=CH), and 6.66-7.0 (4H, C_6H_4). M+ 410.

N-Acetylanilino-N-(4'-hexen-6'-yl)-2-carbethoxycyclopropane (XII). The yield was 3.94 g (60%), bp 213°C (3 mm), n_D^{20} 1.5132. IR spectrum (ν, cm^{-1}): 980, 1640 (trans CH=CH), 1660 (NC=O), and 1725 (CO_2Et). PMR spectrum (δ, ppm): 1.2 multiplet (7H, CH_2, CH in cyclopropane), 1.23 triplet (3H, CH_3, J - 7 Hz), 1.84 singlet (3H, CH_3CO), 2.0 multiplet (2H, $CH_2C=C$), 3.44 multiplet (2H, $NHC_2C=C$), 4.12 quartet (2H, CO_2CH_2), 5.44 multiplet (2H, CH=CH), and 7.15-7.30 (5H, C_6H_5). M+ 329.

N-Acetyl-m-toluidino-N-(4-hexen-6'-yl)-2-carbethoxycyclopropane (XIII). The yield was 0.96 g (14%), bp 206°C (1 mm), n_D^{20} 1.5149. IR spectrum (ν, cm^{-1}): 980, 1640 (trans CH=CH), 1660 (NC=O), and 1725 (CO_2Et). PMR spectrum (δ, ppm): 1.3 multiplet (10H, CH_3, CH_2, CH in cyclopropane), 1.8 singlet (3H, $CH_3C=O$), 2.0 multiplet (2H, $CH_2C=C$), 2.33 singlet (3H, CH_3Ph), 4.02 multiplet (4H, $NCH_2C=C$, CO_2-CH_2), 5.45 multiplet (2H, CH=CH), and 7.05 multiplet (4H, C_6H_4). M+ 343.

N-Methyl-N-(1-vinyl-4-carbethoxymethyl)-5-hexenylaniline (XIV). The yield was 5.89 g (98%), bp 163°C (2 mm), n_D^{20} 1.5195. IR spectrum (ν, cm^{-1}): 920, 1000 (C=CH_2), and 1735 (CO_2Et). PMR spectrum (δ, ppm): 1.12 triplet (3H, CH_3), 1.40 multiplet (4H, CH_2), 2.0 multiplet (3H, CHC=C, CH_2CO_2), 2.8 singlet (3H, NCH_3), 4.08 quartet (2H, CO_2CH_2, J = 7 Hz), 4.2 multiplet (1H, NCHC=C), 4.96 multiplet of triplets (4H C=CH_2), 5.4 multiplet (2H, CH=C), 6.68 multiplet, and 7.08 multiplet (5H, C_6H_5). M+ 302. ^{13}C NMR spectrum (δ, ppm), calculated/experimental: 113.3/114.63 triplet (C^1). 144.5/138.52 doublet (C^2), 39.38/44.58 doublet (C^3), 30.68/26.11 triplet (C^4), 30.05/31.14 triplet (C^5), 71.46/65.21 doublet (C^6), 137.3/138.9 doublet (C^7), 115.10/116.97 triplet (C^8), and 39.12/+33.62 triplet (C^9).

N-ethyl-N-(1-vinyl-4-carbethoxymethyl)-5-hexenylaniline (XV). The yield was 5.67 g (90%), bp 160°C (3 mm), n_D^{20} 1.5180. IR spectrum (ν, cm^{-1}): 920, 1000 (CH=CH_2), and 1740 (CO_2Et). PMR spectrum (δ, ppm): 1.02 triplet (3H, CH_3, J = 7 Hz), 1.2 triplet (3H, CH_3, J = 7 Hz), 1.4 multiplet (4H, CH_2), 2.0 multiplet (3H, CHC=C, CH_2CO_2),3.38 quartet (2H, NCH_2, J = 6 Hz), 4.1 quartet (2H, CO_2CH_2), 4.2 multiplet (2H, NHC_2, C=C), 4.96 multiplet (4H, C=CH_2), 5.5 multiplet (2H, CH=C), 6.78 multiplet, and 7.18 multiplet (5H, C_6H_5). M+ 315.

CONCLUSIONS

The reaction of EDA with N-2,7-octadienyl derivatives of aniline, catalyzed by the complex copper bis[N-(R, S)-α-phenylethylsalicylaldiminate], was studied.

The reaction of N-2,7-octadienylanilines, and also of bis(N-2,7-octadienyl)- and N-acetyl-N-2-7-octadienylanilines, with EDA proceeds with the formation of the products of the cyclopropanation at the terminal vinyl group or the disubstituted double bond. In the case of the N-alkyl-N-2,7-octadienyl anilines, the skeletal isomerization of the octadienyl anilines, the skeletal isomerization of the octadienyl radical in the initial amine with the simultaneous introduction of ethoxycarbonylcarbene at the allylic C–H bond takes place.

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