Reactivity of Primary and Secondary N-2-(1,1-Dichloroalkylidene)anilines. V[1,2]

Norbert De Kimpe*[3] and Niceas Schamp

Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Ghent, Coupure 533 B-9000 Ghent, Belgium

Received February 25, 1975

Treatment of primary N-2-(1,1-dichloroalkylidene)anilines with sodium methoxide in methanol under reflux leads to nucleophilic substitution and a new type of the Favorskii rearrangement, yielding respectively N-2-(1,1-dimethoxyalkylidene)anilines and cis N-aryl α,β-unsaturated imidates. The formation of the latter compounds is explained by a cyclopropylidene amine intermediate, which is formed stereospecifically by disrotative closure of a delocalized zwitterion. Secondary N-2-(1,1-dichloroalkylidene)anilines undergo three types of reaction, i.e., nucleophilic substitution, a nonstereospecific Favorskii-like rearrangement, and a solvolysis leading to N-2-(1,3-dimethoxyalkylidene)anilines. The influence of alkyl substitution, concentration of nucleophilic reagent, reaction medium, nitrogen substituent, and substitution of the aromatic nucleus are discussed.

The base-induced skeletal rearrangement of α-halogeno ketones to carboxylic acid derivatives is known as the Favorskii rearrangement,[4,5] which is most reasonably explained in terms of a cyclopropanone intermediate.[6,7] The semibenzilic mechanism has been found to be important for certain ketone substrates.[8] The direction of opening of the cyclopropanone intermediate is influenced to a limited extent by the base and by the carbanion stabilities[9] of the cleavage intermediates and/or steric factors.[10] The Favorskii rearrangement is often accompanied by solvolysis, which is promoted by introduction of alkyl groups.[11,12]

Recently[13,14] we described the Favorskii rearrangement of 1,1-dichloro-2-alkanones **1a** and **1b**. Treatment of primary dichloromethyl ketones **1a** with sodium methoxide in methanol at ambient temperature gave rise to cis acrylic esters **7a**, next to α-chloromethyl esters **6a** in increasing amount with increasing R_1 group (Scheme I).

The stereospecificity was complete for primary dichloromethyl ketones **1a**, while for secondary derivatives **1b** the ratio between cis and trans acrylic esters **7b** depended on the difference between both alkyl substituents. Introduction of an alkyl group at 3 position caused also solvolysis to occur, yielding varying amounts of 1-chloro-3-methoxy ketones **10b** (Scheme I). These reactions were in full agreement with the mechanisms proposed by Bordwell and coworkers.[11,12]

In order to compare the reactivity of these α,α-halo ketones with their nitrogen analogues, we investigated N-2-(1,1-dichloroalkylidene)anilines **11** and **12**. Starting compounds were prepared by chlorination of appropriate N-2-(alkylidene)anilines with N-chlorosuccinimide as reported in preceding papers.[1,15]

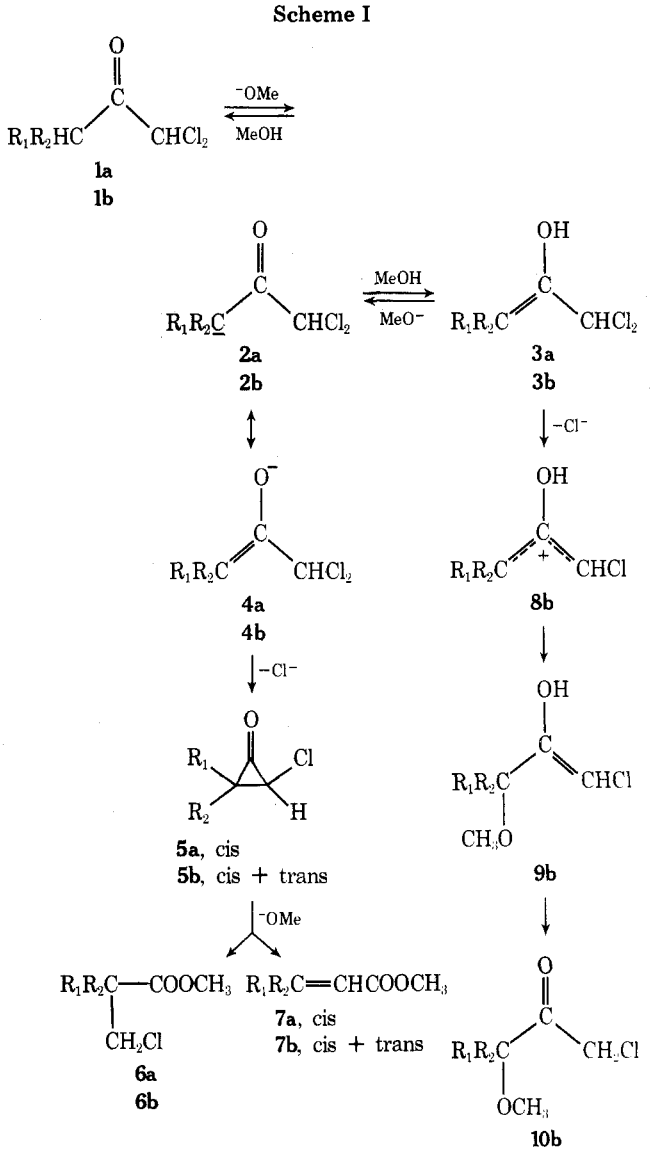
This paper deals with the reactivity of the first members of the new class of α,α-dihalogenated ketimines.

Results

As mentioned in the preliminary communication,[16] reactions of primary N-2-(1,1-dichloroalkylidene)anilines **11** with nucleophilic reagents such as sodium methoxide in methanol led to both nucleophilic substitution and to Favorskii-type rearrangement. Nucleophilic substitution afforded N-2-(1,1-dimethoxyalkylidene)anilines **13** while the new type of the Favorskii rearrangement proceeded stereospecifically with formation of exclusively cis N-aryl α,β-unsaturated imidates **15** (Table I).

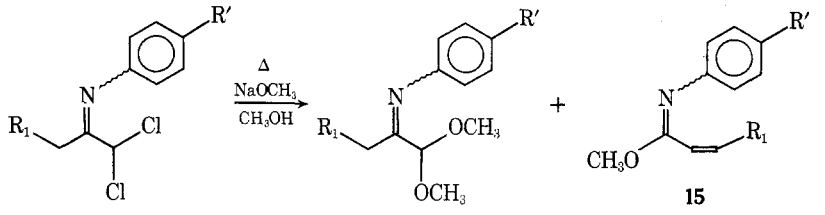
Secondary N-2-(1,1-dichloroalkylidene)anilines **12** underwent in addition to Favorskii rearrangement (**16** and **18**) and nucleophilic substitution (**14**), also solvolysis, yielding N-2-(1,3-dimethoxyalkylidene)anilines **17**. In some cases α,β-unsaturated imidates derived from secondary dichloromethylketimines **12** isomerized partly into β,γ-unsaturated compounds. All four α,β and β,γ cis and trans isomers were separated neatly by capillary column gas chromatography (150 m, OV_1). Besides the base and solvent mentioned, also less polar media (ether, diisopropyl ether) and stronger bases (sodium ethylate, potassium *tert*-butylate) were used. Results are compiled in Table II.

Scheme I



R_1 = alkyl; a, R_2 = H; b, R_2 = alkyl

Table I[a]
Reactivity of Primary Dichloromethylketimines 11

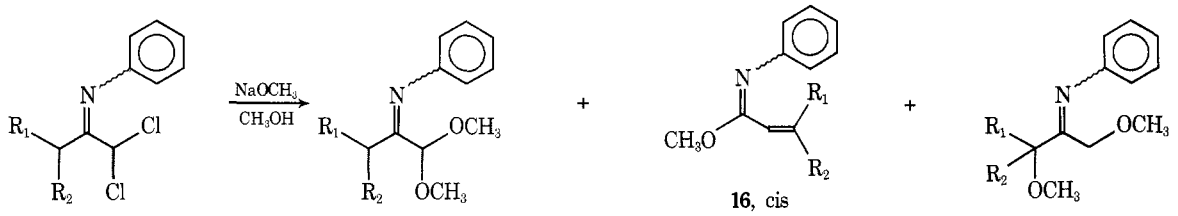


11 13 15

	R_1	R'	Nucleophilic reagent	Concn N (equiv)	Reflux time, hr	Starting material, %	13, %	15, %
11a	*i*-Pr	H	$NaOCH_3$–CH_3OH	0.5 (2)	32	0	48	48
11a	*i*-Pr	H	$NaOCH_3$–CH_3OH	1 (2)	16	0	49	47
11a	*i*-Pr	H	$NaOCH_3$–CH_3OH	2.5 (2)	16	0	45	51
11a	*i*-Pr	H	$NaOCH_3$–Et_2O	(10)	40	20	0	74
11a	*i*-Pr	H	$NaOCH_3$–*i*-Pr_2O	(10)	32	0	0	92
11a	*i*-Pr	H	KO-*t*-Bu–*t*-BuOH	1 (2)	40	100	0	0
11a	*i*-Pr	H	NaOEt–EtOH	1 (3)	32	0	46[b]	28[b]
11b	*i*-Pr	CH_3	$NaOCH_3$–CH_3OH	1 (2)	8	0	42	50
11c	*i*-Pr	OCH_3	$NaOCH_3$–CH_3OH	0.5 (3)	40	2	49	47
11c	*i*-Pr	OCH_3	$NaOCH_3$–CH_3OH	1 (3)	40	0	49	46
11c	*i*-Pr	OCH_3	$NaOCH_3$–CH_3OH	2 (3)	24	1	47	46
11c	*i*-Pr	OCH_3	$NaOCH_3$–Et_2O	(10)	40	14	0	71
11d	Et	H	$NaOCH_3$–CH_3OH	1 (2)	24	0	55	20
11d	Et	H	$NaOCH_3$–CH_3OH	2.5 (2)	24	0	59	19
11e	*t*-Bu	H	$NaOCH_3$–CH_3OH	1 (2)	32	45	43	0
11f	*n*-Bu	H	$NaOCH_3$–CH_3OH	1 (2)	40	0	54	22
11g	*n*-Pe	H	$NaOCH_3$–CH_3OH	1 (2)	32	0	50	20
11g	*n*-Pe	H	$NaOCH_3$–CH_3OH	2.5 (2)	24	0	38	16

[a] Compounds were determined by NMR spectrometry and gas chromatography as imino compounds or, after acidic hydrolysis, as carbonyl compounds. [b] Corresponding ethoxy compounds.

Table II[a]
Reactivity of Secondary Dichloromethylketimines 12



12 14 16, cis 18, trans 17

	R_1	R_2	Nucleophilic reagent[c]	Concn, N (equiv)	Reflux time, hr	Starting material, %	14, %	16 + 18, % cis	16 + 18, % trans	17, %
12a	CH_3	CH_3	$NaOCH_3$–CH_3OH	1 (4)	56	0	16	24		54
12a	CH_3	CH_3	$NaOCH_3$–CH_3OH	2 (4)	58	0	24	28		45
12a	CH_3	CH_3	$NaOCH_3$–Et_2O	(10)	96	65	0	12		0
12b	Et	CH_3	$NaOCH_3$–CH_3OH	2 (3)	96	6	16	35[b]		38
12c	*i*-Pr	CH_3	$NaOCH_3$–CH_3OH	1 (4)	210	29	9	10	25	25
12c	*i*-Pr	CH_3	$NaOCH_3$–CH_3OH	2 (4)	164	9	21	14	34	19
12c	*i*-Pr	CH_3	$NaOCH_3$–*i*-Pr_2O	(10)	60	100	0	0	0	0
12d	Cyclohexyl		$NaOCH_3$–CH_3OH	1 (4)	127	26	26	23		21
12d	Cyclohexyl		$NaOCH_3$–CH_3OH	2 (4)	103	0	50	28		20
12d	Cyclohexyl		$NaOCH_3$–Et_2O	(10)	24	100	0	0		0

[a] Compounds were determined by NMR spectrometry and gas chromatography as imino compounds or, after acidic hydrolysis, as carbonyl compounds. [b] Mixture of four isomers (cis and trans α,β and β,γ-unsaturated imino esters). [c] Mixture of α,β- and β,γ-unsaturated imidate.

α,β-Unsaturated imidates can be isolated by distillation in vacuo from the evaporated reaction mixture. Dimethoxyketimines could be determined only after hydrolysis to the corresponding ketones. The composition of the reaction mixture was measured by gas chromatography; corroborating results were obtained by analysis of the imino compounds, and, after acidic hydrolysis, of the carbonyl compounds. Stereochemistry was determined by NMR spectrometry (J_{AB}) of the reaction mixture, while distillation as well as gas chromatography caused isomerization to the trans compounds. In spite of the rapid isomerization of the cis α,β-unsaturated imino esters **15** (neutral medium), two pure cis derivatives (**15a, 15c**) were isolated by thin layer chromatography.

Varying the concentration of base (0.5, 1, and 2–2.5 *N*) and aromatic substituent (electron-donating groups) does not change the reaction appreciably. Less polar solvents cause the Favorskii product to increase at the expense of nucleophilic substitution, although reaction becomes excessively slow with secondary ketimines. Changing the aro-

matic N substituent into cyclohexyl afforded only nucleophilic substitution.[17]

Comparison with dichloromethyl ketones showed two main differences: (1) dichloromethyl ketones do not exhibit nucleophilic substitution; (2) from dichloromethylketimines only one Favorskii product is formed.

Discussion

From the theoretical point of view the mechanisms concerning the reactivity of 1,1-dichloro-2-alkanones and *N*-2-(1,1-dichloroalkylidene)anilines seem to be analogous. The base abstracts a proton from the 3 position in the dihalogenated ketimine, yielding a mesomeric anion, which then can lead to enamines **19.** This equilibrium is directly related to the equilibrium of a ketone with its enol and enolate.

Ketimines (**11, 12**) are less acidic then ketones (**1a, 1b**), while the anion is less stable owing to the lower electronegativity of nitrogen. The immediate consequence is the much longer reaction time of dichloromethylketimines (20–40 hr at reflux temperature for primary derivatives **11**) as compared to dichloromethyl ketones (<1 min at room temperature).

Secondary dichloromethylketimines **12** possess an even lower reactivity, while ketimines derived from aliphatic amines (X = *N*-cyclohexyl) show no reactivity at all for Favorskii rearrangement.[17] This phenomenon can be envisaged as a better stabilization of the negative charge on nitrogen in the case of *N*-aryl α,α-dichloroketimines. The stability of the ambident ions has a key position in the reactivity of the dichlorocarbonyl and dichloroimino compounds.

For the same reason along with Favorskii rearrangement, *nucleophilic substitution* in imino compounds occurs, which does not take place in dichloro ketones. Nucleophilic substitution (presumably bimolecular) could proceed via the tautomeric enamines, although their presence is not observable in the NMR spectrum. The reactivity of these enamine allylhalogenides and the corresponding ketimines toward methoxide is of comparable magnitude.[18]

On the other hand, in both secondary dichloromethyl ketones and secondary dichloromethylketimines 1-chloro-3-methoxy derivatives **10b** and **22** are yielded by *solvolysis* (Scheme II). The 1-chloro-3-methoxyimino compounds **22** are further converted to the 1,3-dimethoxyketimines by means of a nucleophilic substitution. The intermediacy of the *N*-2-(1-chloro-3-methoxyalkylidene)anilines **22** was proved by spectral evidence as they were detected in the reaction mixture after a short reaction time (approximately half the time required for completion of the reaction). Moreover, acidic hydrolysis of the reaction mixture revealed the presence of 1-chloro-3-methoxy-2-alkanones **10b** along with 1,3-dimethoxy-2-alkanones.

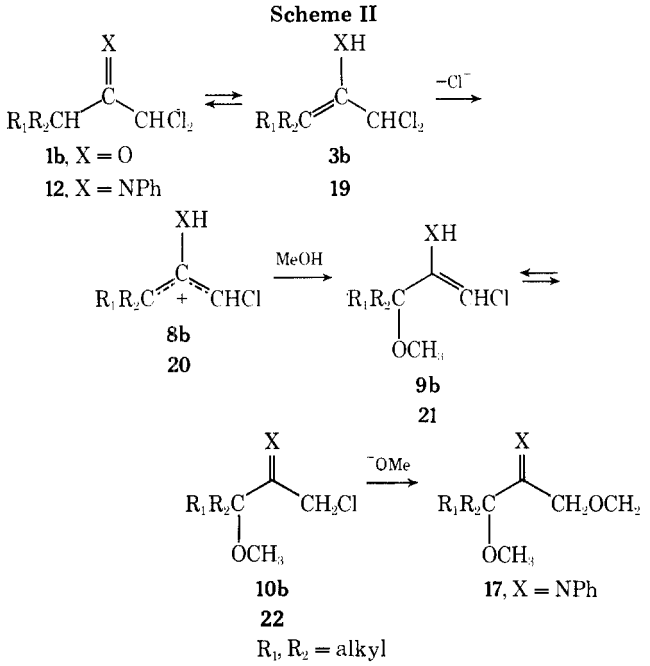
Solvolysis occurs in secondary derivatives only, owing to the enhanced stability of the delocalized carbonium ion (**8b, 20**) produced by loss of a chloride anion from respectively enol allylhalogenide **3b** and enamine allylhalogenide **19.**

It is known that alkyl substitution in either the α or γ position of allylhalogenides enhances the rate of solvolysis by a factor of hundreds or thousands.[19-21] A SN2′ mechanism is rejected while it has been found only in allylhalogenides having no substituents in the γ position.[19]

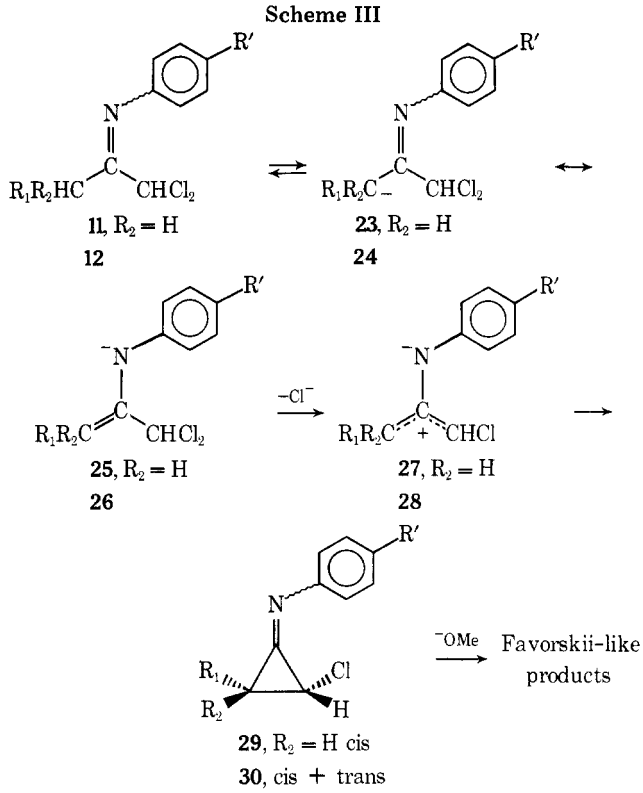
The main reaction in both dichlorinated ketimines and ketones is the *Favorskii rearrangement* (Scheme III). Anions (**2, 23,** and **24**) produced by proton abstraction lose slowly a chloride anion forming a zwitterion, which by a disrotative closure, according to the rules of conservation of orbital symmetry,[22,23] gives rise to a cyclopropanone **5** and cyclopropylidene amine (**29, 30**), respectively. Cyclopropane derivatives are opened by nucleophilic attack, but the opening in cyclopropanones occurs at both sides, while in cyclopropylidene imines only the classical opening (Scheme IV, path A) takes place, leading to a concerted expulsion of a chloride anion.

Thus[14] 1,1-dichloro-4-methyl-2-pentanone (**1a,** R_1 = *i*-Pr) yields via 2-chloro-3-isopropylcyclopropanone *cis*-methyl 4-methyl-2-pentenoate (67%), **7a** (R_1 = *i*-Pr), and methyl 2-chloromethyl-3-methylbutanoate (33%), **6a** (R_1 = *i*-Pr), while the corresponding ketimine *N*-2-(1,1-dichloro-4-methylpentylidene)aniline (**11a**) yields only *cis*-methyl *N*-phenyl 4-methyl-2-pentenoimidate (**15a,** ~50%) (along

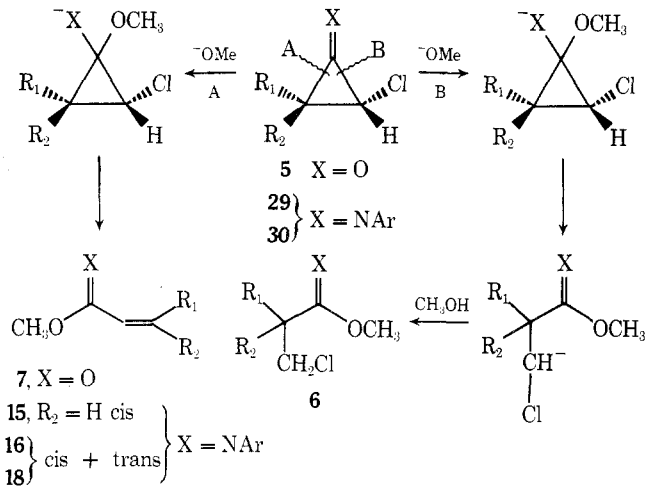
Scheme II



Scheme III



Scheme IV

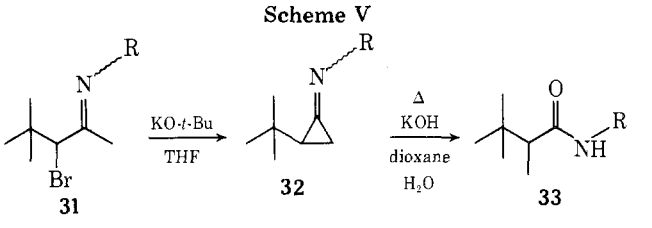


with substitution product **13a**, ~50%). Meanwhile the observation of opening at only one side of the intermediate three-membered ring is an open question.

In both series the classical products of primary derivatives (alkenoates, alkenoimidates) show complete stereospecificity, which is due to the stability of the intermediate zwitterion (**27**), formed by loss of a chloride anion from the least hindered anion **25**. In the case of secondary dichloromethylketimines **12** the formation of cis and trans *N*-phenyl α,β-unsaturated imidates **16** and **18** can be interpreted as derived from a chloride anion expulsion from both *E/Z* isomers of the anion **26**, whereby none of both isomers is extremely favored.

The intermediate cyclopropylideneamines are of recent interest and the synthesis has been described in only a few cases.[24-26] The first reported preparation[24] of such cyclopropylideneamines was executed under Favorskii rearrangement conditions, starting from *N*-2-(3-bromo-4,4-dimethylpentylidene)amines **31** and subsequent treatment with potassium *tert*-butoxide in tetrahydrofuran (Scheme V). When the *N*-1-(2-*tert*-butylcyclopropylidene)amine **32**

Scheme V



was refluxed with potassium hydroxide in dioxane–water, the amide **33** was isolated as the sole product, resulting from the expected opening of the three-membered ring (formation of the most stable anion[9]).

Cyclopropylideneamines, such as the proposed intermediates **29** and **30**, were predicted to exist in equilibrium with aziridines bearing an exocyclic double bond (methyleneaziridines) by means of a valence isomerization. The valence isomerization is similar to the one observed with cyclopropanones (and related alleneoxides),[23,27-29] methylenecyclopropanes[30], diaziridinones (and appropriate oxaziridineimines),[29,31] aziridinones (α-lactams and concordant imino oxiranes and methylene oxaziridines),[29,32] and α-lactones.[29,33] Though several reaction mechanisms have been interpreted to proceed via the already repeatedly postulated valence isomerization (see for instance ref 34 and 35), the occurrence was not adequately proved, until Quast and co-workers observed the phenomenon spectroscopically by NMR or indirectly by thermal decomposition of methylene aziridines.[25] Concerning the intermediacy of the cyclopropylideneamines **29** and **30** mentioned above, no trace of compounds derived from a valence isomerization could be observed. Attempts to trap the intermediate cyclopropylideneamines with furan under various conditions were unsuccessful, in spite of the successful trapping of their O analogues with furan derivatives.[23,36,37]

Experimental Section

Infrared spectra were recorded with a Perkin-Elmer Model 257 spectrophotometer. NMR spectra were measured with Varian T-60 and Varian 300-MHz spectrometers. Mass spectra were recorded with a A. E. I. MS 30 mass spectrometer (70 eV), eventually coupled with a Varian 1200 gas chromatograph (150-m capillary column OV_1). Other GC–MS couplings were executed with a A. E. I. MS 20 mass spectrometer (70 eV) (SE-30 column, 1.5 m).

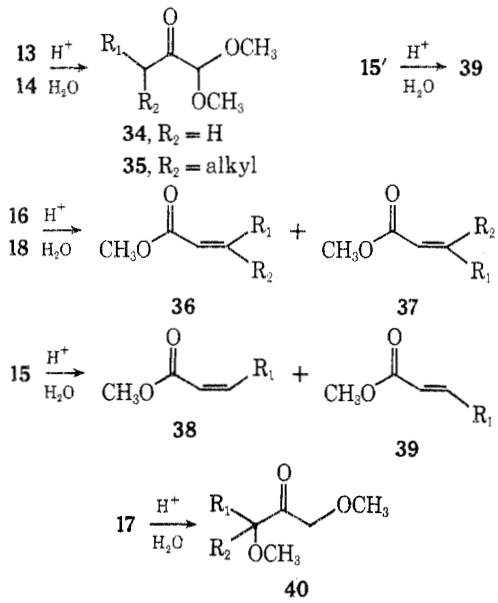
The analysis of the reaction mixtures was executed by gas chromatography using a Varian 1700 apparatus (3-m column, 12% SE-30, Chromosorb W, H_2 carrier gas). The composition was calculated from the area of the peaks, obtained by multiplying the peak height times the width at half-height. The results in the tables were given with respect to internal normalization. Preparative thin layer chromatography was performed with PSC Fertigplatten Merck Kieselgel F 254 (2 mm thickness) with isooctane–carbon tetrachloride–toluene (40:30:30) as eluent. Compounds were located by means of a Chromato-vue apparatus (short-wave uv light).

Preparation of Compounds. Methyl ketones were commercially available compounds or were prepared according to the literature: 2-heptanone,[38,39] methyl cyclohexyl ketone,[40] and 3,4-dimethyl-2-pentanone.[40,41] *N*-2-(1,1-Dichloroalkylidene)anilines **11** and **12** were prepared as described previously.[1,16]

Reaction of Primary *N*-2-(1,1-Dichloroalkylidene)anilines 11 with Sodium Methoxide in Methanol (or Sodium Ethoxide in Ethanol). For all *N*-2-(1,1-dichloroalkylidene)anilines the same general procedure was followed. In a typical experiment, a mixture of 19.52 g (0.080 mol) of freshly prepared[1] *N*-2-(1,1-dichloro-4-methylpentylidene)aniline (**11a**) and 160 ml of 1 *N* sodium methoxide in methanol (0.160 mol) was stirred under reflux (protection by a calcium chloride tube) for 16 hr. The *first half* of the reaction mixture was treated with dry ether in order to precipitate sodium chloride and eventually sodium methoxide. After evaporation of the solvent the residue was treated once more with dry ether and this procedure was repeated till no further precipitate was formed. *cis*-Methyl *N*-phenyl-4-methyl-2-pentenoimidate (**15a**) was isolated by thin layer chromatography. The band at R_f 0.4–0.5 was extracted with dry acetone. Subsequent evaporation at low temperature in vacuo gave pure **15a** as a light yellow oil. A second band contained *N*-2-(1,1-dimethoxy-4-methylpentylidene)aniline (**13a**), which could not be isolated since it decomposed on the slightest contact with air and moisture. During gas chromatographic analysis and distillation **15a** isomerized into *trans*-methyl *N*-phenyl-4-methyl-2-pentenoimidate (**15'a**). Gas chromatographic analysis showed that the residual oil contained 47% **15'a** and 48% **13a** along with minor compounds. Distillation in vacuo (short Vigreux column) gave 3.7 g (45%) of **15'a**, bp 88–90°C (0.4 mmHg), and 3.3 g (35%) of **13a**, bp 92–95°C (0.4 mmHg), which turned black rapidly.[42]

The *second half* of the reaction mixture was neutralized with 2 *N* HCl and 25 ml of 2 *N* HCl was added in excess. After stirring overnight at room temperature, the mixture was extracted four times with ether, and the combined extracts were washed and dried ($MgSO_4$). The dried ethereal extract was evaporated through a 20-cm Vigreux column. Gas chromatographic analysis of the residual mixture of carbonyl compounds[43] revealed the presence of 49% 1,1-dimethoxy-4-methyl-2-pentanone (**34a**), 24% *cis*-methyl 4-methyl-2-pentenoate (**38a**), and 23% *trans*-methyl 4-methyl-2-pentenoate (**39a**). In other batches the cis/trans ratio of both isomeric α,β-unsaturated esters varied between 1:1 and 3:1. All carbonyl compounds were isolated by preparative gas chromatography and were compared with authentic samples.[13,14,17] Distillation in vacuo afforded 2.1 g (42%) of methyl 4-methyl-2-pentenoate (cis + trans, **38a**, **39a**), bp 48–52°C (12 mmHg), and 2.4 g (37%) 1,1-dimethoxy-4-methyl-2-pentanone (**34a**), bp 59–62°C (12 mmHg). A black polymeric material remained in the distillation flask presumably due to decomposition of **34a** (see ref 17).

Reaction of *N*-2-(1,1-Dichloroalkylidene)anilines 11 with Sodium Methoxide in Diethyl Ether or Diisopropyl Ether. The following typical experiment illustrates the procedure which



was used. A mixture of 2.44 g (0.01 mol) of freshly prepared[1] *N*-2-(1,1-dichloro-4-methylpentylidene)aniline (**11a**) and 5.4 g (0.1 mol) of dry sodium methoxide in 25 ml of dry diisopropyl ether was stirred under reflux for 32 hr (protection with a calcium chloride tube). After completion of the reaction, the suspension was filtered and washed with dry ether. Removal of the solvent in vacuo left an oil, which was further purified by preparative TLC. Extraction of the band at R_f 0.4–0.5 with acetone provided 1.8 g (92%) of pure *cis*-methyl *N*-phenyl-4-methyl-2-pentenoimidate (**15a**).

***cis*-Methyl *N*-Phenyl-4-methyl-2-pentenoimidate (15a):** NMR (CCl_4) 0.96 [d, 6, J = 7 Hz, $(CH_3)_2$], 3.15 (m, s, CH_xMe_2), 3.83 (s, 3, OCH_3), 6.5–7.4 (m, 5, C_6H_5), 5.4–5.6 [2 H, **ABX** pattern unresolved at 60 MHz, but completely of first order at 300 MHz: 5.42 (d, 1, J_{ba} = 12, J_{bc} = 0 Hz, $=CH_bC=N$), 5.51 ppm (dd, 1, J_{ab} = 12, J_{ac} = 9.4 Hz, $=CH_aCHMe_2$)]; ir (NaCl) 2850 (OCH_3), 1622 (C=C), 1672 cm^{-1} (C=N). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found: C, 76.61; H, 8.32.

***trans*-Methyl *N*-Phenyl-4-methyl-2-pentenoimidate (15'a):** NMR (CCl_4) 0.95 [d, 6, J = 6.5 Hz, $(CH_3)_2$], 2.2 (m, 1, CH_xMe_2), 3.80 (s, 3, OCH_3), 6.5–7.3 (m, 5, C_6H_5), 5.59 [dd (**AMX**), 1, J_{ab} = 15, J_{ac} = 1 Hz, $=CH_aC=N$], 6.49 ppm (dd, 1, J_{ba} = 15, J_{bc} = 6 Hz, $CH=CHC=N$); ir (NaCl) 2850 (OCH_3), 1672 (C=N), 1622 cm^{-1} (C=C), 1600, 1582–1491 cm^{-1} (aromatic); mass spectrum *m/e* (rel intensity) 203 (M^+, 60), 202 (23), 188 (8), 172 (19), 160 (100), 156 (14), 130 (14), 119 (25), 104 (21), 93 (47), 77 (65), 69 (21), 51 (32). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43. Found: C, 76.65; H, 8.34. Compounds **15a** and **15'a** (and also other imidates mentioned in this paper) did not show syn–anti isomerism, since only one isomer was visible in the NMR spectrum.[44]

***N*-2-(1,1-Dimethoxy-4-methylpentylidene)aniline (13a):** ir (NaCl) (recorded immediately after preparative GLC isolation) 2839 (OCH_3), 1669 (C=N), 1635 cm^{-1} (C=C enaminic form?); mass spectrum[46] (GC–MS coupling, AEI MS 20) *m/e* (rel intensity) 235 (M^+, 4), 204 (2), 203 (2), 160 (100), 118 (6), 104 (21), 77 (17), 75 (23), 57 (8), 51 (6). No analytical data could be obtained owing to decomposition. Acidic hydrolysis yielded **34a.** The reaction of *N*-2-(1,1-dichloro-4-methylpentylidene)aniline (**11a**) with sodium ethoxide was performed in similar manner as described for methoxide–methanol.

***trans*-Ethyl *N*-Phenyl-4-methyl-2-pentenoimidate:** NMR (CCl_4) 0.96 [d, 6, J = 7 Hz, $(CH_3)_2$], 2.2 (m, 1, CH_xMe_2), 4.26 (q, 2, J = 7.5 Hz, OCH_2), 1.36 (t, 3, J = 7.5 Hz, $OCCH_3$), 5.64 (dd, 1, J_{bx} = 1, J_{ba} = 15.5 Hz, $=CH_bC=N$), 6.54 (dd, 1, J_{ab} = 15.5, J_{ax} = 7 Hz, CH_aCHMe_2), 6.5–7.5 ppm (m, 5, C_6H_5). Protons H_a, H_b, and H_x displayed a AMX pattern. Ir (NaCl) 1670 (C=N), 1623 (C=C), 1601, 1585, 1495 cm^{-1} (aromatic); mass spectrum *m/e* (rel intensity) 217 (M^+, 29), 216 (5), 202 (4), 189 (6), 188 (7), 174 (100), 172 (11), 158 (24), 146 (10), 133 (11), 132 (21), 130 (10), 120 (11), 119 (14), 118 (70), 104 (9), 97 (25), 93 (50), 81 (14), 77 (61), 51 (21). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.37; H, 8.81. Found: C, 77.62; H, 8.96.

1,1-Diethoxy-4-methyl-2-pentanone: NMR (CCl_4) 0.89 [d, 6, J = 6 Hz, $(CH_3)_2$], ~2 (m, 1, $CHMe_2$), 2.35 (d degenerated, 2, CH_2CO), 1.21 [t, 6, J = 7 Hz, $(CH_3CO)_2$], 4.33 [s, 1, $CH(OEt)_2$], 3.2–3.8 ppm [ABX_3, 4, $(OCH_2)_2$]; ir (NaCl) 1733 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) no M^+, 143 (3), 105 (13), 104 (12), 103 (100), 97 (8), 85 (6), 75 (75), 73 (10), 57 (13), 47 (83). Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.70. Found: C, 63.60; H, 10.61.

***cis*-Ethyl 4-Methyl-2-pentenoate:** NMR (CCl_4) 1.00 [d, 6, J = 6.5 Hz, $(CH_3)_2$], 3.7 (m, 1, CH_xMe_2), 1.26 (t, 3, J = 7 Hz, CH_3CO), 4.11 (q, 2, J = 7 Hz, CH_2O), 5.55 (dd, 1, J_{ab} = 11.5, J_{bx} = 1 Hz, $=CH_bC=O$), 5.98 ppm (dd, 1, J_{ab} = 11.5, J_{ax} = 9 Hz, $=CH_a-CHMe_2$); ir (NaCl) 1729 (C=O), 1650 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity) 142 (M^+, 40), 127 (2), 114 (64), 99 (39), 97 (100), 81 (22), 73 (14), 71 (17), 69 (87), 67 (34), 59 (73), 56 (35), 43 (62).

***trans*-Ethyl 4-Methyl-2-pentanoate:**[47] NMR (CCl_4) 1.06 [d, 6, J = 7 Hz, $(CH_3)_2$], 2.4 (m, 1, CH_xMe_2), 4.13 (q, 2, J = 7 Hz, OCH_2), 1.27 (t, 3, J = 7 Hz, CH_3CO), 5.70 (dd, 1, J_{ab} = 15.5, J_{bc} = 1 Hz, $=CH_bCO$), 6.88 ppm (dd, 1, J_{ab} = 15.5, J_{ac} = 7 Hz, $=CH_a-CHMe_2$); ir (NaCl) 1725 (C=O), 1660 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity) 142 (M^+, 45), 114 (37), 99 (20), 97 (74), 96 (20), 69 (100), 59 (25), 43 (20).

Reactions with *N*-2-(1,1-Dichloro-4-methylpentylidene)-*p*-toluidine (11b). *trans*-Methyl *N*-*p*-Tolyl-4-methyl-2-pentenoimidate (15'b): NMR (CCl_4) 0.97 [d, 6, J = 6 Hz, $(CH_3)_2$], 2.30 (s, 3, para CH_3), 2.3 (m, 1, CH_xMe_2), 3.80 (s, 3, OCH_3), 5.63 (dd, 1, J_{ab} = 15.5, J_{bx} = 1.0 Hz, $=CH_bC=N$), 6.52 (dd, 1, J_{ab} = 15.5, J_{ax} = 7 Hz, $CH_a=C-C=N$), 6.57 (d, 2, J = 8 Hz, $CH=CN$), 7.01 ppm (d, 2, J = 8 Hz, $CH=C-CN$); ir (NaCl) 2850 (OCH_3), 1672 (C=N), 1620 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity) 217 (M^+, 81), 216 (24), 202 (10), 186 (23), 184 (6), 174 (100), 170 (13), 144 (11), 133 (22), 106 (38), 105 (35), 91 (27), 77 (11), 69 (11), 65 (19), 51 (7).

***cis*-Methyl *N*-*p*-tolyl-4-methyl-2-pentenoimidate (15b)** had the unresolved AB part (NMR, CCl_4) of the ethylenic protons at δ 5.3–5.6 ppm (**ABX**).[48]

Reactions with *N*-2-(1,1-Dichloro-4-methylpentylidene)-*p*-anisidine (11c). *trans*-*N*-*p*-Methoxyphenyl-4-methyl-2-pentenoimidate (15'c): NMR (CCl_4) 0.97 [d, 6, J = 6.5 Hz, $(CH_3)_2$], 2.3 (m, 1, CH_xMe_2), 5.67 (dd, 1, J_{ba} = 15.5, J_{bx} = 1 Hz, $=CH_bC=N$), 6.51 (dd, 1, J_{ab} = 15.5, J_{ax} = 7 Hz, $=CH_aCHMe_2$), 3.79 (s, 3, $CH_3OC=N$), 3.76 (s, 3, para OCH_3), 6.61 (d, 2, J = 8 Hz, $CH=CN$), 6.73 ppm (d, 2, J = 8 Hz, $CH=C-CN$); ir (NaCl) 2840 (OCH_3), 1670 (C=N), 1620 (C=C), 1586, 1510 cm^{-1} (aromatic); mass spectrum *m/e* (rel intensity) 233 (M^+, 100), 232 (24), 218 (21), 202 (27), 190 (96), 160 (15), 149 (39), 148 (12), 134 (21), 123 (33), 122 (21), 108 (18), 77 (21), 69 (21), 53 (15), 51 (10). Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.20. Found: C, 71.92; H, 8.03.

***cis*-*N*-*p*-Methoxyphenyl-4-methyl-2-pentenoimidate (15c):** NMR (CCl_4) 0.93 [d, 6, J = 6.5 Hz, $(CH_3)_2$], 3.1 (m, 1, CH_xMe_2), 3.83 (s, 3, $CH_3OC=N$), 3.67 (s, 3, para OCH_3), 5.3–5.8 (**ABX**, 2, $CH=CH$), 6.71 ppm (s, 4, C_6H_4); ir (NaCl) 2840 (OCH_3), 1660 (C=N), 1611 (C=C), 1610–1509 cm^{-1} (aromatic). Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.20. Found: C, 71.89; H, 7.99.

Reactions with *N*-2-(1,1-Dichloropentylidene)aniline (11d). *trans*-Methyl *N*-Phenyl-2-pentenoimidate (15'd): NMR (CCl_4) 0.96 (t, 3, J = 6.5 Hz, $CH_3C-C=$), 2.07 [m, 2, $(CH_2)_xC=$], 3.83 (s, 3, OCH_3), 6.6–7.4 (m, 5, C_6H_5), 5.70 (dt, 1, J_{ba} = 15.5, J_{bx} = 0.8 Hz, $=CH_bC=N$), ~6.6 ppm (overlapping by aromatic multiplet, J_{ax} = 7, J_{ab} = 15.5 Hz); ir (NaCl) 2850 (OCH_3), 1675 (C=N), 1627 (C=C), 1602, 1586, 1497 cm^{-1} (aromatic); mass spectrum *m/e* (rel intensity) 189 (M^+, 50), 188 (23), 174 (11), 160 (100), 158 (28), 156 (11), 143 (17), 134 (9), 132 (15), 130 (13), 128 (10), 119 (23), 117 (17), 104 (20), 93 (30), 91 (19), 77 (50), 67 (9), 55 (21), 53 (10), 51 (21).

Reactions with *N*-2-(1,1-Dichloroheptylidene)aniline (11f). Both **13f** and **15f** were characterized by acidic hydrolysis, whereby **15f** yielded exclusively trans ester **39f.**

1,1-Dimethoxy-2-heptanone (34f): NMR (CCl_4) 0.89 (t, 3, CH_3), 1.0–1.6 [m, 6, $(CH_2)_3$], 2.43 (t, 2, J = 6.5 Hz, CH_2CO), 4.21 (s, 1, CHCO), 3.36 ppm [s, 6, $(OCH_3)_2$]; ir (NaCl) 2842 (OCH_3), 1737 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) no M^+, 143 (0.6), 99 (3.5), 75 (100), 71 (4), 59 (6), 55 (6).

***trans*-Methyl 2-Heptenoate (39f):** NMR (CCl_4) 0.93 (t, 3, CH_3), 1.1–1.7 [m, 4, $(CH_2)_2$], 2.2 [m, 2, $(CH_2)_xC=$], 3.67 (s, 3, OCH_3), 5.75 (dt, 1, J_{ba} = 15.5, J_{bx} = 1 Hz, $=CH_bCO$), 6.90 ppm (dt, 1, J_{ab} = 15.5, J_{ax} = 6 Hz, $=CH_aCH_2$); ir (NaCl) 2870 (OCH_3), 1735 (C=O), 1665 cm^{-1} (C=C).

Reactions with *N*-2-(1,1-Dichlorooctylidene)aniline (11g). *trans*-Methyl *N*-Phenyl-2-octenoimidate (15'g): NMR (CCl_4) 0.88 (t, 3, CH_3), 1.0–1.6 [m, 6, $(CH_2)_3$], 2.0 [m, 2, $(CH_2)_xC=$], 3.81 (s, 3, OCH_3), 5.67 (dd, 1, J_{ab} = 15, J_{bx} = 1 Hz, $=CH_bC=N$), $CH_a=C-C=N$ covered by the aromatic multiplet, 6.4–7.4 ppm (m,

5, C_6H_5); ir (NaCl) 2850 (OCH_3), 1675 (C=N), 1625 (C=C), 1602, 1585, 1508 cm^{-1} (aromatic).

***trans*-Methyl 2-Octenoate (39g):** NMR (CCl_4) 0.91 (t, 3, J = 7 Hz, CH_3), 1.1–1.6 [m, 6, $(CH_2)_3$], 2.15 [m, 2, $(CH_2)_xC$=], 3.66 (s, 3, OCH_3), 5.72 (dt, 1, J_{ab} = 15, J_{bx} = 1 Hz, CH_bC=O), 6.80 ppm (dt, 1, J_{ab} = 15, J_{ac} = 7 Hz, =CH_aCH_2); uv max (CH_3OH) 217 nm. When the reaction of **11g** was performed in concentrated sodium methylate solution (2.5 N) a small amount of the α,β-unsaturated imidate underwent Michael addition of methylate, yielding the β-methoxy imidate which is characterized by its carbonyl compound (hydrolysis), i.e., methyl 3-methoxyoctanoate.

Methyl 3-Methoxyoctanoate: NMR (CCl_4) 0.90 (t, 3, CH_3), 1.1–1.8 [m, 8, $(CH_2)_4$], 2.35 (**ABX**, 1, J_{ab} = 12, J_{ac} = 6 Hz, CH_aCO), 2.48 (**ABX**, 1, J_{ab} = 12, J_{bx} = 6 Hz, CH_bCO), 3.6 (m, 1, CH_xOMe), 3.65 (s, 3, $COOCH_3$), 3.30 ppm (s, 3, OCH_3); ir (NaCl) 2835 (OCH_3), 1750 cm^{-1} (C=O); mass spectrum m/e (rel intensity) no M^+, 173 (13), 156 (7), 125 (12), 117 (50), 115 (24), 101 (12), 99 (12), 83 (25), 75 (100), 74 (15), 59 (25), 58 (17), 55 (35).

1,1-Dimethoxy-2-octanone (34g): NMR (CCl_4) 0.89 (t, 3, CH_3), 1.0–1.8 [m, s, $(CH_2)_4$], 2.44 (t, 2, J = 6.5 Hz, CH_2CO), 3.37 [s, 6, $(OCH_3)_2$], 4.22 ppm (s, 1, CHCO); ir (NaCl) 2840 (OCH_3), 1735 cm^{-1} (C=O); mass spectrum m/e (rel intensity) no M^+, 157 (2), 115 (3), 85 (5), 75 (100), 55 (11).

Reaction of Secondary *N*-2-(1,1-Dichloroalkylidene)anilines (12) with Sodium Methoxide in Methanol. A mixture of 2.30 g (0.01 mol) of freshly prepared *N*-2-(1,1-dichloro-3-methylbutylidene)aniline (**12a**) and 20 ml of sodium methoxide in methanol (2 N, 0.04 mol) was refluxed during 58 hr. Work-up as described above gave 2.1 g of an oil, which was analyzed by gas chromatography: 28% methyl *N*-phenyl-3-methyl-2-butenoimidate (**16a**, $R_1 = R_2 = CH_3$), 24% *N*-2-(1,1-dimethoxy-3-methylbutylidene)aniline (**14a**), and 45% *N*-2-(1,3-dimethoxy-3-methylbutylidene)aniline (**17a**). The composition of the carbonyl compounds obtained by acidic hydrolysis, as calculated from GLC, was identical with the composition of the imino compounds. Both *N*-2-(1,1-dimethoxyalkylidene)anilines (**13**) and *N*-2-(1,3-dimethoxyalkylidene)anilines (**17**) could not be isolated in pure form owing to rapid decomposition on contact with air. All other reaction mixtures, derived from secondary *N*-2-(1,1-dichloroalkylidene)anilines (**12**), were analyzed in similar manner.

Methyl *N*-Phenyl-3-methyl-2-butenoimidate (16a, $R_1 = R_2 = CH_3$): NMR (CCl_4)[49] 1.76 (d, 3, J = 1.2 Hz, trans CH_3), 1.95 (d, 3, J = 1.2 Hz, cis CH_3), 3.84 (s, 3, OCH_3), 5.44 (m, 1, =CHC=N), 6.5–7.4 ppm (m, 5, C_6H_5); ir (NaCl) 1668 (C=N), 1622 (C=C), 2850 (OCH_3), 1602, 1582, 1495 cm^{-1} (aromatic); mass spectrum m/e (rel intensity) 189 (M^+, 100), 188 (25), 174 (35), 158 (40), 157 (10), 144 (10), 143 (10), 131 (30), 130 (10), 129 (10), 119 (13), 117 (10), 107 (10), 104 (7), 93 (11), 91 (20), 83 (12), 77 (45), 55 (18), 51 (20). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.98. Found: C, 75.99; H, 7.89.

***N*-2-(1,1-Dimethoxy-3-methylbutylidene)aniline (14a):** NMR (CCl_4) 1.18 [d, 6, J = 6.5 Hz, $(CH_3)_2$], 3.0 (m, 1, $CHMe_2$), 3.23 [s, 6, $(OCH_3)_2$], 4.48 [s, 1, $CH(OMe)_2$], 6.4–7.5 ppm (m, 5, C_6H_5); mass spectrum m/e (rel intensity) 221 M^+, 6), 191 (8), 189 (25), 174 (12), 172 (6), 159 (7), 146 (100), 145 (12), 144 (58), 131 (11), 130 (11), 118 (8), 117 (7), 104 (75), 93 (67), 77 (60), 75 (54), 66 (27), 65 (17), 51 (33). Rapidly discoloring liquid.

1,1-Dimethoxy-3-methyl-2-butanone (35a): NMR (CCl_4) 1.02 [d, 6, J = 7.5 Hz, $(CH_3)_2$], 2.95 (septet, 1, J = 7.5 Hz, $CHMe_2$), 4.34 (s, 1, CHCO), 3.37 ppm [s, 6, $(OCH_3)_2$]; ir (NaCl) 2840 (OCH_3), 1730 cm^{-1} (C=O); mass spectrum m/e (rel intensity) no M^+, 115 (7), 87 (10), 75 (100), 71 (4), 55 (10), 43 (15). Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.60; H, 9.50.

1,3-Dimethoxy-3-methyl-2-butanone (40a): NMR (CCl_4) 1.26 [s, 6, $(CH_3)_2$], 3.21 (s, 3, Me_2COCH_3), 3.33 (s, 3, CH_2OCH_3), 4.25 (s, 2, CH_2CO); ir (NaCl) 2835 (OCH_3), 1740 cm^{-1} (C=O); mass spectrum m/e (rel intensity) 146 (M^+, 0.2), 115 (0.5), 73 (100), 69 (4), 55 (6), 45 (17). The most abundant ion m/e 73 is originated either from $(CH_3)_2C{=}O^+CH_3$ or $CH_3OCH_2C{\equiv}O^+$, as both fragment ions are derived from α-cleavage at the C_2–C_3 bond. Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.34; H, 9.49.

***N*-2-(1,3-Dimethoxy-3-methylbutylidene)aniline (17a).** This unstable compound was identified by its corresponding carbonyl compound **40a** (see above) and by its mass spectrum (GC–MS coupling with A. E. I. MS 20): m/e (rel intensity) 221 (M^+, 5) 191 (14), 189 (8), 148 (42), 144 (18), 119 (7), 118 (8), 104 (11), 77 (28), 73 (100), 51 (13), 45 (83).

1-Chloro-3-methoxy-3-methyl-2-butanone (10, $R_1 = R_2 = CH_3$). When *N*-2-(1,1-dichloro-3-methylbutylidene)aniline (**12a**) was refluxed with sodium methylate in methanol (1 N, 4 equiv) during 16 hr, subsequent acidic hydrolysis afforded, along with the normal products, 1-chloro-3-methoxy-3-methyl-2-butanone (**10**, $R_1 = R_2$ = Me), which is derived from the corresponding imino compound **22** ($R_1 = R_2 = CH_3$). It was compared with authentic material.[14]

Methyl 3-Methyl-2-butenoate (36a). Compound **36a** arose from **16a** and was a known compound.[52] Similar to the case mentioned above, α,β-unsaturated imidate **16a** was found to undergo (2 N NaOMe–MeOH) Michael addition (only a small amount) yielding a β-methoxy imidate, which was hydrolyzed to **methyl 3-methoxy-3-methylbutanoate** (see similarly 3-methoxyoctanoate): NMR (CCl_4) 1.25 [s, 6, $(CH_3)_2$], 2.41 (s, 2, CH_2), 3.19 (s, 3, OCH_3), 3.65 ppm (s, 3, $COOCH_3$); ir (NaCl) 1747 (C=O), 2838 cm^{-1} (OCH_3); mass spectrum m/e (rel intensity) no M^+, 131 (17), 116 (7), 115 (4), 99 (11), 89 (33), 83 (7), 75 (11), 73 (100), 71 (17), 59 (13), 48 (42), 55 (8).

Reaction of *N*-2-(1,1-Dichloro-3-methylbutylidene)aniline (12a) with Sodium Methoxide in Diethyl Ether. Preparation of Methyl *N*-Phenyl-3-methyl-2-butenoimidate (16a, $R_1 = R_2 = CH_3$). A mixture of 1.15 g (0.005 mol) of freshly prepared[1] *N*-2-(1,1-dichloro-3-methylbutylidene)aniline (**12a**) and 2.7 g (0.05 mol) of dry sodium methoxide in 15 ml of dry diethyl ether was stirred under reflux for 96 hr. The suspension was filtered and washed with dry diethyl ether and the solvent evaporated in vacuo. The residual oil was chromatographed by means of TLC (see experimental conditions above), affording 0.61 g (65%) of methyl *N*-phenyl-3-methyl-2-butenoimidate (**16a**, $R_1 = R_2 = CH_3$). Spectroscopic and analytical data were given above.

Reactions with *N*-2-(1,1-Dichloro-3-methylpentylidene)-aniline (12b). The Favorskii rearrangement of compound **12b** afforded a mixture of α,β- and β,γ-unsaturated imino esters, each present as cis and trans isomers.[53] Some NMR data were given, obtained from the NMR spectrum of the mixture of isomers (bp 72–76° C, 0.03 mmHg).

***trans*-Methyl *N*-Phenyl-3-methyl-2-pentenoimidate (18b):** mass spectrum m/e (rel intensity) 203 (M^+, 100), 202 (16), 188 (18), 174 (20), 172 (26), 156 (8), 148 (1), 145 (15), 130 (9), 119 (13), 111 (30), 97 (20), 93 (20), 91 (20), 77 (53), 69 (13), 51 (27); NMR (CCl_4) 0.9 (t, 3, J = 7 Hz, CH_3), 1.90 (d, 3, J = 1.2 Hz, CH_3C=), 5.40 (m, 1, CH=), 3.81 (s, 3, OCH_3), 6.4–7.4 ppm (m, 5, C_6H_5), CH_2 covered.

***cis*-Methyl *N*-Phenyl-3-methyl-2-pentenoimidate (16b):** mass spectrum m/e (rel intensity) 203 (M^+, 100), 202 (21), 188 (33), 174 (8), 172 (17), 156 (8), 148 (3), 145 (12), 130 (8), 119 (21), 111 (92), 97 (17), 93 (25), 91 (29), 77 (67), 69 (25), 51 (33); NMR (CCl_4) 0.9 (t, 3, J = 7 Hz, CH_3), 1.72 (d, 3, J = 1.2 Hz, CH_3C=), 5.4 (m, 1, CH=), 3.81 (s, 3, OCH_3), 6.4–7.4 ppm (m, 5, C_6H_5), CH_2 covered.

***trans*-Methyl *N*-Phenyl-3-methyl-3-pentenoimidate (41):** NMR (CCl_4) 2.83 (s, broadened, 2, N=C-CH_2C=C), 3.75 (s, 3, OCH_3), 1.6 (CH_3C=), 5.1 ppm (m, 1, CH=); mass spectrum m/e (rel intensity) 203 (M^+, 47), 202 (44), 188 (71), 174 (3), 172 (5), 170 (3), 148 (11), 134 (41), 119 (100), 111 (21), 110 (21), 93 (9), 91 (27), 77 (27), 69 (22), 51 (18).

***cis*-Methyl *N*-Phenyl-3-methyl-3-pentenoimidate (42):** mass spectrum m/e (rel intensity) 203 (M^+, 42) 202 (43), 188 (63), 174 (3), 172 (4), 170 (3), 148 (1), 134 (46), 119 (100), 111 (25), 110 (25), 93 (12), 91 (29), 77 (33), 69 (25), 51 (21); NMR (CCl_4) 2.92 (s broadened, 2, N=CCH_2C=), 3.75 (s, 3, OCH_3), 1.55 (CH_3C=), 5.1 ppm (m, 1, CH=). Attempts to separate the isomeric compounds by thin layer chromatography were unsuccessful (R_f 0.3–0.4, silica gel F254 Merck, isooctane–CCl_4–toluene, 40:30:30).

***trans*-Methyl 3-methyl-2-pentenoate (36b) and *cis*-methyl 3-methyl-2-pentenoate (37b)** were previously described.[14]

***N*-2-(1,3-Dimethoxy-3-methylpentylidene)aniline (17b).** The unstable compound **17b** was identified by its mass spectrum (obtained from GC–MS coupling) and by hydrolysis to **40b:** mass spectrum of **17b** m/e (rel intensity) 235 (M^+, 2), 204 (10), 158 (9), 148 (20), 119 (8), 118 (6), 104 (9), 87 (100), 77 (22), 55 (24), 51 (11), 45 (9).

1,3-Dimethoxy-3-methyl-2-pentanone (40b): NMR (CCl_4) 0.77 (t, 3, J = 7.5 Hz, CH_3CCO), 1.61 (m, 2, CH_2), 1.20 (s, 3, CH_3CO), 4.23 (s, 2, CH_2O), 3.19 (s, 3, CH_3OCMe), 3.32 ppm (s, 3, OCH_3); ir (NaCl) 2835 (OCH_3), 1738 cm^{-1} (C=O); mass spectrum m/e (rel intensity) 160 (M^+, 1.2), 131 (1.5), 129 (2), 128 (3), 115 (4), 98 (4), 87 (100), 83 (20), 75 (20), 71 (5), 59 (7), 57 (7), 56 (7), 55 (75).

***N*-2-(1,1-Dimethoxy-3-methylpentylidene)aniline (14b):** bp

80–86°C (0.03 mmHg); rapidly decomposing liquid; mass spectrum *m/e* (rel intensity) 235 (M^+, 6), 160 (100), 130 (3), 104 (87), 77 (35), 75 (41), 57 (11), 51 (11). Acidic hydrolysis afforded **35b**.

1,1-Dimethoxy-3-methyl-2-pentanone (35b): NMR (CCl_4) 1.83 (t, 3, J = 7 Hz, CH_3CCCO), 1.6 (m, 2, CH_2), 2.8 (m, 1, CHMe), 1.02 (d, 3, J = 6 Hz, CH_3CCO), 4.30 [s, 1, $CH(OMe)_2$], 3.38 ppm [s, 6, $(OCH_3)_2$]; ir (NaCl) 2842 (OCH_3), 1730 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) no M^+, 129 (3), 114 (25), 101 (3), 96 (9), 85 (4), 75 (100), 71 (16), 69 (25), 68 (16), 67 (12), 57 (6), 55 (25).

Reactions with *N*-2-(1,1-Dichloro-3,4-dimethylpentylidene)aniline (12c). The Favorskii rearrangement of **12c** afforded a mixture of cis and trans α,β-unsaturated imidate **16c** and **18c**. Preparative gas chromatography transformed **16c** partially into the trans derivative **18c**; no trace of β,γ-unsaturated imino esters was found.

***trans*-Methyl *N*-Phenyl-3,4-dimethyl-2-pentenoimidate (18c):** NMR (CCl_4) 0.92 [d, 6, J = 6.5 Hz, $(CH_3)_2$], 2.20 (m, 1, $CHMe_2$), 1.84 (d, 3, J = 1.5 Hz, CH_3C=), 3.83 (s, 3, OCH_3), 5.45 (m, 1, =CHC=N), 6.5–7.3 ppm (m, 5, C_6H_5); ir (NaCl) 2845 (OCH_3), 1663 (C=N), 1620 (C=C), 1601, 1583, 1494 cm^{-1} (aromatic); mass spectrum *m/e* (rel intensity) 217 (M^+, 93), 216 (16), 202 (56), 186 (20), 174 (53), 171 (10), 170 (21), 159 (15), 144 (16), 143 (13), 142 (18), 134 (13), 131 (11), 130 (13), 125 (96), 124 (49), 119 (42), 117 (15), 111 (17), 110 (8), 109 (16), 104 (12), 93 (62), 91 (49), 81 (18), 77 (100), 73 (10), 67 (28), 66 (20), 65 (19), 55 (51), 53 (17), 51 (44).

***cis*-Methyl *N*-Phenyl-3,4-dimethyl-2-pentenoimidate (16c):** NMR (CCl_4) 0.90 [d, 6, J = 6 Hz, $(CH_3)_2$], 1.58 (d, 3, J = 1.5 Hz, CH_3C=), 5.4 (m, 1, CH=C), 3.79 (s, 3, OCH_3), 6.4–7.4 ppm (m, 5, C_6H_5); ir (NaCl) 2845 (OCH_3), 1663 (C=N), 1620 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity 217 (M^+, 54), 216 (15), 125 (100), 109 (20), 93 (20), 77 (42), 67 (13), 55 (20), 51 (20).

***cis*-Methyl 3,4-dimethyl-2-pentenoate (36c) and *trans*-methyl 3,4-dimethyl-2-pentenoate (37c)** were obtained by acidic hydrolysis of **16c** and **18c** and were described previously.[14]

***N*-2-(1,1-Dimethoxy-3,4-dimethylpentylidene)aniline (14c):** mass spectrum *m/e* (rel intensity) 249 (M^+, 1), 217 (2), 207 (4), 174 (31), 172 (6), 104 (18), 93 (5), 87 (100), 77 (14), 75 (19), 71 (5), 69 (4), 55 (17), 51 (5), 43 (12) (GC–MS coupling). Acidic hydrolysis gave **35c**.

1,1-Dimethoxy-3,4-dimethyl-2-pentanone (35c); NMR (CCl_4) 0.90 [d, 6, J = 6 Hz, $(CH_3)_2$], 1.90 (m, 1, $CHMe_2$), 0.95 (d, 3, J = 7 Hz, CH_3CCO), 3.36 and 3.38 (2 s, 6, 2 OCH_3), 4.27 [s, 1, $CH(OMe)_2$], 2.77 ppm (quintet, 1, J = 7 Hz, CHCO); ir (NaCl) 2840 (OCH_3), 1730 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) no M^+, 143 (0.5), 100 (1), 87 (2), 83 (1), 75 (100), 71 (2), 55 (2).

***N*-2-(1,3-Dimethoxy-3,4-dimethylpentylidene)aniline (17c):** mass spectrum *m/e* (rel intensity) 249 (M^+, 52), 217 (54), 202 (50), 174 (100), 117 (41), 104 (56), 101 (51), 99 (62), 93 (32), 77 (73), 75 (75), 69 (33), 51 (26). GC–MS coupling revealed the presence of a small amount of the intermediate ***N*-2-(1-chloro-3-methoxy-3,4-dimethylpentylidene)aniline (22c,** R_1 = *i*-Pr; R_2 = CH_3): mass spectrum *m/e* (rel intensity) 253/255 (M^+, 1), 210/212 (3), 152/154 (6), 117 (29), 101 (100), 77 (20), 69 (23), 51 (6). Compound **17c** was hydrolyzed to **10** (R_1 = *i*-Pr; R_2 = CH_3).[14]

1,3-Dimethoxy-3,4-dimethyl-2-pentanone (40c): NMR (CCl_4) 0.78 (d, 3, J = 7 Hz, CH_3CCCO), 0.91 (d, 3, J = 7 Hz, CH_3CCCO), 1.14 (s, 3, CH_3CCO), 3.19 (s, 3, CH_3OCMe), 3.34 (s, 3, OCH_3), 4.18 (s, 2, OCH_2), 2 ppm (m, 1, $CHMe_2$); ir (NaCl) 2830 (OCH_3), 1738 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) 174 (M^+, 0.4), 131 (0.5), 129 (2), 101 (100), 69 (72), 59 (8), 55 (4), 43 (14).

Reactions with *N*-1-(2,2-Dichloro-1-cyclohexylethylidene)aniline (12d). The Favorskii-type rearrangement of **12d** (2 *N*/4 equiv NaOMe–MeOH) gave rise to 28% imidate, which consisted of 16% α,β- and 12% β,γ-unsaturated imidate, respectively methyl *N*-phenylcyclohexylideneacetoimidate (**16d**) and methyl *N*-phenyl-1′-cyclohexenylacetoimidate (VPC analysis). The structure was further proved by hydrolysis to methyl cyclohexylideneacetate (**36d**) and methyl 1′-cyclohexenylacetate, which were compared with authentic material.[14]

Methyl *N*-Phenylcyclohexylideneacetoimidate (16d): NMR (CCl_4) 1.2–2.5 [m, 10, $(CH_2)_5$], 5.3 (m, 1, =CHC=N), 6.3–7.4 (m, 5, C_6H_5), 3.76 ppm (s, 3, OCH_3); ir (NaCl) 2842 (OCH_3), 1671 (C=N), 1625 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity) 229 (M^+, 100), 228 (50), 214 (44), 200 (16), 199 (62), 198 (62), 197 (29), 196 (69), 195 (37), 187 (19), 186 (19), 184 (44), 182 (12), 181 (12), 180 (62), 170 (16), 156 (19), 134 (29), 119 (62), 118 (37), 104 (16), 93 (75), 91 (25), 81 (25), 79 (25), 77 (94), 66 (25), 65 (19), 51 (37).

Methyl *N*-Phenyl-1′-cyclohexenylacetoimidate: NMR (CCl_4) 1.2–2.5 [m, 8, $(CH_2)_4$], 5.3 (m, 1, CH=), 6.3–7.4 (m, 5, C_6H_5), 3.76 (s, 3, OCH_3), 2.75 ppm (s broadened, 2, CH_2C=N); mass spectrum *m/e* (rel intensity) 229 (M^+, 86), 228 (40), 214 (29), 134 (53), 119 (100), 77 (24).

***N*-2-(2,2-Dimethoxy-1-cyclohexylethylidene)aniline (14d)** decomposed immediately after preparative GLC to a tarry material. Compound **14d** was identified by GC–MS coupling and by acidic hydrolysis to 1-cyclohexyl-2,2-dimethoxyethanone (**35d**): mass spectrum *m/e* (rel intensity) of **14d** 261 (M^+, 4), 186 (100), 104 (79), 83 (9), 77 (39), 75 (32), 55 (32), 51 (11).

1-Cyclohexyl-2,2-dimethoxyethanone (35d). This compound has been described in one of our previous papers.[17]

***N*-1-[1-(1′-Methoxy)cyclohexyl-2-methoxyethylidene]aniline (17d).** The same remarks were valid as given for **14d:** mass spectrum *m/e* (rel intensity) 261 (M^+, 1.5), 229 (31), 214 (17), 184 (100), 158 (8), 113 (15), 104 (18), 81 (21), 77 (46), 55 (8), 53 (14), 51 (20). Acidic hydrolysis afforded **40d.**

1-(1′-Methoxy)cyclohexyl-2-methoxyethanone (40d): NMR (CCl_4) 1.2–1.8 [m, 10, $(CH_2)_5$], 3.16 (s, 3, OCH_3), 3.34 (s, 3, CH_2OCH_3), 4.21 ppm (s, 2, CH_2); ir (NaCl) 2835 (OCH_3), 1735 cm^{-1} (C=O); mass spectrum *m/e* (rel intensity) no M^+, 113 (100), 81 (58), 71 (10), 67 (5), 55 (10), 53 (5), 45 (52), 41 (13). GC–MS coupling revealed the presence of a small amount of 1-(1′-methoxy)cyclohexyl-2-chloroethanone, which was identified by comparison with authentic material.[14]

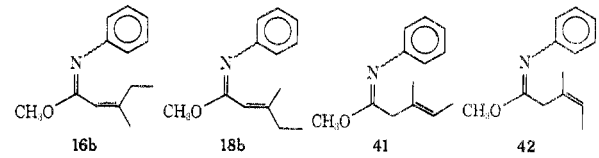
Acknowledgments. N. De Kimpe is indebted to the Belgian "Nationaal Fonds voor Wetenschappelijk Onderzoek" for an aspirant fellowship. The authors wish to thank Professor M. Anteunis and Mr. G. Verhegge for recording the 300-MHz spectra. The authors acknowledge the assistance of Mr. J. De Laet in performing the mass spectra and GC–MS couplings. We are grateful to the "Nationaal Fonds voor Wetenschappelijk Onderzoek", the "Fonds voor Kollektief Fundamenteel Onderzoek", the "Instituut tot Aanmoediging van het Wetenschappelijk Onderzoek in Nijverheid en Landbouw", and the Ministry of Scientific Research and Programmation for financial support to the laboratory.

Registry No.—**11a,** 54884-65-0; **11b,** 54884-66-1; **11c,** 56829-89-1; **11d,** 54913-00-7; **11e,** 54884-70-7; **11f,** 54884-68-3; **11g,** 54884-69-4; **12a,** 56829-90-4; **12b,** 56829-91-5; **12c,** 56829-92-6; **12d,** 56829-93-7; **13a,** 54884-71-8; **14a,** 56829-94-8; **14b,** 56829-95-9; **14c,** 56829-96-0; **14d,** 56829-97-1; **15a,** 54884-78-5; **15′a,** 56829-98-2; **15b,** 54884-79-6; **15′b,** 56830-26-3; **15c,** 54884-80-9; **15′c,** 56829-99-3; **15′d,** 56830-00-3; **15′g,** 56830-01-4; **16a,** 56830-02-5; **16b,** 56830-03-6; **16c,** 56830-04-7; **16d,** 56830-05-8; **17a,** 56830-06-9; **17b,** 56830-07-0; **17c,** 56830-08-1; **17d,** 56830-09-2; **18b,** 56830-10-5; **18c,** 56830-11-6; **22c,** 56830-12-7; **34f,** 6344-11-2; **34g,** 6956-55-4; **35a,** 56830-13-8; **35b,** 56830-14-9; **35c,** 56830-15-0; **39f,** 38693-91-3; **39g,** 7367-81-9; **40a,** 56830-16-1; **40b,** 56830-17-2; **40c,** 56830-18-3; **40d,** 56830-21-8; **41,** 56830-19-4; **42,** 56830-20-7; sodium methoxide, 124-41-4; sodium ethoxide, 141-52-6; *trans* ethyl *N*-phenyl-4-methyl-2-pentenoimidate, 56830-22-9; 1,1-diethoxy-4-methyl-2-pentanone, 56830-23-0; *cis* ethyl 4-methyl-2-pentenoate, 15790-85-9; *trans* ethyl 4-methyl-2-pentenoate, 15790-86-0; methyl 3-methoxyoctanoate, 56830-24-1; methyl 3-methoxy-3-methylbutanoate, 56830-25-2; methyl *N*-phenyl-1′-cyclohexenylacetoimidate, 56868-51-0.

References and Notes

(1) Part IV: N. De Kimpe and N. Schamp, *Bull. Soc. Chim. Belg.*, **84,** 235 (1975).
(2) Presented in part at the International Symposium on Nucleophilic Substitution, Pocono Manor, Pa., 1975, Abstract 11A.
(3) Part of the Ph.D. thesis of N. De Kimpe.
(4) A. S. Kende, *Org. React.*, **11,** 267 (1960).
(5) A. A. Akhrem, T. K. Ustynyuk, and Yu. A. Titov, *Russ. Chem. Rev.*, **39,** 732 (1970).
(6) R. Loftfield, *J. Am. Chem. Soc.*, **72,** 633 (1950).
(7) R. Loftfield, *J. Am. Chem. Soc.*, **73,** 4707 (1951).
(8) B. Tchoubar and O. Sackur, *C. R. Acad. Sci.*, **208,** 1020 (1939).
(9) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N.Y., 1965.
(10) C. Rappe, L. Knutsson, N. J. Turro, and R. Gagosian, *J. Am. Chem. Soc.*, **92,** 2032 (1970).
(11) F. Bordwell and M. Carlson, *J. Am. Chem. Soc.*, **91,** 3951 (1969).
(12) F. Bordwell, M. Carlson, and A. Knipe, *J. Am. Chem. Soc.*, **91,** 3949 (1969).
(13) N. Schamp and W. Coppens, *Tetrahedron Lett.*, 2697 (1967).

(14) N. Schamp, N. De Kimpe, and W. Coppens, *Tetrahedron*, **31**, 2081 (1975).
(15) N. De Kimpe, N. Schamp, and W. Coppens, *Bull. Soc. Chim. Belg.*, **84**, 227 (1975).
(16) N. De Kimpe and N. Schamp, *Tetrahedron Lett.*, 3779 (1974).
(17) N. De Kimpe and N. Schamp, *Bull. Soc. Chim. Belg.*, **83**, 507 (1974).
(18) D. Cantacuzène and M. Tordeux, *Tetrahedron Lett.*, 4807 (1971).
(19) R. H. de Wolfe and W. G. Young, *Chem. Rev.*, **56**, 786 (1956).
(20) A. Streitwieser, "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962.
(21) C. Vernon, *J. Chem. Soc.*, **423**, 4462 (1954).
(22) R. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970.
(23) N. Turro, *Acc. Chem. Res.*, **2**, 25 (1969).
(24) H. Quast, E. Schmitt, and R. Frank, *Angew. Chem.*, **83**, 728 (1971).
(25) H. Quast and W. Rissler, *Angew. Chem.*, **85**, 411 (1973).
(26) F. Greene, R. Camp, V. Abegg, and G. Pierson, *Tetrahedron Lett.*, 4091 (1973).
(27) R. Camp and F. Greene, *J. Am. Chem. Soc.*, **90**, 7349 (1968).
(28) D. Sclove, J. Pazos, R. Camp, and F. Greene, *J. Am. Chem. Soc.*, **92**, 7488 (1970).
(29) J. Liebman and A. Greenberg, *J. Org. Chem.*, **39**, 123 (1974).
(30) E. Ullman and W. Fanshawe, *J. Am. Chem. Soc.*, **83**, 2379 (1961).
(31) F. Greene and J. Pazos, *J. Org. Chem.*, **34**, 2269 (1969).
(32) J. Sheehan and I. Lengyel, *J. Am. Chem. Soc.*, **86**, 746 (1964).
(33) W. Adam, J.-C. Liu, and O. Rodriguez, *J. Org. Chem.*, **38**, 2269 (1973).
(34) J. Deyrup and R. Greenwald, *Tetrahedron Lett.*, 5091 (1966).
(35) H. U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1966).
(36) N. Turro, S. Edelson, J. Williams, and T. Darling, *J. Am. Chem. Soc.*, **90**, 1926 (1968).
(37) K. Srinivasan and J. Boyer, *J. Chem. Soc., Chem. Commun.*, 379 (1974).
(38) C. Marvel and F. Hager, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1948, p 248.
(39) J. Johnson and F. Hager, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1948, p 351.
(40) W. Coppens and N. Schamp, *Bull. Soc. Chim. Belg.*, **81**, 643 (1972).
(41) S. O. Lawesson et al., *Recl. Trav. Chim. Pays-Bas*, **83**, 462 (1964).
(42) The NMR spectrum of **13a** (obtained from preparative gas chromatography or distillation in vacuo) showed a complex pattern of methoxy peaks at δ 3.2–3.4 ppm, which immediately collapsed to a single peak on addition of a few drops of 2 *N* HCl; this trituration with acid resulted in the spectrum of the appropriate dimethoxymethyl ketone, i.e., 1,1-dimethoxy-4-methyl-2-pentanone (**34a**), in pure form.
(43) In general cis α,β-unsaturated imidates **15** were converted into a mixture of cis and trans α,β-unsaturated esters **38** and **39**, while trans imidates **15'** were transformed into exclusively trans α,β-unsaturated esters **39**. Contrary to the immediate hydrolysis of dimethoxymethylketimines, the α,β-unsaturated imidates were hydrolyzed in a slower way. In a typical standardized experiment, *trans*-methyl *N*-phenyl-4-methyl-2-pentenoimidate (**15'a**) was dissolved in CCl_4 and treated with excess 2 *N* HCl (in an undegassed and unsealed NMR tube). The emulsion was shaken regularly, followed by NMR measurement of the organic layer. Compound **15'a** showed a half-life period of 105 min at 35°C.
(44) The imidates were most probably existing in the *Z* form (i.e., the one with the aryl group cis with respect to the methoxy group) based on accepted concepts of steric considerations, although a recent paper, concerning *E/Z* isomerism (syn/anti) of saturated imidates, reported that steric influences as well as dipole interactions play a role in the determination of the equilibrium.[45]
(45) C. O. Meese, W. Walter, and M. Berger, *J. Am. Chem. Soc.*, **96**, 2259 (1974).
(46) The mass spectrum of **13a** clearly supports the structure: expulsion of a dimethoxymethyl radical ($CH_3OCH{=}\dot{O}CH_3$) provides the base peak *m/e* 160. Also the dimethoxymethyl cation *m/e* 75 is typical for this compound. Contrary to this observation, the corresponding O analogues, 1,1-dimethoxy-2-alkanones, are characterized by the base peak *m/e* 75 ($CH_3OCH{=}O^+CH_3$)[17].
(47) (a) E. Abderhalden, *Hoppe-Seylers Z. Physiol. Chem.*, **251**, 164 (1938); (b) L. A. Yanovskaya and V. F. Kucherov, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, **7**, 1341 (1964); *Chem. Abstr.*, **61**, 11887 (1964).
(48) All cis *N*-aryl α,β-unsaturated imidates **15** showed the unresolved AB part (NMR, 60 MHz, CCl_4) of the ethylenic protons at δ 5.3–5.6 ppm (**ABX** or $\mathbf{ABX_2}$). Since the structural assignment of **15a** and **15c** was fully established, the correspondance of spectral analysis, especially the typical AB line pattern, allowed us to determine the cis *N*-aryl α,β-unsaturated imidates **15** by analogy.
(49) The δ values of the β-methyl groups allowed us to distinguish cis and trans isomers **16** and **18**. Similar to α,β-unsaturated carbonyl compounds[50,51] the methyl group cis with respect to the carbon–nitrogen double bond in α,β-unsaturated imidates resonated at lower field than when trans, the cis methyl group being deshielded because of the anisotropy of the C=N function.
(50) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed, Pergamon Press, Elmsford N.Y., 1969.
(51) H. Günther,: "NMR Spektroskopie", Georg Thieme Verlag, Stuttgart, 1973.
(52) R. B. Wagner, *J. Am. Chem. Soc.*, **71**, 3214 (1949).
(53) These four isomeric compounds were characterized by their mass spectrum, obtained by GC–MS coupling (Varian 1200, AEI MS 30 OV_1 capillary column 150 m, temperature 80 → 160°C, 0.5°C/min). The observation that β,γ-unsaturated imino esters were more volatile than the α,β-unsaturated isomers and that cis isomers were more volatile than trans isomers allowed us to classify the imino esters as follows (increasing volatility with percent amount in parentheses): **18b** (45%) < **16b** (15%) < **41** (28%) < **42** (12%).



16b 18b 41 42

Solvolytic Rearrangement of Quadricyclyl-7-carbinol[1]

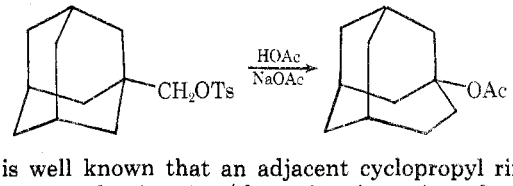
William G. Dauben* and John W. Vinson

Department of Chemistry, University of California, Berkeley, California 94720

Received July 29, 1975

Quadricyclyl-7-carbinol was synthesized from 7-benzyloxymethylnorbornenone via 7-benzyloxynorbornadiene. The triflate ester of the carbinol upon solvolysis in buffered trifluoroethanol rearranged via a cyclopropylethyl carbonium ion pathway. This result indicates that the energy gained by rearrangement from a primary to a secondary carbonium ion to form a quadricyclooctyl system is insufficient to overcome the strain engendered in the new ring system.

Much work has been reported on the solvolysis of strained ring systems,[2] and the usual result has been the formation of less strained ring systems. A problem which has been less thoroughly investigated is the use of carbonium ion rearrangements to incorporate strain into the ring system. Considerable energy can be released when a less stable primary carbonium ion rearranges to the highly stabilized tertiary carbonium ion, and it should be possible to salvage some of this energy in the form of higher skeletal strain. One such case of such energy salvage is found in the solvolysis of 1-adamantylcarbinyl tosylate.[3] In this case, the stabilization energy gained in going to the tertiary carbonium ion outweighs the increased skeletal strain of the homoadamantyl ring system.



It is well known that an adjacent cyclopropyl ring can stabilize a carbonium ion,[4] but a less investigated problem is how early in the process of rearrangement does the assistance of a neighboring group take effect. A compound that