in pentanol and apparently approaches the polarity of ethanol, as indicated by the finding of a magnetic effect on the intensity of exciplex fluorescence and position of its maximum.

If we assume that the (I)/(III) ratio for the microemulsion is determined by the average of only two positions of pyrene in the interphase and hydrophobic region (i.e., $n_I + n_0 = 1$, where n_I and n_0 indicate the mole fractions of pyrene in the interphase and "oil"), then the fraction of pyrene localized in the interphase may be determined using this simple model. The observed (I)/(III) ratio in the microemulsion $(I)/(III)_M = n_I(I)/(III)_I + n_0(I)/(III)_P$. We assumed that $(I)/(III)_I \gtrsim (I)/(III)_E = 1.10$. Hence, we readily obtain that about 30% of pyrene is related to the interphase.

This conclusion is in accord with the results of Backer and Whitten [6], who found that during the lifetime of the excited electronic state, pyrene is distributed between the interphase and hydrophobic phase of the reverse micellar solution H_2O/OT Aerosol/heptane.

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[2.2]PARACYCLOPHANE AS A MODEL FOR THE CONSTRUCTION OF "PERPENDICULAR" STYRENE

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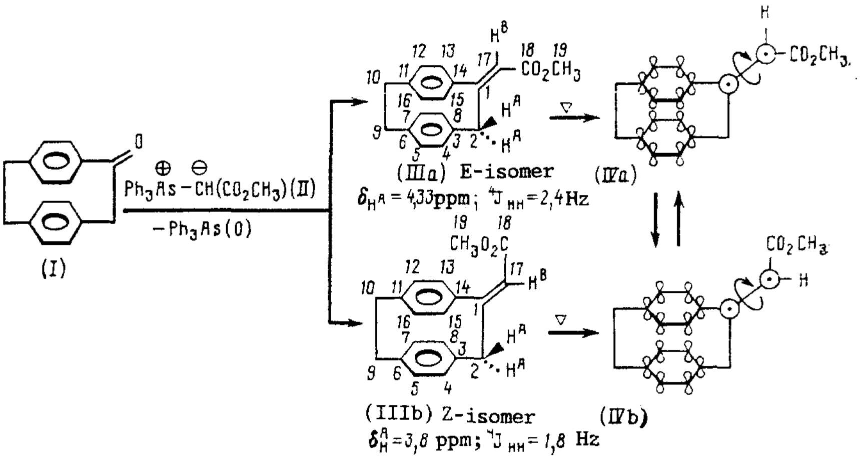
1-Methoxycarbonylmethylene[2.2]paracyclophane was synthesized starting from [2.2]paracyclophane and $Ph_3As^+\bar{C}H(CO_2CH_3)$. This product is a mixture of Z and E isomers, whose structures and configurations were established by NMR spectroscopy using the nuclear Overhauser effect.



(I)

(IIIa) E-isomer (IVa)

(IIIb) Z-isomer (IVb)

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In our investigation of rotational (and redox-rotational [1]) isomerization of twisted and perpendicularly constructed extended heteroorganic σ,π and π,π conjugation chains, the need arose for the molecular construction of vinylbenzene (styrene) derivatives, in which the adjacent π systems of the aromatic ring and double bond would be oriented perpendicularly to each other. In the present work, a scheme for the construction of this unusual class of compounds is proposed, based on the introduction of the exocyclic double bond (containing a methoxycarbonyl group in its terminal position as an electron-withdrawing group and, concurrently, stereochemical label) into the rigid [2.2]paracyclophane skeleton using the Wittig reaction [2]. The three-dimensional structure of this skeleton [3] unequivocally gives the required fixation of the aromatic ring π systems. As a result of our reaction of [2.2]paracyclophane (I) with $Ph_3As^+\bar{C}H(CO_2CH_3)$ (II) in $CHCl_2$ at 20°C over 24 h, two stereoisomeric products were obtained in 100% yield: (IIIa) with R_f 0.67 and mp 149-150°C and (IIIb) with R_f 0.31 and mp 126.5-127.5°C were isolated by thin-layer chromatography on silica gel with benzene as the eluent. The (IIIa)/(IIIb) ratio was 1.8:1. The structures of these isomers were indicated by elemental analysis and NMR spectroscopy. The geometric configurations were assigned on the basis of the δ_{H^A} values and $^4J_{HH}$ coupling constants in the cis and trans conjugation chains CH_2^A–C=C–H^B and finally confirmed for the stereoisomers examined by measurement of the homonuclear Overhauser effect for the ^1H nuclei. Thus, an increase in the intensity of the H^B triplet by 6% is observed upon radio-frequency irradiation for the doublet of the $C^2H_2^A$ group of minor isomer (IIIb), while analogous irradiation in the case of predominant isomer (IIIa) leads to an increase in the intensity of the corresponding H^B triplet by only 1%. Therefore, H^A and H^B in isomer (IIIb) are indeed closer, in accord with the Z configuration, than in isomer (IIIa), which, thus, has E configuration. In this regard, the somewhat reduced chemical shift of the OCH_3 group of Z isomer (IIIb) (3.64 ppm) in comparison with E isomer (IIIa) (3.83 ppm) may be attributed to the possibility of its location in the negative region of the shielding cone of the aromatic ring, which is specific only for the given class of compounds due to its unique structure. Finally, relative to the use of ^{13}C NMR spectroscopy for configurational assignment in this series of compounds, it is interesting to note that of all the 19 observed carbon atom signals of the molecules examined, the signals for C^2 are relatively sensitive to stereoisomerism: δ = 42.29 ppm for E isomer (IIIa) and 45.95 ppm for Z isomer (IIIb).

According to thin-layer chromatography, interconversion of the stereoisomers occurs upon their photoirradiation in CCl_4 using a PRK-4 lamp for 2 h at 20°C. This permits us to regard diradicals (IVa) and (IVb) as the corresponding intermediates. The structural core of these intermediates is the perpendicularly fixed fragment of the substituted benzyl radical. Products (III) may be considered as potential monomers and synthones as well as new π-ligands for the study of the stereochemistry of heteroorganic reactions.

EXPERIMENTAL

The PMR spectra were taken on a Bruker WP-200 spectrometer at 200 MHz. The ^{13}C NMR spectra were taken on a Varian VXR-400 spectrometer at 400 MHz in $CDCl_3$ with TMS as the internal standard. The IR spectra were taken on a UR-20 spectrometer in CH_2Cl_2. The mass spectra were taken on an MS 890 mass spectrometer at 40 eV. A sample of [2.2]paracyclophan-1-one (I) was obtained according to Cram and Helgeson [4], while (carbomethoxymethylene)triphenylarsorane (II) was obtained according to our previous work [6].

Reaction of [2.2]paracyclophan-1-one with (methoxycarbonylmethylene)triphenylarsorane. A sample of 0.3 g (0.8 mmole) ylid (II) was added to a solution of 0.13 g (0.58 mmole) (I) in 5 ml CH_2Cl_2 and left for 24 h at room temperature. The reaction was monitored relative to the νC=O band of (I) at 1706 cm^{-1}. The solvent was distilled off in vacuum and the residue was treated with ether. The insoluble triphenylarsine was filtered off. The yield of this compound was 0.17 g (87%). The ethereal filtrate was separated by thin-layer chromatography on silica gel with benzene as the eluent, taking the fractions with R_f 0.31 and 0.67. Recrystallization from heptane gave 0.06 g (38%) (IIIa) and 0.03 g (19%) (IIIb).

<u>(IIIa):</u> R_f 0.67. IR spectrum in CH_2Cl_2 (ν, cm^{-1}): 1720 (C=O) and 1640 (C=C). PMR spectrum (δ, ppm, J, Hz): 3.08 s (4H, CH_2CH_2), 3.83 s (OCH_3), 4.33 d (2H, CH_2, J = 2.44), 6.17 t (1H, CH, J = 2.38), 7.5 m (8H, Ar). ^{13}C NMR spectrum (δ, ppm): 35.04, 35.07, 42.29, 51.21, 115.33, 131.25, 132.66, 133.16, 133.60, 138.30, 139.24, 140.09, 140.11, 163.80, 167.01. Mass spectrum, m/z 278, mp 149-150°C. Found: C, 81.89; H, 6.53%. Calculated for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52%.

<u>(IIIb)</u>: R_f 0.31. IR spectrum in CH_2Cl_2 (ν, cm^{-1}): 1730 (C=O) and 1650 (C=C). PMR spectrum (δ, ppm, J, Hz): 3.08 s (4H, CH_2CH_2), 3.64 s (3H, OCH_3), 3.89 d (2H, CH_2, J = 1.85),

6.10 t (1H, CH, J = 1.82), 7.5 m (8H, Ar). ^{13}C NMR spectrum (δ, ppm): 35.20, 35.23, 45.95, 51.16, 115.33, 131.03, 132.98, 133.16, 133.66, 136.75, 138.73, 139.26, 140.00, 161.71, 166.32. Mass spectrum, m/z 278, mp 126.5-127.5°C. Found: C, 81.79; H, 6.53%. Calculated for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52%.

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MECHANISM OF THE HYDROAMINATION OF ALCOHOLS AND CARBONYL COMPOUNDS ON A FUSED IRON CATALYST

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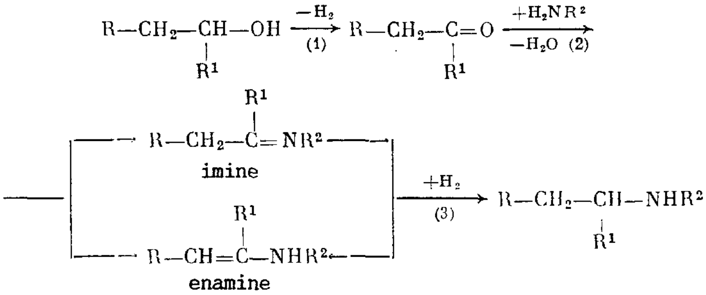
In a study of the reaction of 2,2-dimethyl-1-propanol, 2-ethyl-1-hexanol, 2-octanol, and 4-heptanol or 4-heptanone and 2-octanone with aminating agents such as ammonia, dimethylamine, and propylamine in the presence of hydrogen on a fused iron catalyst, we showed that the desired amines are formed through both "imine" and "enamine" mechanisms.

An "imine" mechanism has been proposed for a promoted reduced fused iron catalyst (PRFIC) [1] and an "enamine" mechanism has been proposed for a copper catalyst [2] in the hydroamination of alcohols and carbonyl compounds in the presence of metal catalysts.



Each of these mechanisms involves three major steps: 1) dehydration of the starting alcohol to give a carbonyl compound, 2) reaction of the aldehyde or ketone and an aminating agent to give an intermediate imine or enamine, and 3) reduction of the imine or enamine by hydrogen to give an amine. Kinetic and isotope data obtained in a study of the hydroamination of alcohols [2-5] have permitted establishment of the nature of major step (1) and the results of the hydroamination of ketones [1, 6] have permitted establishment of the nature of major step (3). On the other hand, establishment of the nature of major step (2) using kinetic, isotope, or spectral data involves considerable experimental difficulties. In the case

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