Cyclocotrimerization of Pyridyl Nitriles IVa-c with Acetylene. A solution of the catalyst obtained as indicated above was added to a steel autoclave of the C type, to which 0.1 mole of pyridyl nitrile IVa-c and 100 ml of toluene had been previously added, after which 0.3 mole of acetylene was fed in. The autoclave was heated at 150°C for 15 h, after which it was cooled. The reaction mixture was treated with methanol, and the mixture was filtered and distilled in vacuo to give the corresponding dipyridyl-substituted Va-c.

Cyclocotrimerization of Propionitriles with Acetylene in the Presence of Added Alkylthiopropionitriles. A 120-mmole sample of $Al(C_2H_5)_2$ was added at 0°C in a stream of argon to a solution of 40 mmole of $Co(2\text{-ethylhexanoate})_2$ in 15 ml of toluene, and the mixture was stirred for 15 min. An 80-mmole sample of the corresponding nitrile I*l*, m or pyridine II*l*, m was added, and the mixture was stirred for 20 min. The resulting solution of the catalyst was transferred to a 1-liter steel autoclave, to which 0.1 mole of nitrile Ia and 100 ml of toluene had been previously added, and 0.3 mole of acetylene was fed in. The autoclave was heated at 150°C for 10 h, after which it was cooled. The reaction mixture was decomposed with methanol, and the mixture was filtered in vacuo. Depending on the additive used, the yield of pyridine IIa was 23, 20, 19, or 20%, respectively.

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CONDENSATION OF AZOMETHINES WITH DIMETHYL ACETYLENEDICARBOXYLATE

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UDC 547.462.8'26'551.2'592.12.2'
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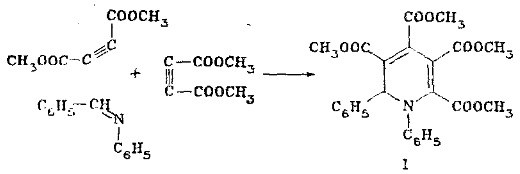
The condensation of dimethyl acetylenedicarboxylate with benzylidene- and cyclohexylideneaniline, as well as with cyclohexylidene-p-toluidine and cyclohexylidene-p-anisidine, under various conditions gave 1:1, 1:2, and 1:3 adducts. The structures of the isolated substances, which are formed as a result of the addition of the ester to the azomethines with subsequent 1,5-prototropic rearrangement (arylcyclohexenylvinylamines), as well as by cycloaddition (substituted dihydropyridines and spiro-cyclohexanedihydropyridines), are discussed.

Information regarding reactions involving the cycloaddition of dimethyl acetylenedicarboxylate (DMAD) to azomethines, which are promising methods for the synthesis of various heterocyclic compounds, is limited. It has been reported [1] that DMAD reacts with benzylidenebenzylamine but does not react with benzylideneaniline. We have studied the latter reaction in absolute ether at room temperature or at 0°C, as well as in hot toluene. It all cases we isolated an adduct of cycloaddition of two molecules of DMAD to benzylideneaniline, viz., 1,2-diphenyl-3,4,5,6-tetramethoxycarbonyl-1,2-dihydropyridine (I), in low yield by means of chromatographic separation of the reaction products. Its structure was confirmed by analytical and spectral (Table 1) data.



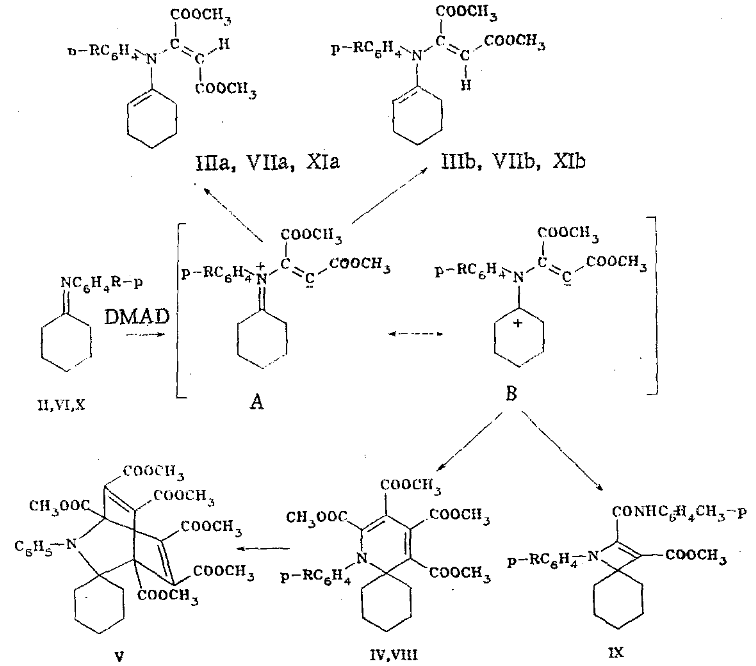
I

Patrice Lumumba People's Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 366-371, March, 1984. Original article submitted July 12, 1983.

Cyclohexylideneaniline, cyclohexylidene-p-toluidine, and cyclohexylidene-p-anisidine were also used in reactions with DMAD (the azomethine:DMAD ratio was 1:2). The composition of the complex mixtures of substances formed depend on the reaction conditions. Adducts with 1:1 and 1:2 compositions are obtained when the reaction is carried out in ether at 0°C, whereas 1:3 adducts are also formed when mixtures of the reagents in toluene are heated.

Two 1:1 adducts, viz., trans and cis isomers of N-(cyclohexen-1-yl)-N-(1,2-dimethoxycarbonylvinyl)aniline (IIIa, b), and a 1:2 adduct, viz., cyclohexane-spiro-2-(1-phenyl-3,4,5,6-tetramethoxycarbonyl-1,2-dihydropyridine) (IV), were isolated when the condensation of DMAD with cyclohexylideneaniline (II) was carried out by the first method. According to data from the UV, IR, and PMR spectra (Tables 1-3), IIIb was identical to the compound described in [1], the formation of which, as assumed by Huisgen and Herbig [1], occurs via 1,5-prototropic rearrangement of zwitterion A, which is formed in the addition of DMAD to the starting azomethine.

The structure of adduct III was confirmed by data from the ^{13}C NMR spectrum in the case of isomer IIIb. Five signals (166.40, 164.64, 152.14, 141.01, and 139.83 ppm) of quaternary carbon atoms and five signals (129.89, 126.06, 125.76, 125.58, and 92.77 ppm) of seven ternary carbon atoms are observed in the case of incomplete double resonance. The peaks at 166.40 and 164.54 ppm are related to the carbon atoms of ester C=O groups. The signal at 141.01 ppm belongs to the quaternary carbon atom of an aryl radical [coupling of this carbon atom with two meta protons with spin-spin coupling constant $\sim$6 Hz is observed in the high-resolution spectrum]. The signals at 152.14 and 139.83 ppm are related to quaternary carbon atoms attached to double bonds. Broadening of these signals, evidently due to small $J_{^{13}C-H}$ SSCC values, is observed in the high-resolution spectrum. The signals at 128.89 and 125.58 ppm belong in pairs to the two carbon atoms of the benzene ring in the ortho and meta positions relative to the nitrogen-containing substituents. Of the two signals at 126.06 and 125.76 ppm, one is related to the carbon atom in the para position of the phenyl ring, and the other is related to the carbon atom attached to the double bond of the vinyl fragment. The signal at 92.77 ppm is related to the tertiary carbon atom of the cyclohexene ring. The signals at strong field at 51.47 and 49.88 ppm are related to the carbon atoms of the methoxy groups. The four signals at 26.24, 24.22, 21.98, and 20.99 ppm belong to the cyclohexene carbon atoms [2].



II—IV R=H; VI—IX R=CH_3; X, XI R=OCH_3

On the basis of calculations of the chemical shifts of the olefin protons [3, 4], in which the constants of shielding of the vinyl proton by the substituents in the dimethoxycarbonylvinyl group [singlets in the PMR spectra at 5.60 (IIIa) and 4.74 ppm (IIIb)] are taken into account, it may be concluded that IIIa, b are geometrical isomers: IIIa has a trans configuration, and IIIb has a cis configuration.

TABLE 1. Data from the IR and UV Spectra

Compound	IR spectrum, ν, cm⁻¹				UV spectrum, λ, nm (log ε)
	aliphatic and aromatic CH	ester CO	C=C	ester C—O—C	
I	2960—3065	1710, 1750	1500, 1590—1600	1185—1245	264 (4,14): 390 (3.50)
IIIa	2845—3070	1705, 1725 s	1495 s 1600	1170—1280	260 (4,09); 370 (4,03)
IIIb	2839—3064	1705, 1748	1494 vs 1577	1149—1257	258 (4,12), 320 (4,03)
IV	2865—3060	1694, 1734	1504, 1574	1159, 1205, 1230 s	240 (4,56), i., 280 (4,34); 353 (4,32)
V	2865—3060	1702, 1750	1442, 1502, 1570	1163—1239	240 (4,50), sh., 280 (4,36); 334 (4,06)
VIIa	2840—3020	1713 s, 1733 s	1433, 1500, 1600	1173—1273	260 (4,40); 364 (3,96)
VIIb	2833—3020	1694, 1733	1420, 1500, 1569 s	1140—1260	262 (4,20); 314 (4,30)
VIII	2858—3043	1699, 1744 br.s	1434, 1505, 1574 br.s	1156—1282	242 (4,13), sh, 280 (4,03); 350 (3,98)
XIa	2830—3060	1710, 1745	1520, 1615	1125—1285	242 (4,47); 257 (4,37); 324 (4,43)
XIb	2960—2845	1710, 1750	1450, 1520, 1610	1170—1260	250 (4,10); 306 (4,20)

TABLE 2. Data from the Mass Spectra

Compound	m/z values (relative intensities of the peaks, %)										
	$M^{+\cdot}$	$[M-CH_3]^+$	$[M-OCH_3]^+$	$[M-COOCH_3]^+$	$[NH-Ar-C(COOCH_3)=CHCOOCH_3]^+$	$[M-COOCH_3-OCH_3]^+$	$[M-COOCH_3-CH_3OH]^+$	$[M-COOCH_3-COOCH_3]^+$	$[M-COOCH_3-COOCH_3-H]^+$	$[CH-COOCH_3 = CH-COOCH_3]^+$	$[Ar]^+$
IIIa	315 (20,06)	300 (1,9)	284 (6,6)	256 (100)	235 (8,5)	225 (4,7)	224 (24,2)	197 (6,1)	196 (12,4)	144 (20,0)	77 (27,2)
IIIb	315 (16,0)	300 (2,8)	284 (9,1)	256 (100)	235 (9,8)	225 (5,5)	224 (25,8)	197 (7,4)	196 (14,7)	144 (28,3)	77 (34,4)
IV	457 (51,6)	442 (3,2)	426 (27,0)	398 (100)	—	367 (10,3)	366 (35,3)	339 (5,6)	338 (17,5)	—	77 (34,1)
V	599 (32,6)	584 (2,3)	568 (24,6)	540 (40,6)	—	509 (8,0)	508 (18,3)	481 (6,0)	480 (15,4)	144 (28,6)	77 (100)
VIIa	329 (1.9)	314 (0,4)	298 (0,8)	270 (8,9)	249 (100)	239 (0,8)	238 (2,1)	211 (0,8)	210 (1,3)	144 (5,1)	91 (35,0)
VIIb	329 (9,3)	314 (1,3)	298 (6,0)	270 (100)	249 (8,0)	239 (7,3)	238 (31,6)	211 (5,6)	210 (21,3)	144 (28,0)	91 (53,8)
VIII	471 (10,3)	456 (0,8)	440 (5,4)	412 (36,7)	—	381 (4,2)	380 (10,0)	353 (2,9)	352 (6,3)	—	91 (100)
XIa	345 (11,6)	—	314 (5,8)	286 (46,5)	265 (100)	255 (9,3)	254 (19,8)	227 (14,0)	226 (16,3)	144 (16,3)	107 (83,7)
XIb	345 (26,0)	330 (1,0)	314 (10,0)	286 (100)	—	255 (4,0)	254 (24,0)	227 (5,0)	226 (12,0)	—	107 (2,0)

Spiro compound IV (Tables 1 and 2), which is an analog of dihydropyridine I, is evidently formed in the reaction of DMAD with zwitterion B.

A 1:3 adduct was isolated in an experiment in which the reaction of DMAD with azomethine II was carried out by heating in toluene. The 2-aza-2-phenyl-3,4,5,6,7,8-hexamethoxycarbonyl-4,7-dienebicyclo[2.2.2]-hexane-1-spiro-cyclohexane structure (V) was assigned to it on the basis of spectral data (Tables 1 and 2). This compound is probably formed in the diene synthesis of spiran IV with DMAD.

Similar compounds, viz., the trans and cis isomers of N-(cyclohexen-1-yl)-N-(1,2-dimethoxycarbonylvinyl)-p-toluidine (VIIa, b) and cyclohexane-spiro-2-[1-(p-tolyl)-3,4,5,6-tetramethoxycarbonyl-1,2-dihydropyridine] (VIII) (Tables 1-3), were obtained in the reaction of DMAD with cyclohexylidene-p-toluidine (VI) in ether at 0°C.

Signals of protons at 4.0-6.5 ppm are not observed in the PMR spectrum (Table 3) of spiro compound VIII, and methylidene protons attached to double bonds are consequently absent in its molecule. Only the signal at 61.5 ppm is not split in the ^{13}C NMR spectrum of VIII measured under incomplete double resonance conditions; the other signals are split as a consequence of coupling with protons. The signal at 61.5 ppm is therefore related to a quaternary sp^3-hydridized carbon atom (a spiro carbon atom). The assignment of the other

TABLE 3. Data from the PMR Spectra (δ, ppm)

Compound	Cyclohexene CH_2, m	p-CH_3; p-OCH_3, s, 3H	$COOCH_3$, s, 3H each	Vinyl protons		Aromatic protons
				$=CHCOOCH_3$, s, 1H	cyclohexene, m, 1H	
IIIa[a]	2,11—1,44, 8H	—	3,63; 3,17	5,60	5,32	7,20—6,71, m, 5H
IIIb[a]	2,14—1,37, 8H	—	3,65; 3,47	4,74	5,58	7,25—6,92, m, 5H
VIIa[b]	2,15—1,43, 8H	2,23	3,68; 3,25	5,60	5,33	7,03—6,63, m, 4H
VIIb[b]	2,20—1,43, 8H	2,30	3,75; 3,55	4,80	5,68	7,03, s, 4H
VIII[a]	2,11—1,18, 10H	2,24	3,70; 3,62; 3,56; 3,38	—	—	6,94, s, 4H
XIa[b]	2,30—1,45, 8H	3,74, 6H (p-OCH_3, $1COOCH_3$)	3,34	5,70	5,53—5,28	6,93—6,36, m, 4H
XIb[b]	2,20—1,32, 8H	3,71, 6H (p-OCH_3, $1COOCH_3$)	3,53	4,70	5,62	7,02—6,72, A_2B_2, 4H

[a] With tetramethylsilane as the internal standard. [b] Hexamethyldisiloxane.

signals of the strong-field part of the spectrum of spiro compound VIII is presented in Fig. 1.

A crystalline substance, which corresponds to a 1:1 adduct, was also isolated in the condensation of DMAD with cyclohexylidene-p-toluidine (VI). A molecular-ion peak with m/z 404 is present in its mass spectrum. The band in the IR spectrum at 1700 cm^{-1} is related to stretching vibrations of an ester CO group, and the band at 1645 cm^{-1} is related to an amide CO group. A broad signal at 7.85 ppm, which is related to the signal of the proton attached to the nitrogen atom of the monosubstituted amide group, is present in the PMR spectrum. The signals at 7.01 and 6.88 ppm with intensities of 4H each correspond to the aromatic protons of two p-tolyl fragments. The signals at 3.52, 2.32, and 2.24 ppm with intensities of 3H each are related to the signals of the protons of a $COOCH_3$ group and two CH_3 groups of tolyl radicals, respectively. The complex multiplet at 0.95-1.85 ppm corresponds to the signals of protons of a cyclohexane fragment.

On the basis of these data it may be concluded that the isolated crystalline substance with mp 221-222.5°C has the cyclohexane-spiro-2-[1-(p-tolyl)-3-methoxycarbonyl-4-(p-tolyl)-carbamoyl-3-azetine] structure (IX). We assume that this spiro compound is formed in the condensation of cyclohexylidene-p-toluidine with methoxycarbonyl-p-tolylcarbamoylacetylene — the product of partial ammonolysis of DMAD by p-toluidine, which may be present in the starting azomethine. A band of stretching vibrations of a carbonyl group at 1710-1720 cm^{-1}, the intensity of which increased during storage of the azomethines due to the generation of the starting ketone and amine from them, was always present in the IR spectra of the freshly distilled Schiff bases that were used in this research.

Only adducts (1:1) with trans and cis configurations, viz., N-(cyclohexen-1-yl)-N-(1,2-dimethoxycarbonylvinyl)-p-anisidine (XIa, b) (Tables 1-3), were isolated in the reaction of cyclohexylidene-p-anisidine (X) (a very unstable azomethine) in ether at 0°C.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ were measured with a Brucker WP-80 spectrometer (80 MHz) with tetramethylsilane as the internal standard. The ^{13}C NMR spectra of solutions in $CDCl_3$ were obtained with Varian CFT-20 and Brucker WP-80 spectrometers with accumulation under pulse conditions and with subsequent Fourier transformation with TMS as the internal standard. The high-resolution ^{13}C NMR spectra were obtained under conditions of pulse modulation of the broad-band suppression with retention of the intensification due to the Overhouser internuclear effect. The UV spectra of solutions in ethanol were measured with a Specord UV-vis spectrometer. The IR spectra of KBr pellets were recorded with a UR-20 spectrometer. The mass spectra were obtained with an MKh-1303 spectrometer at an ionization voltage of 70 eV. Thin-layer chromatography (TLC) was carried out on activity II aluminum oxide in an ethyl acetate—heptane system (1:2).

1,2-Diphenyl-3,4,5,6-tetramethoxycarbonyl-1,2-dihydropyridine (I). A) A solution of 1 g (5.5 mmole) of benzylideneaniline and 1.3 g (9.2 mmole) of DMAD in 20 ml of absolute ether

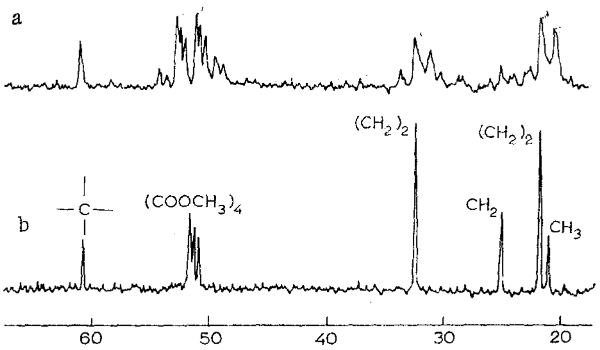


Fig. 1. Fragments of the C NMR spectrum of VII (CDCl , tetramethylsilane): a) under-conditions of noise decoupling of the protons; b) under incomplete double-resonance conditions.

was alllowed to stand for 24 h, after which the ether was removed by distillation, 10 ml of toluene was added to the residue, and the mixture was refluxed for 10 h. The toluene was removed by distillation, and the residue (2.3 g) was chromatographed [aluminum oxide, l = 44 cm, d = 3.5 cm, ethyl acetate–heptane (1:5)] to give 0.15 g (6.5%) of I in the form of bright-yellow crystals with mp 62.5-65°C and R_f 0.18. PMR spectrum: 7.03-7.53 (m, aromatic protons); 5.97 (1H, s, 2-H); 3.88, 3.73, 3.65, 3.60 ppm (3H, s, 4 OCH_3). Found: N 3.3%; M 465. $C_{25}H_{23}NO_8$. Calculated: N 3.0%; M 465.

B) A solution of 0.5 g (2.7 mmole) of benzylideneaniline and 0.65 g (4.6 mmole) of DMAD in 10 ml of absolute ether was maintained at room temperature for 20 days, after which the ether was removed by distillation, and the residue was chromatographed [Al_2O_3, l = 42 cm, d = 1.5 cm, ethyl acetate–heptane (1:5)] to give, after crystallization from petroleum ether, 0.015 g (1.2%) of I with mp 62.5-65°C and R_f 0.18.

trans- and cis-N-(Cyclohexen-1-yl)-N-(1,2-dimethoxycarbonylvinyl)aniline (IIIa, b), Cyclohexane-spiro-2-(1-phenyl-3,4,5,6-tetramethoxycarbonyl-1,2-dihydropyridine) (IV), and 2-Aza-2-phenyl-3,4,5,6,7,8-hexamethoxycarbonyl-4,7-dienebicyclo[2.2.2]hexane-1-spiro-cyclohexane (V). A) A solution of 1.2 g (8.4 mmole) of DMAD in 5 ml of ether was added gradually at 0°C to a solution of 0.7 g (4.1 mmole) of freshly distilled cyclohexyldeneaniline (II) in 5 ml of absolute ether at 0°C, and the resulting solution was maintained at –5°C for 24 h. The ether was removed by distillation, 10 ml of toluene was added to the residue, and the mixture was refluxed for 8 h. The toluene was removed by distillation, and the residue (1.9 g) was chromatographed (Al_2O_3, l = 31 cm, d = 3 cm) by elution with ethyl acetate–heptane (1:15) to give 0.11 g (6%) of IIIa in the form of an oily orange substance with R_f 0.75. Found: N 4.6%; M 315. $C_{18}H_{21}NO_4$. Calculated: N 4.4%; M 315. Subsequent elution with ethyl acetate–heptane (1:10) gave 0.42 g (22%) of IIIb in the form of a vitreous yellow substance with R_f 0.58. Found: N 4.4%; M 315. $C_{18}H_{21}NO_4$. Calculated: N 4.4%; M 315. Further elution gave 0.3 g of a substance with an unknown structure, the mass spectrum of which contained a molecular-ion peak with m/z 315. These results, together with the percentage of nitrogen found (4.3%), constituted evidence that this substance was a 1:1 adduct. Final elution with a mixture of the same solvents in a ratio of 1:1 gave 0.02 g (1.5%) of yellow crystals of mp 43-45°C (from hexane) and R_f 0.22. Found: M 599. $C_{30}H_{33}NO_{12}$. Calculated: M 599.

B) A solution of 0.3 g (1.7 mmole) of cyclohexylideneaniline and 0.5 g (3.5 mmole) of DMAD in 6 ml of absolute ether was maintained at –5°C for 24 h, after which the ether was removed by distillation, and the reaction products were isolated by chromatography to give 0.35 g (43%) of IIIa and 0.12 g (15%) of IIIb. Final elution with ethyl acetate–heptane (1:10) gave 0.03 g (3.7%) of pale-yellow crystals of IV with mp 160-161.5°C (from heptane) and R_f 0.26. Found: N 3.2%; M 475. $C_{24}H_{27}NO_8$. Calculated: N 3.1%; M 475.

trans- and cis-N-(Cyclohexen-1-yl)-N-(1,2-dimethoxycarbonylvinyl)-p-toluidine (VIIa, b), Cyclohexane-spiro-2-[1-(p-tolyl)-3,4,5,6-tetramethoxycarbonyl-1,2-dihydropyridine] (VIII), and Cyclohexane-spiro-2-[1-(p-tolyl)-3-methoxycarbonyl-4-(p-tolyl)carbamoyl-3-azetine] (IX). A solution of 1.77 g (9.5 mmole) of cyclohexylidene-p-toluidine (VI) and 2.75 g (19 mmole) of DMAD in 16 ml of absolute ether was maintained at –5°C for 1 day, after which the ether was removed by distillation, and the residue (4.4 g) was chromatographed (Al_2O_3, l = 74 cm, d = 3 cm) as the ratio of ethyl acetate to heptane was gradually changed from 1:15 to 1:10 (with final elution with ethyl acetate). This procedure gave 0.95 g (22%) of VIIa [an oily orange substance with R_f 0.75. Found: N 4.0%; M 329. $C_{19}H_{23}NO_4$. Calculated: N 4.3%; M 329 and 0.65 g (15%) of VIIb [a yellow oily substance with R_f 0.60. Found: N 4.1%; M 329. $C_{19}H_{23}NO_4$. Calculated: N 4.3%; M 329]. A mixture of ethyl acetate and heptane in a ratio of 1:10 gave 0.06 g (15%) of colorles crystals of IX with mp 221-222.5°C (from heptane) and R_f 0.44. Mass spectrum*: $[M]^+$ 404 (100), $[M-OCH_3]^+$ 373 (4.3), $[M-CH_3OH]^+$ 372 (7.5), $[M-CH_3OH-H]^+$ 371 (10.6), $[M-COOCH_3]^+$ 345 (66), $[M-NHC_6H_4CH_3]^+$ 298 (4.3), $[M-CONHC_6H_4CH_3]^+$ 270 (16.0), $[M-COOCH_3-CONHC_6H_4CH_3]^+$ 211 (3.2), $[CH_3C_6H_4]^+$ 91 (13.8). Found: N 6.7%. $C_{25}H_{28}NO_3$. Calculated: N 6.0%; M 404.

Final elution gave 0.15 g (3.4%) of pale-yellow crystals of VIII with mp 164-166°C (from hexane) and R_f 0.22. Found: N 3.3%; M 471. $C_{25}H_{29}NO_8$. Calculated: N 3.0%; M 471.

trans- and cis-N-(Cyclohexen-1-yl)-N-(1,2-dimethoxycarbonylvinyl)-p-anisidine (XIa, b). A) A mixture of 28.42 g (0.29 mole) of cyclohexanone and 21.3 g (0.173 mole) of p-anisidine in 30 ml of dry toluene was refluxed with a water separator in the presence of 0.5 ml of glacial acetic acid for 5 h. Fractional distillation gave 16.4 g (47%) of cyclohexylidene-p-anisidine (X) in the form of a yellowish viscous liquid with bp 143°C (1 mm) and n_D^{21} 1.5592. IR spectrum: 1760 cm^{-1} (C=N). Found: N 6.99%. $C_{13}H_{17}NO$. Calculated: N 6.9%. This Schiff base decomposed readily (it became turbid, after which crystals of p-anisidine developed) during storage in air.

B) Condensation (carried out as in the case of VII) of 1.6 g (7.8 mmole) of azomethine X and 2.22 g (15.6 mmole) of DMAD in 15 ml of absolute ether at 0°C gave 0.66 g (25%) of XIa and 0.25 g (9.2%) of XIb. trans-Isomer XIa was an oily red-orange substance with R_f 0.79. Found: C 65.8; H 6.4; N 4.1%; M 345. $C_{19}H_{23}NO_5$. Calculated: C 66.1; H 6.7; N 4.1%; M 345. cis-Isomer XIb was obtained in the form of grayish crystals with mp 92-93°C [from hexane–ethyl acetate (5:1)] and R_f 0.5. ^{13}C NMR spectrum: 167.65 and 165.51 (two C=O), 158.42 [phenylene $C_{(1)}$], 153.52 [cyclohexene $C_{(1)}$], 140.6 and 127.78 [vinyl $C_{(1)}$ and $C_{(2)}$], 134.1 [phenylene $C_{(4)}$], 125.78 [phenylene $C_{(3)}$ and $C_{(5)}$], 114.65 [phenylene $C_{(2)}$ and $C_{(6)}$], 91.57 [cyclohexene $C_{(2)}$], 52.17 and 50.56 (two ester OCH_3), 55.23 (p-anisidine OCH_3), and 26.61, 24.67, 22.43, and 21.41 ppm (four aliphatic cyclohexene carbon atoms). Found: C 65.9; H 6.94; N 4.1%; M 345. $C_{19}H_{23}NO_5$. Calculated: C 66.1; H 6.7; N 4.1%; M 345. In addition, 1.2 g of a complex mixture of substances with unidentified structures was isolated from the column.

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*Here and subsequently, the m/z ratios and the relative intensities in percent are given.