Facile Synthesis of Stable Analogues of 2-Oxocyclobutanecarboxylates: 2-[(Diphenylmethylene)amino]cyclobutenecarboxylates, Derivatives, and Reactions[1]

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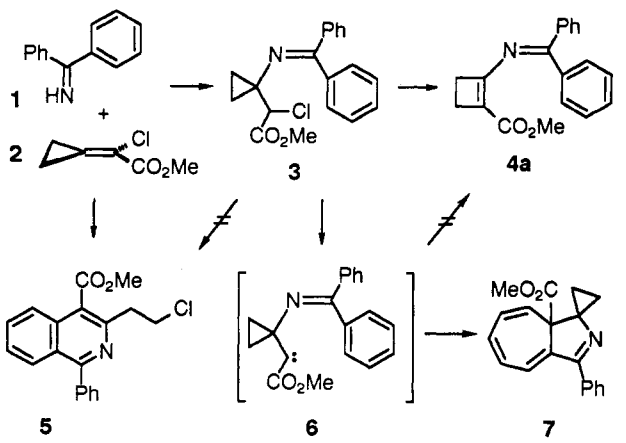
An efficient two-step synthesis of 2-[(diphenylmethylene)amino]cyclobutenecarboxylate (**4a**) and some analogous derivatives from 2-chloro-2-cyclopropylideneacetates **2**, **17**, **22**, and **25** and nonenolizable ketimines, especially diphenylmethyleneamine (DPMA-H), is described. A likely mechanism for the formation of **4a** from the primary Michael adduct **3** of DPMA-H to **2** and its substituted analogues is presented. The unique neighboring group effect of the DPMA moiety to allow formation of an azaspiropentane intermediate and its regioselective rearrangement to cyclobutenamine derivatives is discussed and further exemplified by an extremely facile SET α-chlorination. Compound **4a** and derivatives undergo a thermal ring-opening reaction to the corresponding butadienes with subsequent formation of 1,3-disubstituted 3,4-dihydroisoquinolines **39**. Further transformations of **4a** and some derivatives include transesterification, hydrolysis to methyl 2-oxocyclobutanecarboxylates, and addition of *N*-phenyltriazolinedione.

Recently we have described a new isoquinoline synthesis proceeding via the formal [4 + 2] cycloaddition of an aromatic 1-azadiene, represented by diphenylmethyleneamine (benzophenone imine, DPMA-H, **1**) and the activated Michael acceptor methyl 2-chloro-2-cyclopropylideneacetate (**2**) (Scheme I).[2]

During our investigation of the proposed tandem Michael addition mechanism, the intermediate **3**, i.e. the simple Michael adduct of DPMA-H(**1**) onto **2**,[3] was treated with strong bases under aprotic conditions (e. g. LDA/THF). Instead of the desired isoquinoline **5**, the enolate ion of **3** gave the 2-azaazulene derivative **7**, presumably via the carbene intermediate **6**.[2] Although the formation of the cyclopropylcarbene **6** itself was not a surprise, its efficient internal addition onto the aromatic ring system to give **7** instead of rearranging to cyclobutene **4a** was unexpected.[2]

Nevertheless, we were confident that compound **3**[3] could also act as a precursor for synthetically useful cyclobutenecarboxylates of the type **4**. This compound and its ring-substituted analogues are protected 2-aminocyclobutanecarboxylic acids and appeared as desirable targets for various reasons. They could help to extend recent efforts in the synthesis of small ring amino acids[3,4,5,6] to β-amino acids with four-membered rings. They may also

Scheme I



be considered as enamine derivatives of the notoriously unstable 2-oxocyclobutanecarboxylates. Furthermore they were envisaged as precursors to various biologically active cyclobutane compounds,[7] e.g. the recently described antiviral carbocyclic oxetanocine analogues.[8]

Results and Discussion

As the conversion of **3** to **4a** involves a formal dehydrochlorination, various basic conditions were applied to **3**, most of which gave **7** or complex product mixtures with less than 5% **4a**.[2,6,9] It was therefore proposed that since **4a** is not formed via the carbene **6**, it may arise via the stabilized iminium cation **8**, which in turn may be formed

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(2) Wessjohann, L.; Skattebøl, L.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1990**, 574.

(3) Wessjohann, L.; McGaffin, G.; de Meijere, A. *Synthesis* **1989**, 359.

(4) (a) Wessjohann, L.; Krass, N.; Yu, D.; de Meijere, A. *Chem. Ber.* **1992**, *125*, 867. (b) Krass, N.; Wessjohann, L.; Yu, D.; de Meijere, A. In *Strain and its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; Kluwer Academic Publ.: Dordrecht 1989; NATO-ASI Series C, Vol. 253, p 509.

(5) de Meijere, A.; Wessjohann, L. *Synlett* **1990**, *1*, 20, and refs cited therein.

(6) Wessjohann, L. Ph.D. Dissertation, Univ. Hamburg (FRG) 1990.

(7) (a) Belluš, D.; Ernst, B. *Angew. Chem.* **1988**, *100*, 820; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 797. (b) Adlington, R. M.; Baldwin, J. E.; Jones, R. H.; Murphy, J. A.; Parisi, M. F. *J. Chem. Soc., Chem. Commun.* **1983**, 1479.

(8) (a) Johnson, C. R.; De Jong, R. L. *J. Org. Chem.* **1992**, *57*, 594. (b) Hsiao, C. N.; Hannick, S. M. *Tetrahedron Lett.* **1990**, *31*, 6609.

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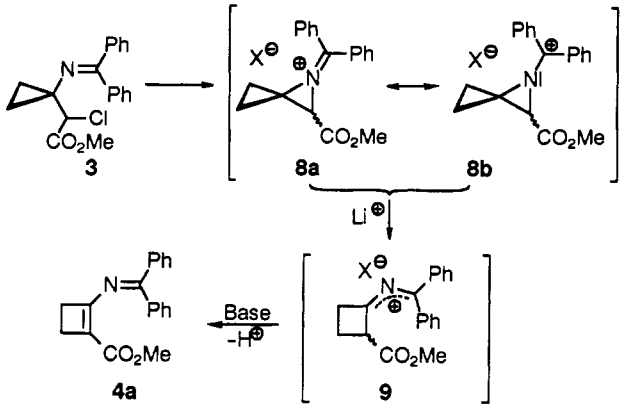
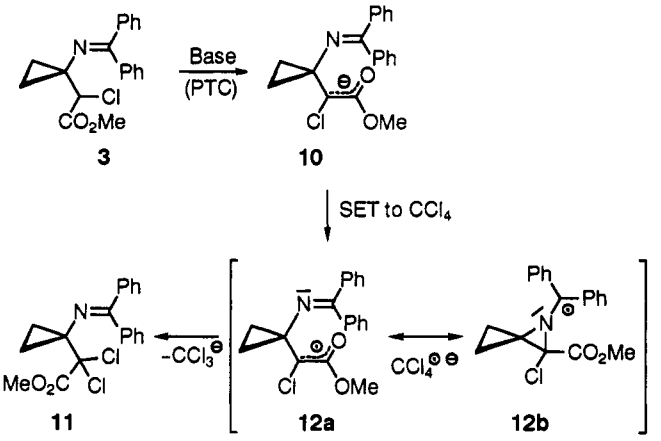
Scheme II



Scheme III



by an intramolecular displacement of chloride (Scheme II). The lithium cation may then serve as a Lewis-acid to catalyze the azaspiropentane to cyclobutanone imine rearrangement.[10]

Lithium iodide is known to catalyze similar reactions, especially the more common oxaspiropentane to cyclobutanone rearrangement.[11,12] Furthermore, the iodide anion may catalyze the S_N1-reaction via a Finkelstein-type process.

Thus, when the adduct **3** was treated with triethylamine and lithium iodide in methanol, cyclobutenecarboxylate **4a** became the major product. Although conversion of **3** reproducibly was more than 93%, the isolated yield was only 65%, apparently due to the long reaction times (7 d, reflux), which led to the formation of a sensitive methanol adduct of **4a**. This adduct partly reforms **4a** on silica gel or upon heating. Although this adduct could be isolated in 14% yield with a purity of about 90%, its exact constitution could not be elucidated with complete certainty. On the basis of its spectral data, it is clearly not the 1,4-adduct of methanol to the acrylic ester moiety in **4a**, but most probably the 1,2-adduct to the C–N double bond.[13]

In the less-polar acetonitrile such undesired adducts are not formed, but prolonged reaction times and higher temperatures (9 d, 82 °C) are required. Complete conversion of starting material was impossible in acetonitrile without accepting some decomposition of the product, which could be isolated in 68% yield. The best yield (73%) was obtained with triethylamine in 2-propanol (7 d, 82 °C). With this sterically more demanding alcohol, no addition product was observed.

The C=N group in methyl 2-[(diphenylmethylene)-amino]cyclobutenecarboxylate **4a** is surprisingly unreactive as compared to other imines[3,4,6] including the starting material **3**. It is not very susceptible to hydrolysis; nevertheless, pretreated silica gel[3] should be used for chromatography.

This unusual stability must be due to the push-pull type resonance with extensive π-delocalization, which also accounts for the intense yellow color and the unexpected magnetic equivalence of the *syn*- and *anti*-phenyl carbons in the ^{13}C NMR spectrum of **4a** at room temperature. The cyclobutyl protons of **4a** in $CDCl_3$ give rise to a singlet at 2.34 ppm in the ^1H NMR spectrum.

The unique neighboring group effect of the DPMA group is not only exerted to formal β-cations or β-anions as in **10**,[9] but apparently also to β-radicals. This becomes evident in the extremely facile chlorination of the anion of **3**, i.e. the carbenoid **10**, with polychlorinated hydrocarbons.[14,15] This reaction is believed to proceed via a single electron transfer (SET) from the anion onto the chlorohydrocarbon followed by abstraction of a chlorine atom from the solvent anion radical to give the chlorinated product.

Accordingly **3**, when treated with 50% sodium hydroxide solution in tetrachloromethane/dichloromethane (3:1) under phase transfer conditions,[15] was converted to the corresponding dichloroacetate **11** in 88% yield in only 20 min. Ring-opening of the assumed intermediate cyclopropylmethyl radical, known to be an extremely fast reaction for simple alkyl-substituted systems,[16] was not observed.[17] In this case the proposed radical is stabilized not only by the neighboring methoxycarbonyl group,[18] but probably even more by the β-effect of the DPMA group, as represented by the resonance structure **12b** (Scheme III). The β-DPMA ester **3** not only reacts much faster and in better yields than comparable compounds without

(9) The enolate anion **10** derived from **3**, especially when lithium is the counterion, proved to be extremely stable, although it is a carbenoid. This stability (e.g. several days in THF/LDA at rt) might stem from the complexation of the counterion by the DPMA nitrogen or even reversible addition of the ester enolate anion onto the C–N double bond to give the six-membered cyclic hemiaminal.

(10) (a) Crandall, J. K.; Conover, W. W. *J. Org. Chem.* **1974**, *39*, 63. (b) Aue, D. H.; Lorens, R. B.; Helwig, G. S. *Tetrahedron Lett.* **1973**, 4795.

(11) Salaün, J. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; John Wiley & Sons, Ltd.: New York 1987; p 809. Cf. also: Gajewsky, J. J.; Oberdier, J. P. *J. Am. Chem. Soc.* **1972**, *94*, 6053.

(12) (a) Erden, I.; de Meijere, A.; Rousseau, G.; Conia, J. M. *Tetrahedron Lett.* **1980**, *21*, 2501. (b) Crandall, J. K.; Conover, W. W. *J. Org. Chem.* **1978**, *43*, 3533. (c) Aue, D. H.; Meshishneck, M. J.; Shellhamer, D. F. *Tetrahedron Lett.* **1973**, 4799.

(13) The formation of 1,2-adducts of imines, at least with nucleophiles like lithium dimethylcuprate and butyllithium, is well documented. Cf. (a) Böhme, H.; Plappert, P. *Chem. Ber.* **1975**, *108*, 3574. (b) Emling, B. L.; Horvath, R. J.; Saraceno, A. J.; Ellermeyer, E. F.; Haile, L.; Hudac, L. D. *J. Org. Chem.* **1959**, *24*, 657. (c) Gilman, H.; Kirby, J. E. *J. Am. Chem. Soc.* **1933**, *55*, 1265. (d) Giller, K. Ph.D. Dissertation, Univ. Hamburg (FRG) 1991.

(14) (a) Meyers, C. Y.; Kolb, V. M. *J. Org. Chem.* **1978**, *43*, 1985. (b) Meyers, C. Y.; Matthews, W. S.; Ho, L. L.; Kolb, V. M.; Parady, T. E. In *Catalysis in Organic Syntheses*; Smith, G. V., Ed.; Academic Press: New York, 1977; p 197.

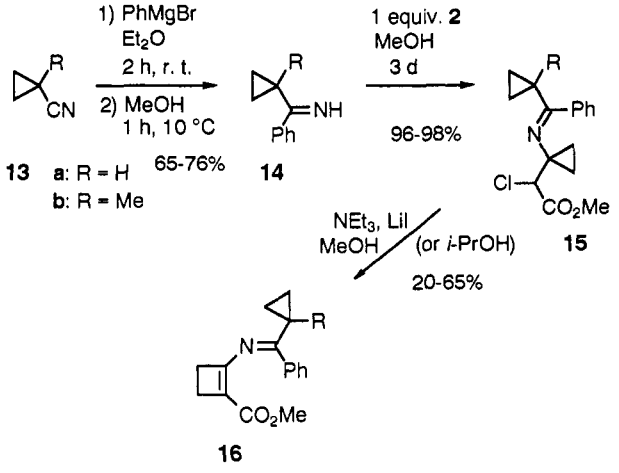
(15) Lauritzen, S. E.; Rømming, C.; Skattebøl, L. *Acta Chem. Scand., Ser. B* **1981**, *35*, 263.

(16) (a) Maillard, B; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. (b) Newcomb, M.; Glenn, A. G. *Ibid.* **1989**, *111*, 275, and refs cited therein.

(17) It can not be ruled out that a rapid second SET takes place and then the cyclopropyl-stabilized α-methoxycarbonyl cation is trapped by chloride. Cf. Schmittel, M.; Röck, M. *Chem. Ber.* **1992**, *125*, 1611.

(18) Cf. Suckling, C. J. In *Strain and its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; Kluwer Publ.: Dordrecht, 1989; NATO ASI Series C, Vol. 273, p 177.

Scheme IV

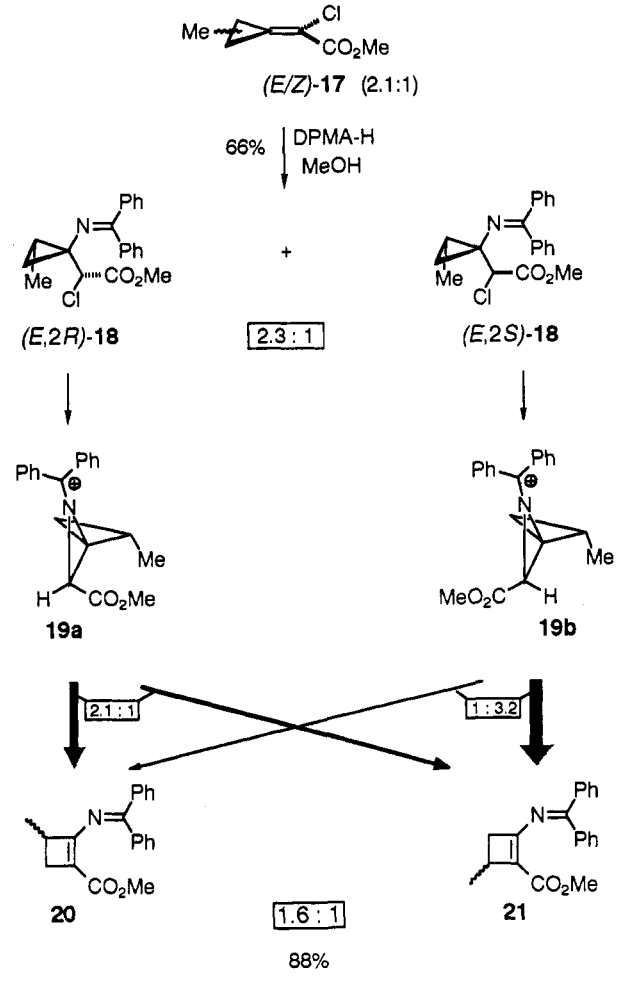


the DPMA group (e.g. 2-phenylacetic ester gives 21% yield after 48 h[16]), but also reacts in solvents usually inefficient as chlorine donors, e.g. refluxing dichloromethane, which gives 52% of **11** in 45 min.[19]

The scope of the (methyleneamino)cyclopropyl-α-chloroacetate to 2-(methyleneamino)cyclobutenecarboxylate transformation was widened in two ways. First, one of the phenyl groups in DPMA-H was replaced by a cyclopropyl group, since the latter can stabilize a positive charge on the adjacent carbon atom in a cationic intermediate of type **8** and **9** as well as a phenyl group.[20] Cyclopropyl-substituted imines **14a,b** can be prepared from cyclopropanecarbonitrile (**13a**) and 1-methylcyclopropanecarbonitrile (**13b**), respectively, by addition of phenylmagnesium bromide.[21] Michael addition of **14a,b** to compound **2** occurs readily,[22a] and the adducts **15a,b**, when treated with triethylamine/lithium iodide in methanol or 2-propanol, gave the corresponding cyclobutenecarboxylates **16a,b**, albeit in lower yields than compound **4a** with the DPMA substituent (Scheme IV). Obviously, further reactions involving the cyclopropyl imine moiety can occur in **15** and **16**. The less sterically protected **15a** and **16a**[13d,22a] showed reactions attributed to methanol addition, hydrolysis, and cyclopropylmethyleneamine to dihydropyrrole rearrangement. The importance of a sterically protected imino group was confirmed by the observation that the benzaldimine adduct of **2**[22b] could not be rearranged to the corresponding cyclobutenecarboxylate.

Secondly, alterations were made on the rearranging cyclopropyl ring in the Michael adducts of DPMA-H (**1**) (Scheme V). Methyl (2′-methylcyclopropylidene)acetates **17**,[23] which consisted of two diastereomers, react with DPMA-H to give the two (*E*)-diastereomers (*E*,2-*rac*)-**18** exclusively (2.3:1), as shown by NOE measurements and correlation to similar compounds.[3,5,6,13d] The rearrangement of (*E*,2-*rac*)-**18** proceeded as expected, much faster

Scheme V



and in higher yield (88%) than that of the unsubstituted derivative **3**. The two possible regioisomers of **20** and **21** were formed in a ratio of 1.6:1. The mixture of regioisomers **20** and **21** could not be fully separated, but was only enriched up to a ratio of approximately 3:1. The assignment of the isomers by NMR spectroscopy proved difficult and required CH-correlation and COLOC spectroscopy (C–H long-range coupling). The similarity of the ratios (*E*,2*R*)-**18** to (*E*,2*S*)-**18** and **20** to **21** (2.3:1 and 1.6:1, respectively) suggests that each regioisomer is preferentially formed from one corresponding diastereomer. This could be verified with small amounts of the separated isomers of **18**. Thus (*E*,2*R*)-**18** gave **20** with a preference of 2.1:1 and (*E*,2*S*)-**18** yielded **21** with a preference of 3.2:1 (Scheme V).

Apparently the more highly substituted methine carbon of the cyclopropyl group migrates preferentially (3.2 vs 2.1) as was previously observed for the analogous oxaspiropentane rearrangements.[12] On the other hand, the steric or stereoelectronic influence of the ester group appears to be slightly more important so that **19a** preferentially rearranges to **20** (2.1:1) with migration of the less-substituted carbon. Since neither the absolute configuration at C-2 nor the identity of the diastereomers is known, it is unclear whether the ester group exhibits a *syn*- or an *anti*-effect on the migration (a positive *anti*-effect is arbitrarily depicted for **19a,b** in Scheme V), nor do we know whether the configuration at C-2′ in **18** is retained during migration, although this is very likely (*vide infra*). Nevertheless, the dominating influence of the

(19) In cold dichloromethane, however, the reaction becomes so slow that hydrolysis of the ester (cf. ref 15) and/or DPMA group predominate. Analytical grade solvent was used to avoid impurities of tri- and tetrachloromethane. These may, however, be formed during the reaction: Jonczyk, A.; Balcerzak, P. *Tetrahedron Lett.* **1989**, *30*, 4697.

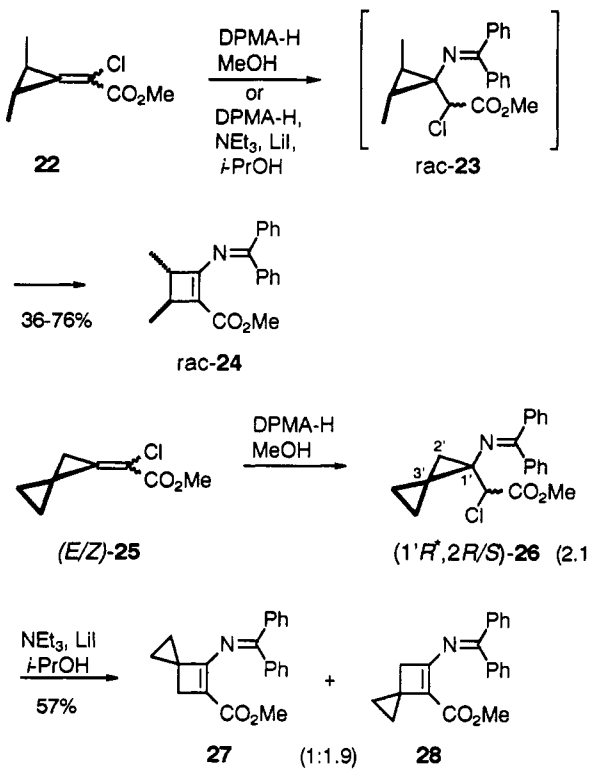
(20) A cyclopropyl group is well known to stabilize an adjacent positive charge. Cf. review: de Meijere, A. *Angew. Chem.* **1979**, *91*, 867. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 809, and refs cited therein.

(21) (a) Cloke, J. B. *J. Am. Chem. Soc.* **1929**, *51*, 1174. (b) Gothis, D.; Cloke, J. B. *Ibid.* **1934**, *56*, 2710. (c) Stevens, R. V.; Ellis, M. C.; Wentland, M. P. *Ibid.* **1968**, *90*, 5576.

(22) (a) Giller, K.; Baird, M. S.; de Meijere, A. *Synlett* **1992**, 524. (b) Schreiber, J. Ph.D. Dissertation, Univ. Hamburg (FRG) 1992.

(23) Liese, T.; Teichmann, S.; de Meijere, A. *Synthesis* **1988**, 25.

Scheme VI

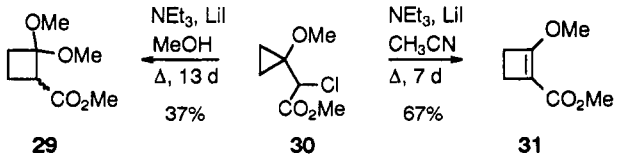


stereochemistry at C-2 on the migration shows that the amount of positive charge developed during reaction on C-2 is small, as proposed by Aue et al.[12c] for the oxaspiropentane rearrangement.

When treated with DPMA-H (1) in methanol, methyl 2-(*trans*-2',3'-dimethylcyclopropylidene)-2-chloroacetate (**22**)[23] yields the *trans*-2,3-disubstituted cyclobutenecarboxylate *rac*-**24** directly (36%), even without added lithium iodide; the yield, however, is much better (76%) when **22** is reacted with DPMA-H in 2-propanol in the presence of triethylamine and lithium iodide (Scheme VI). The two diastereomeric adducts (2-*rac*)-**23** could not be isolated, but were detected in the mixture during the reaction in low concentration (up to 21%) by their typical signals in the ^{1}H NMR spectrum. The *trans*-orientation of the methyl groups in **22** is retained in the product *rac*-**24**. This is in accord with an azaspiropentane intermediate of type **8**, with a delocalized positive charge, which would not allow for an inversion at the migrating carbon. This retention of the configuration in the DPMA-substituted systems like **23** contrasts observations of Crandall et al.[12b] in the corresponding oxaspiropentane rearrangements which give *cis*/*trans* mixtures of 2,3-dimethylcyclobutanones. Some of Crandall's systems did allow for weak neighboring group effects by an ester group, but not for an efficient charge delocalization, as exerted by the DPMA-substituent in intermediates of type **8**.

It is particularly interesting that even the highly strained spiropentane derivative (1'*R**,2*R*/*S*)-**26** (ratio 2.1:1) gives the two regioisomeric spiro[2.3]hexenecarboxylates **27** and **28** (ratio 1:1.9) in an astonishing total yield of 57% (Scheme VI). The preferential migration of the substituted carbon is in accord with observations in the oxaspiropentane series,[11,12] but at first sight contradictory to the results obtained with the methyl derivative (*E*,2*R*/*S*)-**18**. However, since the identity of the two diastereomers of (1'*R**,2*R*/*S*)-**26** is not known, it would be speculation to discuss a different migratory preference for the cyclopropyl group.[20] It is noteworthy that the migrating cyclopropyl residue does not ring-open, which would be an extremely fast and facile process if a significant amount of positive charge would develop on the cyclopropyl spirocarbon in the intermediate.[11,18] This totally excludes the existence of a long-lived cationic center at the migrating carbon in contrast to the suggestion of Crandall et al.[12] for the oxaspiropentane system and again demonstrates the high probability for the proposed intermediate of type **8** with its efficient charge delocalization by the DPMA group.

Scheme VII



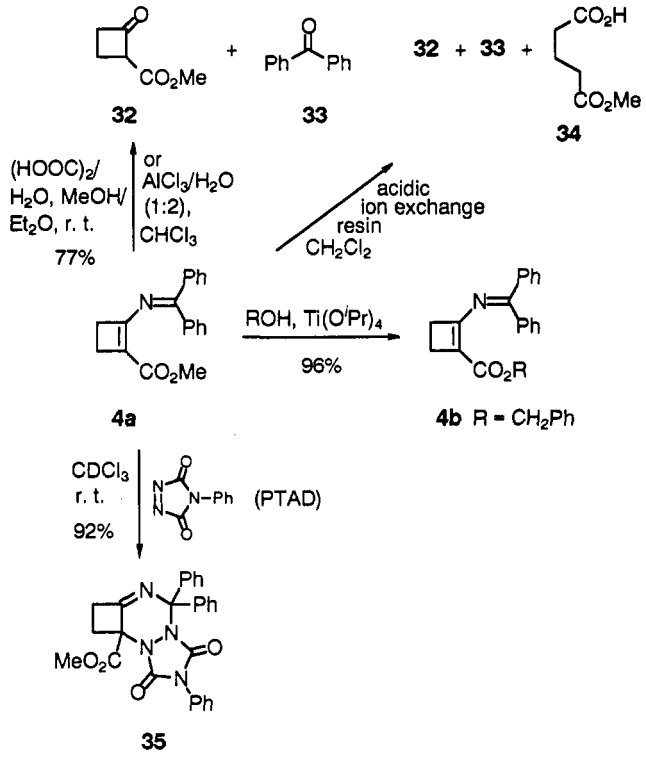
Eventually, the Michael adduct **30**, easily obtained from **2** and methanol under basic conditions,[23] was treated with triethylamine/lithium iodide. In refluxing methanol **30** slowly (13 d) rearranged to give the dimethyl acetal **29** in 37% yield.[24] In refluxing acetonitrile the reaction of **30** proceeded faster and gave 2-methoxycyclobut-1-enecarboxylate **31** in 67% yield without the possibility of subsequent acetal formation (Scheme VII). This process is likely to proceed via a cationic intermediate by a mechanism more closely related to that observed for oxaspiropentanes.[12] In this case a neighboring group participation of the carboxylate may be competitive with that of the methoxy substituent. A butadiene was isolated as a byproduct in 14% yield, but not fully characterized.

Due to its unusual stability towards nucleophiles, 2-DPMA-cyclobutenecarboxylate **4a** can easily be transesterified under catalysis of titanium tetraisopropoxide,[25] e.g. to the benzyl ester **4b** in 96% yield (Scheme VIII). Hydrolysis of **4a** could not be achieved under neutral conditions, e.g. with phosphate buffer and ultrasound promotion. However, under acidic conditions [oxalic acid/water in methanol/ether or aluminum trichloride/water (1:2 equiv) in chloroform] the known methyl 2-oxocyclobutane-1-carboxylate (**32**) is formed in less then 2 h (Scheme VIII). Although the conversion of **4a** to **32** appears to be quantitative, a retro-Dieckmann reaction of **32** to give monomethyl glutarate (**34**) may occur, if the reaction is not monitored carefully. With an acidic ion-exchange resin (e.g. wet Lewatit SPC 108) in methylene chloride, monoester **34** was formed during hydrolysis of **4a** (ratio **34**/**32** 1.6:1). Timely ether extraction of the reaction mixture and rapid drying gives **32** together with benzophenone (**33**) in 77% yield, which is better than that of known procedures.[24] On standing in moist air or upon attempted chromatography, fast ring-opening of **32** to monomethyl glutarate (**34**) occurred. The obvious separation of **32** from benzophenone by vacuum distillation can only be applied when operating on a larger scale.

(24) 2,2-Dialkoxycyclobutanecarboxylates can more easily be obtained from ketene acetals and acrylates: (a) Amice, Ph.; Conia, J. M. *Bull. Soc. Chim. Fr.* **1974**, 1015. (b) Amice, Ph.; Conia, J. M. *Tetrahedron Lett.* **1974**, 479. (c) Snider, B. B.; Roush, D. M.; Rodini, D. J.; Gonzalez, D.; Spindell, D. *J. Org. Chem.* **1980**, *45*, 2773. (d) Ficini, J.; Krief, A. *Tetrahedron Lett.* **1970**, 885. (e) Ficini, J.; Dureault, A. *Tetrahedron Lett.* **1977**, 809.

(25) Cf. Seebach, D.; Hungerbühler, E.; Naef, R.; Schnurrenberger, P.; Weidmann, B.; Züger, M. *Synthesis* **1982**, 138.

Scheme VIII



4-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) reacts with **4a** at room temperature in a [2 + 4]-cycloaddition to yield **35** (92%).

Compounds of type **36** (e.g. **4a**) are not only enamines derived from cyclobutanones, but also cyclobutenes which should be capable of opening up to the corresponding butadienes.[26] When compounds **4a**, **16a,b**, and **21** were subjected to flash vacuum pyrolysis (FVP, $p \sim 10^{-4}$ Torr, 500 °C, ca. 15 ms), the expected dihydroisoquinoline derivatives **39** were formed (Scheme IX). **39a** and **39c** were obtained in 68% yield; the more sensitive **16a** still gave 50% of the corresponding dihydroisoquinoline derivative **39b**. The DPMA-methylcyclobutene **21** yielded 53% of the (*Z*)-crotonate-substituted isoquinoline **39d**.

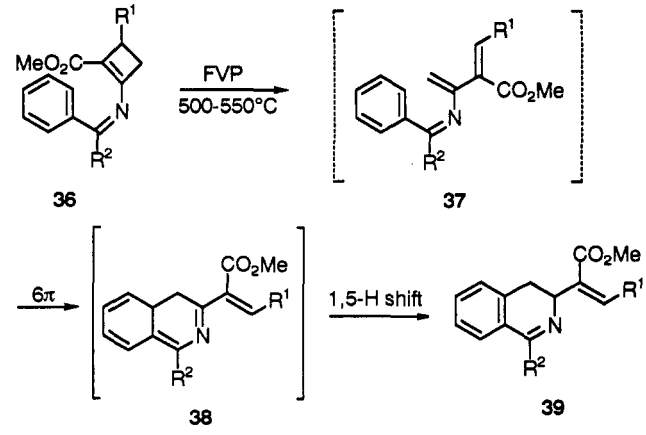
The reactions of compounds **36** probably proceed via the expected ring-opened products **37**, which subsequently undergo 6π-electrocyclization followed by 1,5-H shift as known for 3-azatrienes of type **37**.[27] A very unstable byproduct in the reaction of **4a** shows spectroscopic features in full accordance with the intermediate **37a**, but purification to give analytically pure material proved to be impossible. Compound **37a** is the main monomeric product upon FVP at 400 °C. It dimerizes upon standing and reacts with methyl acrylate to give the expected Diels–Alder products.[13d]

Conclusions

The reported variant of an azaspiropentane to cyclobutanone imine rearrangement appears to be synthetically useful, as it leads to unusually substituted cyclobutenes and cyclobutanones, butadienes, and dihydroisoquinolines. The [(diphenylmethylene)amino]cyclobutenecarboxylates of type **4** are 2-azabutadienes and as such can be applied in [4 + 2] cycloadditions.

Further improvement on the synthesis of compounds **4** and derivatives with shorter reaction times and higher yields are conceivable by the introduction of more nucleophilic, i.e. donor-substituted DPMA-H derivatives.[5,6,22] These may also help to elucidate the proposed mechanism by further enhancing the stability of cationic intermediates. Applications include the syntheses of new derivatives of isoquinolines and 2-azaazulenes.[2,22] Small ring amino acids derived from compounds of type **4** are also under current investigation.

Scheme IX



R¹	R²	Starting Material	Product	Yield (%)
H	Phenyl	**4a**	**39a**	68
H	Cyclopropyl	**16a**	**39b**	50
H	1-Methylcyclopropyl	**16b**	**39c**	68
Me	Phenyl	**21**	**39d**	53

Experimental Section

General Methods. NMR chemical shifts were measured in $CDCl_3$ or C_6D_6 (standards: $\delta = 0$ for TMS, $\delta = 7.26$ for $CHCl_3$, $\delta = 77.0$ for $CDCl_3$, $\delta = 7.16$ for C_6HD_5, $\delta = 128.0$ for C_6D_6). Elemental analyses were performed by the Mikroanalytisches Labor der Universität Hamburg. The preparation of starting materials **1–3**, **17**, and **22** has been described previously,[3,5,23,28] and that of ketimines **14a,b** in the literature.[21] For chromatographic separations, Merck Kieselgel 60 (70–230 mesh) dried at 100 °C/0.1 Torr and treated with triethylamine (1 vol%) was used. Dry ether was used as an eluent; all eluents contained 1 vol % of triethylamine if not stated otherwise. Abbreviations used: PE = petroleum ether, bp 30–50 °C.

Methyl 2-[(Diphenylmethylene)amino]cyclobutenecarboxylate (4a). (A) Crude **3** (0.85 g, 2.6 mmol), 20 mg (0.15 mmol) of dried LiI, and 0.5 mL of dry triethylamine in 20 mL of dry methanol were refluxed under N_2 until the starting material was consumed (approximately 7 d). Column chromatography (silica gel, ether/PE 1:8) gave fraction I ($R_f = 0.31$ in ether/PE 1:4), containing 120 mg (14%) of a methanol adduct onto **4a**, which decomposes readily, e.g., on wet silica gel, to give **4a**: mp 89 °C; ^{1}H NMR (250 MHz, $CDCl_3$) 2.00 (t, 2 H), 2.35 (t, 2 H), 3.24 (s, 3 H, OCH_3), 3.73 (s, 3 H, CO_2CH_3), 7.14–7.33 (m, 6 H, H_{Ph}), 7.55–7.60 (m, 4 H, H_{Ph}); ^{13}C NMR (62.9 MHz, $CDCl_3$) 23.6 (t, CH_2), 29.8 (t, CH_2), 49.5 (q, OCH_3*), 50.4 (q, CO_2CH_3*), 90.3 (s), 98.7 (s), 126.0 (d, 4 C, *m*-C_{Ph}*), 127.7 (d, 2 C, *p*-C_{Ph}), 128.6 (d, 4 C, *o*-C_{Ph}*), 143.3 (s, 2 C, *i*-C_{Ph}), 159.0 (s), 164.8 (s, C=O); IR

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(neat) 3384, 2938, 1632 cm^{-1}; MS (70 eV) 323 (M^+, 0.2), 292 (M^+ – OCH_3, 3), 291 (M^+ – CH_3OH), 197 ($Ph_2C{=}NOH^+$, 100); MS (CI, NH_3) *m/z* 324 (MH^+, 6), 292 (M^+ – OCH_3, 68), 197 ($Ph_2C{=}NOH^+$, 100). Fraction **II** (R_f = 0.24 in ether/PE 1:4): 490 mg (65%) of **4a**, yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) 2.34 (s, 4 H, 2 CH_2), 3.63 (s, 3 H, OCH_3), 7.36–7.54 (m, 10 H, H_{Ph}); ^{1}H NMR (300 MHz, C_6D_6) 2.20 (t, J = 3.4 Hz, 2 H, *c*-BuCH_2), 2.33 (t, J = 3.4 Hz, 2 H, *c*-BuCH_2), 3.40 (s, 3 H, OCH_3), 7.05–7.18 (m, 6 H, *m*-, *p*-H_{Ph}), 7.50–7.55 (m, 4 H, *o*-H_{Ph}); ^{13}C NMR (75.4 MHz, $CDCl_3$) 23.2 (t), 30.8 (t), 50.8 (q, OCH_3), 113.3 (s, C-1*), 128.1 (d, 4 C, *m*-C_{Ph}*1), 128.9 (d, 4 C, *o*-C_{Ph}*1), 130.5 (d, 2 C, *p*-C_{Ph}), 137.3 (s, 2 C, *i*-C_{Ph}), 158.4 (s, C-2*), 163.1 (s, C=O), 168.7 (s, C=N); ^{13}C NMR (75.4 MHz, C_6D_6) 23.8 (t), 31.1 (t), 50.3 (q, OCH_3), 113.1 (s, C-1*), 127.7 (d, 2 C, C_{Ph}), 128.0 (d, 2 C, C_{Ph}), 128.3 (d, 4 C, C_{Ph}), 129.2 (d, 2 C, C_{Ph}), 130.4 (d, C_{Ph}), 137.9 (s, 2 C, *i*-C_{Ph}), 158.3 (s, C-2*), 162.7 (s, C=O), 168.1 (s, C=N); IR (neat) 3057, 1702, 1640 cm^{-1}; MS (70 eV) *m/z* 291 (M^+, 63), 276 (M^+ – CH_3, 11), 260 (M^+ – OCH_3, 11), 232 (M^+ – CO_2CH_3, 26), 231 (25), 230 (37), 165 (100). Anal. Calcd for $C_{19}H_{17}NO_2$ (291.35): C, 78.33; H, 5.88; N, 4.81. Found: C, 78.52; H, 5.95; N, 4.80.

(B) A mixture of 1.00 g (3.0 mmol) of **3**, 50 mg (0.37 mmol) of dried LiI, and 1.5 mL of dry triethylamine in 20 mL of dry acetonitrile was refluxed until the starting material had been consumed (approximately 9 d). Pentane and ether (25 mL each) were added, and the precipitated salts were filtered off. Column chromatography (silica gel, ether/PE 1:8) yielded 590 mg (68%) of **4a**.

(C) A solution of 200 mg (0.61 mmol) of **3**, 40 mg (0.30 mmol) of dried LiI, and 186 mg (1.84 mmol) of dry triethylamine in 20 mL of dry 2-propanol was refluxed for 7 d. The solvent was removed in vacuo, the residue was triturated with 40 mL of dry ether, and the insoluble salts were filtered off. After removal of the ether in vacuo, column chromatography (silica gel, ether/PE 1:3) of the residue gave 130 mg (73%) of **4a**.

Methyl 2,2-Dichloro-2-[1′-[(diphenylmethylene)amino]-cyclopropyl]acetate (11). To a solution of 1.29 g (3.94 mmol) of **3** and 0.31 g (1.34 mmol) of triethylbenzylammonium chloride in a mixture of 30 mL of CCl_4 and 10 mL of CH_2Cl_2 was added with stirring 20 mL of freshly prepared, hot 50% NaOH. After 20 min the reaction mixture was diluted with 50 mL of ice–water and 20 mL of CH_2Cl_2. The organic layer was separated, and the aqueous layer was extracted twice with 10 mL of CH_2Cl_2. The combined organic phases were washed with 10 mL of water. After drying ($MgSO_4$), the solvent was removed in vacuo, and the crude product was purified by column chromatography (silica gel, ether/PE 1:20) to yield 1.25 g (88%) of **11**: mp 89 °C; ^{1}H NMR (250 MHz, $CDCl_3$) 0.76 (m, 2 H), 1.46 (m, 2 H), 3.97 (s, 3 H), 7.17–7.34 (m, 5 H), 7.39–7.49 (m, 5 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 15.7 (t), 53.3 (s), 54.3 (q), 90.0 (s), 127.8 (d, 2 C), 128.1 (d, 2 C), 128.4 (d, 4 C), 128.8 (d), 130.3 (d), 136.6 (s), 140.1 (s), 164.8 (s), 167.2 (s); IR (neat) 3055, 1766, 1650 cm^{-1}; MS (70 eV) *m/z* 362 (MH^+, 80), 326 (M^+ – Cl, 100), 298 (M^+ – Cl – C_2H_4, 17). Anal. Calcd for $C_{19}H_{17}Cl_2NO_2$: C, 63.00; H, 4.73; Cl, 19.57; N, 3.87. Found: C, 63.29; H, 4.66; Cl, 19.70; N, 3.94.

General Procedure for the Preparation of (Cyclopropylphenylmethylene)amines 14a,b (GP 1). The procedure is similar to that reported by Cloke and Stevens.[21] To a solution of 55 mmol of phenylmagnesium bromide in 70 mL of dry ether kept under nitrogen was added dropwise with stirring 55 mmol of the appropriate cyclopropanecarbonitrile dissolved in 20 mL of dry ether. After complete addition, the mixture was stirred for 2 h at rt. Dry methanol (15 mL) was added slowly at 10 °C, and the mixture was stirred for 1 h at rt. The precipitate was filtered off and washed with three 30-mL portions of dry ether. The solvent was removed in vacuo at rt, and the residue was purified by bulb to bulb distillation into a cold trap at 0.05 mm. Yields: **14a**, 65%; **14b**, 76%. Analytical data are in accordance with those reported.[21]

General Procedure for the Preparation of Methyl 2-Chloro-2-[1′-(methyleneamino)cyclopropyl]acetates (GP 2). To a 0.1–0.2 M solution of the respective ketimine in dry methanol was added 1 equiv of the appropriate 2-chloro-2-cyclopropylideneacetate. The solution was stirred at rt for 3 d. The solvent was removed in vacuo. The crude products were used without further purification. For analytical purposes the substances were purified by column chromatography (silica gel, ether/PE 1:3).

Methyl 2-Chloro-2-[1′-[(cyclopropylphenylmethylene)-amino]cyclopropyl]acetate (15a). According to GP 2, a mixture of two diastereomers (1:1) was obtained in 98% yield (2.83 g) as a yellowish oil (crude product) from 1.44 g of **2**: ^{1}H NMR (250 MHz, $CDCl_3$) 0.70–1.35 (m, 16 H), 1.75 (m, 1 H), 2.37 (m, 1 H), 3.83 (s, 6 H), 4.22 (s, 1 H), 4.66 (s, 1 H), 7.18–7.21 (m, 2 H), 7.24–7.32 (m, 5 H), 7.35–7.39 (m, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 7.2 (t), 7.3 (t), 8.5 (t), 8.8 (t), 13.7 (t), 14.0 (t), 14.3 (t), 15.1 (d), 16.0 (t), 21.3 (d), 43.7 (s), 45.4 (s), 52.8 (q), 53.0 (q), 62.1 (d), 64.7 (d), 126.7 (d), 127.6 (d), 127.8 (d), 128.1 (d), 128.3 (d), 128.4 (d), 138.2 (s), 139.1 (s), 168.6 (s), 168.8 (s), 174.7 (s), 181.2 (s); IR (neat) 3007, 1757, 1626 cm^{-1}; MS (70 eV) *m/z* 197 (M^+ – Cl – CO_2CH_3, 4), 146 ($C_6H_7ClO_2^+$, 16), 115 (3), 111 (3), 106 (6), 105 (100), 77 (50), 71 (6), 69 (9), 57 (8), 55 (5), 51 (13). Anal. Calcd for $C_{16}H_{18}ClNO_2$: C, 65.86; H, 6.22; Cl, 12.15; N, 4.80. Found: C, 65.73; H, 6.16; Cl, 12.22; N, 4.76.

Methyl 2-chloro-2-{1′-[[(1″-methylcyclopropyl)phenylmethylene]amino]cyclopropyl}acetate (15b) was obtained in 96% yield (1.74 g) as a yellowish oil (crude product) from 869 mg of **2** according to GP 2: ^{1}H NMR (250 MHz, $CDCl_3$) 0.43–0.65 (m, 4 H), 0.69–0.80 (m, 1 H), 0.86–0.93 (m, 1 H), 0.98–1.03 (m, 2 H), 1.12 (s, 3 H), 3.82 (s, 3 H), 4.17 (s, 1 H), 7.06–7.12 (m, 3 H), 7.30–7.38 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 13.6 (t), 14.6 (t), 15.0 (t), 15.9 (t), 22.0 (q), 24.5 (s), 46.1 (s), 52.8 (q), 65.3 (d), 127.2 (d), 127.9 (d), 128.0 (d), 137.3 (s), 169.0 (s), 176.0 (s); IR (neat) 2955, 1740, 1676 cm^{-1}; MS (70 eV) *m/z* 306 (M^+ + H, 41), 270 (M^+ – Cl, 86), 242 (M^+ – Cl – C_2H_4, 97), 210 (94), 182 (49), 170 (89), 160 (74), 143 (35), 128 (70), 115 (89), 105 (100), 96 (34), 91 (29), 83 (96), 77 (88), 51 (35). Anal. Calcd for $C_{17}H_{20}ClNO_2$: C, 66.77; H, 6.59; Cl, 11.59; N, 4.58. Found: C, 66.96; H, 6.68; Cl, 11.64; N, 4.40.

Methyl 2-Chloro-2-[2′-methyl-1′-[(diphenylmethylene)-amino]cyclopropyl]acetate ((*E*,2*R*/*S*)-18). According to GP 2, a mixture of two diastereomers (*E*,2*R*)-**18** and (*E*,2*S*)-**18** in the ratio of 2.3:1 was obtained in 66% yield (472 mg) as a yellow oil from 335 mg of (*E*/*Z*)-**17** (2.1:1). (*E*,2*R*)-**18**: ^{1}H NMR (250 MHz, $CDCl_3$) 0.85–1.02 (m, 6 H), 3.90 (s, 3 H), 4.37 (s, 1 H), 7.26–7.34 (m, 4 H), 7.39–7.45 (m, 4 H), 7.51–7.59 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 14.3 (d), 22.4 (q), 25.5 (t), 51.1 (s), 53.0 (q), 65.3 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.5 (d), 128.6 (d), 130.0 (d), 137.7 (s), 140.4 (s), 166.2 (s), 169.1 (s); IR (neat) 2953, 1762, 1699, 1630 cm^{-1}; MS (70 eV) *m/z* 306 (M^+ – Cl, 46), 274 (7), 264 (M^+ – C_6H_5, 27), 246 (19), 232 (49), 204 (23), 197 (12), 166 (46), 165 (100), 128 (6), 115 (9), 104 (6), 91 (4), 77 (15), 65 (4), 59 (7).

(*E*,2*S*)-**18**: ^{1}H NMR (250 MHz, $CDCl_3$) 0.43 (dd, J = 6.5, 7.8 Hz, 1 H), 0.79 (dd, J = 6.5, 9.2 Hz, 1 H), 1.12 (m, 1 H), 1.28 (d, J = 7.1 Hz, 3 H), 3.92 (s, 3 H), 4.42 (s, 1 H), 7.21–7.36 (m, 4 H), 7.39–7.46 (m, 4 H), 7.48–7.57 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 15.5 (d), 22.9 (t), 27.5 (q), 52.8 (s), 53.1 (q), 65.7 (d), 127.9 (d), 128.1 (d), 128.39 (d), 128.41 (d), 130.0 (d), 130.1 (d), 137.1 (s), 140.3 (s), 156.6 (s), 168.8 (s); IR (neat) 2953, 1760, 1660 cm^{-1}; MS (70 eV) *m/z* 306 (M^+ – Cl, 52), 264 (M^+ – C_6H_5, 36), 246 (18), 240 (16), 232 (63), 204 (28), 166 (52), 165 (100), 164 (30), 161 (25), 128 (10), 115 (14), 105 (12), 102 (7), 77 (21), 69 (12), 59 (13), 51 (9); HRMS (70 eV, mixture (*E*,2*R*/*S*)-**18**) calcd for $C_{20}H_{20}ClNO_2$ 341.1178, found 341.1171.

General Procedure for the Preparation of Methyl 2-(Methyleneamino)cyclobutene-1-carboxylates (GP 3). To a 0.1–0.2 M solution of the respective methyl 2-chloro-2-[(methyleneamino)cyclopropyl]acetate in dry 2-propanol was added 0.5 equiv of anhydrous LiI and 3 equiv of dry triethylamine. The reaction mixture was heated for 5 d at 85–90 °C. After cooling to rt the solvent was removed in vacuo. The residue was triturated with dry ether, the insoluble salts were filtered off, and the ether was removed in vacuo. The crude material was purified by column chromatography (silica gel, ether/PE 1:3).

Methyl 2-[(Cyclopropylphenylmethylene)amino]cyclobutene-1-carboxylate (16a). A solution of 0.62 g (2.12 mmol) of **15a**, 142 mg (1.06 mmol) of dried LiI, and 0.64 g (6.33 mmol) of dry triethylamine in 30 mL of methanol was heated under reflux for 4 d. The mixture was cooled to rt, and the solvent was removed in vacuo. Column chromatography (silica gel, ether/PE 1:3) of the crude product yielded 108 mg (20%) of **16a** as a yellow oil: ^{1}H NMR (250 MHz, $CDCl_3$) 1.01 (m, 1 H), 1.03–1.06

(m, 2 H), 1.08 (m, 1 H), 1.98 (tt, J = 5.2, 7.9 Hz, 1 H), 2.37 (m, 2 H), 2.47 (m, 2 H), 3.62 (s, 3 H), 7.34–7.39 (m, 3 H), 7.47–7.52 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 9.9 (t), 18.8 (d), 22.8 (t), 30.8 (t), 50.7 (q), 110.8 (s), 127.2 (d), 128.1 (d), 129.8 (d), 138.2 (s), 159.0 (s), 163.2 (s), 173.7 (s); IR (neat) 3090, 1730, 1666 cm^{-1}; MS (70 eV) m/z 255 (M^+, 100), 254 (M^+ – H, 81), 240 (M^+ – CH_3, 17), 224 (M^+ – OCH_3, 17), 222 (26), 196 (M^+ – CO_2CH_3, 26), 194 (66), 180 (10), 168 (6), 167 (6), 156 (11), 130 (6), 129 (35), 128 (23), 115 (20), 111 (5), 103 (10), 102 (54), 90 (6), 83 (6), 77 (7), 68 (3), 59 (4), 53 (6). Anal. Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 74.87; H, 6.75; N, 5.25.

Methyl 2-[[(1′-Methylcyclopropyl)phenylmethylene]amino]cyclobutene-1-carboxylate (16b). According to GP 3, 860 mg (65%) of **16b** was obtained as a yellow oil from 1.50 g of **15b**: ^{1}H NMR (250 MHz, $CDCl_3$) 0.79 (m, 2 H), 1.15 (m, 2 H), 1.31 (s, 3 H), 2.29 (m, 2 H), 2.40 (m, 2 H), 3.64 (s, 3 H), 7.30–7.36 (m, 5 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 15.5 (t), 22.1 (q), 22.9 (t), 23.1 (s), 31.2 (t), 50.6 (q), 100.7 (s), 127.2 (d), 127.9 (d), 129.2 (d), 136.7 (s), 159.2 (s), 163.1 (s), 175.5 (s); IR (neat) 3067, 1732, 1653 cm^{-1}; MS (70 eV) m/z 269 (M^+, 84), 268 (M^+ – H, 75), 254 (M^+ – CH_3, 14), 238 (M^+ – OCH_3, 16), 210 (M^+ – CO_2CH_3, 27), 208 (45), 175 (49), 160 (29), 143 (30), 129 (57), 128 (70), 116 (60), 115 (100), 105 (96), 91 (29), 86 (33), 84 (51), 77 (88), 69 (76), 51 (54), 49 (86), 39 (45). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.59; H, 7.15; N, 5.11.

Methyl 2-[(Diphenylmethylene)amino]-3-methylcyclobutene-1-carboxylate (20) and Methyl 2-[(Diphenylmethylene)amino]-4-methylcyclobutene-1-carboxylate (21). According to GP 3, 200 mg of (*E*,2*R*/*S*)-18 (2.3:1) gave 157 mg (88%) of a mixture (1.6:1) of **20** and **21**.

20: ^{1}H NMR (250 MHz, C_6D_6) 0.94 (d, J = 7.1 Hz, 3 H), 1.97 (bd, J = 10.7 Hz, 1 H), 2.54–2.67 (m, 2 H), 3.39 (s, 3 H), 7.01–7.11 (m, 6 H), 7.49–7.60 (m, 4 H); ^{13}C NMR (62.9 MHz, C_6D_6) 16.9 (q), 31.3 (t), 39.0 (d), 50.8 (q), 109.1 (s), 128.1 (d), 129.0 (d), 130.4 (d), 137.3 (s), 162.8 (s), 163.7 (s), 167.8 (s).

21: ^{1}H NMR (250 MHz, C_6D_6) 1.17 (d, J = 6.8 Hz, 3 H), 1.73 (bd, J = 14.0 Hz, 1 H), 2.49 (dd, J = 14.0, 5.3 Hz, 1 H), 2.77 (m, 1 H), 3.38 (s, 3 H), 7.01–7.11 (m, 6 H), 7.49–7.60 (m, 4 H); ^{13}C NMR (62.9 MHz, C_6D_6) 18.4 (q), 31.4 (d), 39.1 (t), 50.7 (q), 117.8 (s), 128.1 (d), 129.0 (d), 130.4 (d), 137.3 (s), 157.7 (s), 162.8 (s), 168.0 (s).

Mixture of **20** and **21**: IR (neat) 3060, 1743, 1641 cm^{-1}; MS (70 eV) m/z 305 (M^+, 53), 304 (M^+ – H, 27), 290 (M^+ – CH_3, 24), 274 (M^+ – OCH_3, 20), 246 (M^+ – CO_2CH_3, 26), 244 (28), 243 (13), 198 (12), 197 (75), 167 (13), 166 (40), 165 (100), 164 (20), 163 (12), 128 (10), 115 (10), 105 (13), 104 (6), 77 (17), 65 (6), 59 (5); HRMS (70 eV) calcd for $C_{20}H_{19}NO_2$ 305.1416, found 305.1418. Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 77.77; H, 6.28; N, 4.33.

Methyl *trans*-3,4-Dimethyl-2-[(diphenylmethylene)amino]cyclobutene-1-carboxylate (*rac*-24). To a solution of 208 mg (1.15 mmol) of benzophenoneimine (**1**) and 200 mg (1.15 mmol) of **22** in 10 mL of dry 2-propanol were added 77 mg (0.58 mmol) of anhydrous LiI and 348 mg (3.44 mmol) of dry triethylamine. The solution was stirred for 2 d at 60 °C. The solvent was removed in vacuo and the crude material was purified by column chromatography (silica gel, ether/PE 1:4) to yield 276 mg (76%) of *rac*-**24** as a yellow oil: ^{1}H NMR (250 MHz, $CDCl_3$) 1.03 (d, J = 7.1 Hz, 3 H), 1.08 (d, J = 6.8 Hz, 3 H), 2.09 (dq, J = 7.1, 1.2 Hz, 1 H), 2.26 (dq, J = 6.8, 1.2 Hz, 1 H), 3.63 (s, 3 H), 7.32–7.57 (m, 10 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 15.7 (q), 17.3 (q), 39.8 (d), 47.7 (d), 50.6 (q), 113.9 (s), 128.0 (d), 129.0 (d), 130.4 (d), 137.3 (s), 162.0 (s), 163.6 (s), 167.8 (s); IR (neat) 3060, 1700, 1631 cm^{-1}; MS (70 eV) m/z 319 (M^+, 20), 318 (M^+ – H, 10), 304 (M^+ – CH_3, 20), 272 (7), 260 (M^+ – CO_2CH_3, 20), 258 (13), 244 (12), 230 (4), 182 [$(C_6H_5)_2CNH_2^+$, 14], 166 (33), 165 (M^+ – C_6H_5 – C_6H_5, 100), 139 [M^+ – $(C_6H_5)_2CN$, 10], 129 (12), 115 (14), 105 (20), 104 (10), 91 (12), 79 (13), 77 (45), 67 (7), 63 (9), 59 (19). Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 78.97; H, 6.72; N, 4.25.

1-Chloro-1-(trichloroethenyl)spiropentane. The previously published procedure[29] was modified in the following way to give better yields: A mixture of 13.5 g (0.25 mol) of methylenecyclopropane, 88.9 g (0.50 mol) of tetrachlorocyclopropene,[30] and 1.0 g of dry potassium carbonate was heated with constant shaking in a sealed glass ampoule for 14 d at 120 °C. The black viscous mixture was dissolved in 30 mL of CH_2Cl_2, the solution was trap-to-trap distilled in vacuo and then fractionated over a 20-cm Vigreux column to give 37.1 g (64%) of 1-chloro-1-(trichloroethenyl)spiropentane, bp 54 °C/0.08 Torr. Spectroscopic data were in accord with those in the literature.[29]

Methyl 2-Chloro-2-spiropentylideneacetate ((*E*/*Z*)-25). To a solution of sodium methanolate freshly prepared from 200 mL of dry methanol and 15.0 g (0.65 mol) of sodium was added with stirring at 65 °C 30.0 g (129 mmol) of 1-chloro-1-(trichloroethenyl)spiropentane, and the mixture was heated under reflux for 72 h. After cooling the mixture to rt, 150 mL of ice–water was added, and the mixture was extracted with three portions of ether (150 mL each). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated to yield 25.9 g (92%) of crude trimethyl 2-chloro-2-spiropentylideneorthoacetate, which was not purified further.

The crude orthoester (25.9 g, 119 mmol) was dissolved in 80 mL of CH_2Cl_2 and the solution stirred with 10 g of strongly acidic ion-exchange resin (e.g. BAYER LEWATIT SPC 118, macroporous) for 48 h at room temperature. After having been collected on a filter, the resin was washed thoroughly with CH_2Cl_2, and the combined solutions were dried over $MgSO_4$. The solvent was evaporated and the residue purified by chromatography (silica gel, ether/PE 1:10) to give 14.5 g (70% based on chloro-1-(trichloroethenyl)spiropentane) of (*E*/*Z*)-**25** (*E*/*Z* 1:1.7 by GLC). (*E*)-**25**: ^{1}H NMR (250 MHz, $CDCl_3$) 1.41 (m, 4 H, 4′,5′-H), 1.79 (s, 2 H, 2′-H), 3.77 (s, 3 H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT) 10.7 (–, 2 C, C-4′,5′), 11.7 (–, C-2′), 17.3 (C_{quat}, C-3′), 52.8 (+, CH_3), 110.0 (C_{quat}, C-2), 147.1 (C_{quat}, C-1′), 162.9 (C_{quat}, C-1).

(*Z*)-**25**: ^{1}H NMR (250 MHz, $CDCl_3$) 1.41 (m, 4 H, 4′,5′-H), 2.01 (s, 2 H, 2′-H), 3.85 (s, 3 H, CH_3); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT) 10.3 (–, 2 C, C-4′,5′), 15.3 (–, C-2′), 14.3 (C_{quat}, C-3′), 52.8 (+, CH_3), 110.2 (C_{quat}, C-2), 145.6 (C_{quat}, C-1′), 162.6 (C_{quat}, C-1).

Mixture of (*E*/*Z*)-**25**: IR (neat) 3085, 2954, 1731 cm^{-1}; MS (70 eV) m/z 172 (M^+, 19), 157 (M^+ – CH_3, 58), 144 (M^+ – C_2H_4, 26), 137 (M^+ – Cl, 18), 129 (33), 115 (22), 114 (23), 113 (M^+ – CO_2CH_3, 52), 109 (33), 101 (21), 79 (21), 78 (30), 77 (100), 71 (28), 65 (33), 59 (36), 51 (37), 50 (26). Anal. Calcd for $C_8H_9ClO_2$: C, 55.67; H, 5.26; Cl, 20.54. Found: C, 55.75; H, 5.23; Cl, 20.58.

Methyl 2-[1′-[(Diphenylmethylene)amino]spiropentyl]-2-chloroacetate ((1′*R,2*R*/*S*)-26).** A solution of 3.18 g (18.4 mmol) of (*E*/*Z*)-**25** and 3.34 g (18.4 mmol) of benzophenoneimine in 25 mL of dry methanol was stirred for 4 d at rt under argon. The solvent was removed in vacuo, and the residue was triturated with 25 mL of ether. The insoluble white solid was filtered off, and the solvent was removed in vacuo to give 6.27 g (96%) of crude (1′*R**,2*R*/*S*)-**26**, which was of sufficient purity for further reactions. For spectroscopic analysis, chromatography of 2.45 g (silica gel, ether/PE 1:3) gave 2.20 g (90%) of (1′*R**,2*R*/*S*)-**26** as a pale yellow oil, mixture (2.1:1) of isomers A/B: ^{1}H NMR (250 MHz, $CDCl_3$) 0.57 (m, 2 H), 0.70–0.90 (m, 6 H), 0.98 (m, 1 H, B), 1.06 (m, 1 H, A), 1.44 (m, 2 H), 3.77 (s, 3 H, B), 3.84 (s, 3 H, A), 4.47 (s, 1 H, A), 4.57 (s, 1 H, B), 7.20–7.60 (m, 20 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 4.9 (t, A), 5.0 (t, B), 6.2 (t, B), 6.7 (t, A), 20.3 (t, A, B), 27.8 (s, A, B), 48.5 (s, B), 52.0 (s, A), 52.7 (q, B), 53.0 (q, A), 64.3 (d, B), 68.4 (d, A), 127.8 (d, A, B), 127.9 (d, A, B), 128.1 (d, A, B), 128.2 (d, A, B), 128.4 (d, A, B), 128.6 (d, A, B), 130.0 (d, A, B), 130.1 (d, A, B), 132.4 (d, A, B), 137.2 (s, A, B), 140.5 (d, A, B), 166.4 (s, B), 168.7 (s, A); IR (neat) 3061, 2997, 1762, 1734, 1640 cm^{-1}; MS (70 eV) m/z 353 (M^+, 0.1), 319 (18), 318 (M^+ – Cl, 88), 259 (M^+ – Cl – CO_2CH_3, 51), 257 (12), 198 (14), 197 (100), 167 (12), 166 (13), 165 (58), 115 (12), 77 (16).

Methyl 4-(diphenylmethyleneamino)spiro[2.3]hex-4-ene-5-carboxylate (27) and methyl 5-(diphenylmethyleneamino)-spiro[2.3]hex-4-ene-4-carboxylate (28) were obtained in 20% (520 mg) and 37% (936 mg) yield, respectively, as yellow oils from 2.90 g of a mixture of both isomers (2.1:1) of (1′*R**,2*R*/*S*)-**26** according to GP 3: **27**: ^{1}H NMR (250 MHz, $CDCl_3$) 0.86 (m, 2

(29) Weber, M.; de Meijere, A. *Chem. Ber.* **1985**, *118*, 2450.

(30) Tetrachloropropene is commercially available from *Aldrich*, *Kodak*, and *Merck-Schuchardt*. For preparative procedures see: Tobey, S. W.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 2481. Glück, C.; Piognee, V.; Schwager, H. *Synthesis* **1987**, 260.

H), 0.88 (m, 2 H), 2.57 (s, 2 H), 3.57 (s, 3 H), 7.31–7.55 (m, 10 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 8.5 (t), 30.4 (s), 33.6 (t), 50.6 (q), 106.8 (s), 128.0 (d), 129.1 (d), 130.6 (d), 137.0 (s), 162.1 (s), 163.6 (s), 169.1 (s); IR (neat) 3061, 2997, 1695, 1634 cm^{-1}; MS (70 eV) *m/z* 317 (M^+, 48), 316 ($M^+ - H$, 8), 302 ($M^+ - CH_3$, 4), 286 ($M^+ - OCH_3$, 5), 259 (11), 258 ($M^+ - CO_2CH_3$, 64), 256 (14), 197 (52), 182 (7), 180 (7), 166 (25), 165 (100), 164 (10), 127 (3), 115 (10), 105 (27), 91 (4), 77 (28), 65 (2), 59 (3), 51 (8).

28: ^{1}H NMR (250 MHz, $CDCl_3$) 0.59 (m, 2 H), 0.96 (m, 2 H), 2.35 (s, 2 H), 3.63 (s, 3 H), 7.35–7.58 (m, 10 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 6.7 (t), 24.9 (s), 41.3 (t), 50.6 (q), 119.3 (s), 128.2 (d), 129.1 (d), 130.4 (d), 137.6 (s), 155.7 (s), 161.9 (s), 168.9 (s); IR (neat) 2998, 1741, 1698 cm^{-1}; MS (70 eV) *m/z* 317 (M^+, 86), 316 ($M^+ - H$, 35), 302 ($M^+ - CH_3$, 19), 286 ($M^+ - OCH_3$, 18), 284 (13), 258 ($M^+ - CO_2CH_3$, 48), 256 (38), 242 (13), 197 (100), 182 (11), 180 (7), 166 (24), 165 (85), 164 (15), 139 (5), 127 (4), 115 (6), 105 (32), 103 (6), 91 (4), 77 (26), 65 (2), 59 (4), 51 (7); HRMS (70 eV, mixture **27** and **28**) calcd for $C_{21}H_{19}NO_2$ 317.1416, found 317.1414. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.48; H, 6.24; N, 4.59.

Methyl 2,2-Dimethoxycyclobutanecarboxylate (29). To a solution of 100 mg (0.56 mmol) of **30** in 10 mL of dry methanol were added 75 mg (0.56 mmol) of dried LiI and 170 mg (1.68 mmol) of dry triethylamine. The solution was heated at reflux for 13 d. The solvent was distilled off, the residue was triturated with 10 mL of dry ether, and the insoluble salts were filtered off. The ether was distilled off, and the remaining oil was purified by Kugelrohr distillation at 80–100 °C/0.1 Torr to give 36 mg (37%) of **29**: ^{1}H NMR (250 MHz, $CDCl_3$) 1.78–1.92 (m, 1 H), 1.94–2.21 (m, 2 H), 2.26–2.41 (m, 1 H), 3.14 (s, 3 H,), 3.24–3.34 (m, 1 H), 3.28 (s, 3 H), 3.70 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 14.1 (t), 29.8 (t), 48.5 (q), 48.6 (q), 49.2 (q), 51.7 (d), 102.8 (s), 171.3 (s); IR (neat) 2954, 1741 cm^{-1}; MS (70 eV) *m/z* 175 ($M^+ + H$, 1), 159 ($M^+ - CH_3$, 1), 158 ($M^+ - CH_4$, 4), 146 ($M^+ - C_2H_4$, 18), 143 ($M^+ - OCH_3$, 50), 142 (7), 129 (15), 128 ($M^+ - OCH_3 - CH_3$, 9), 123 (10), 115 ($M^+ - C_2H_4 - OCH_3$, 33), 111 (33), 101 (46), 100 (23), 89 (14), 88 [$CH_2C(OCH_3)_2^+$, 90], 85 (11), 83 (25), 75 (38), 71 (12), 69 (32), 59 (94), 58 (51).

Methyl 2-Methoxycyclobutenecarboxylate (31). To a solution of 114 mg (0.64 mmol) of **30** in 5 mL of dry acetonitrile were added 88 mg (0.66 mmol) of dried LiI and 200 mg (1.98 mmol) of dry triethylamine. The mixture was kept at 65 °C for 7 d. The solution was then slowly concentrated at 50 °C/20 Torr to a volume of 0.5 mL. Column chromatography (silica gel, ether/PE 1:2) gave 61 mg (67%) of **31** as a colorless liquid: ^{1}H NMR (250 MHz, $CDCl_3$) 2.02 (m, 2 H), 2.15 (m, 2 H), 3.43 (s, 3 H), 3.67 (s, 3 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 20.0 (t), 28.6 (t), 50.3 (q), 58.7 (q), 102.8 (s), 161.4 (s), 161.9 (s); IR (neat) 2950, 1704 cm^{-1}; MS (70 eV) *m/z* 142 (M^+, 76), 141 ($M^+ - H$, 12), 128 (7), 127 ($M^+ - CH_3$, 100), 115 (15), 113 (19), 112 (7), 111 ($M^+ - OCH_3$, 80), 110 (16), 101 (9), 99 (8), 97 (5), 88 (23), 83 ($M^+ - CO_2CH_3$, 35), 82 (8), 69 (14), 68 (14), 59 (18), 55 (10); HRMS (70 eV) calcd for $C_7H_{10}O_3$ 142.0627, found 142.0633.

Benzyl 2-[(Diphenylmethylene)amino]cyclobutene-1-carboxylate (4b). A solution of 0.61 g (2.1 mmol) of **4a** and 0.51 g (1.8 mmol) of $Ti(O^iPr)_4$ in 15 mL of dry benzylic alcohol was heated to 95 °C for 15 h. The benzylic alcohol was distilled off at 0.2 mm, and the residue was purified by column chromatography (silica gel, ether/PE 1:3) to yield 0.74 g (96%) of **4b** as a yellow oil: ^{1}H NMR (250 MHz, $CDCl_3$) 2.39 (m, 4 H), 5.09 (s, 2 H), 7.12–7.22 (m, 3 H), 7.23–7.48 (m, 12 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 23.2 (t), 31.2 (t), 65.2 (t), 112.5 (s), 127.7 (d, 3 C), 128.1 (d, 4 C), 128.3 (d, 2 C), 128.9 (d, 4 C), 130.4 (d, 2 C), 136.5 (s), 137.3 (s, 2 C), 159.1 (s), 162.4 (s), 168.4 (s); IR (neat) 3040, 2930, 1690, 1630 cm^{-1}; MS (70 eV) *m/z* 367 (M^+, 13), 276 ($M^+ - CH_2Ph$, 57), 233 (22), 232 ($M^+ - CO_2CH_2Ph$, 31), 230 (18), 180 (14), 91 ($C_7H_7^+$, 100); HRMS (70 eV) calcd for $C_{25}H_{21}NO_2$ 367.1567, found 367.1575.

Methyl 2-Oxocyclobutanecarboxylate (32). (A) To a solution of 640 mg (2.2 mmol) of **4a** in 15 mL of methanol and 5 mL of ether was added a solution of 600 mg (4.8 mmol) of oxalic acid dihydrate in 10 mL of water. The mixture was stirred for 2 h at rt. Ether (40 mL) and water (30 mL) were added. The organic layer was separated, washed with saturated NH_4Cl, and dried over $MgSO_4$. After removal of the solvent a crude mixture of **32** and benzophenone (**33**) was obtained. The yield calculated from NMR is 77%. Analytical data are in accordance with those reported by Conia et al.[24a,b]

(B) To a solution of 30 mg (0.103 mmol) of **4a** in 5 mL of CH_2Cl_2 was added 0.36 g of wet ion-exchange resin (type LEWATIT SPC 108, strongly acidic). After stirring the mixture for 46 h at rt, the resin was filtered off and washed with CH_2Cl_2. The combined solutions were dried over $MgSO_4$. Removal of the solvent gave 24 mg of a mixture of **32**, **33**, and monomethyl glutarate (**34**) in a ratio of 1:3.2:1.6 according to the ^{1}H NMR spectrum.

(C) To a solution of 85 mg (0.292 mmol) of **4a** in 5 mL of $CHCl_3$ was added 39 mg (0.3 mmol, 1 equiv) of $AlCl_3$ and 11 mg (0.6 mmol, 2 equiv) of water. The mixture was stirred for 3 h at rt and poured into 10 mL of ether and 5 mL of water. The organic layer was separated, the aqueous layer was extracted with 5 mL of ether, and the combined organic phases were dried over $MgSO_4$. Removal of the solvent and subsequent Kugelrohr distillation of the residue gave 10 mg (10%) of a mixture of **32** and **33** in a ratio of 1:1.1.

Methyl 1,3,8,10-Tetraaza-9,11-dioxo-2,2,10-triphenyltricyclo[6.3.0.0^{4,7}]undec-3-ene-7-carboxylate (35). To a solution of 98 mg (0.34 mmol) of **4a** in 1 mL of $CDCl_3$ was added at 0 °C under N_2 59 mg (0.34 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD). The mixture was allowed to warm to rt and stirring was continued for 2 h. After the reaction was complete, as indicated by TLC, the solvent was removed in vacuo to give 145 mg (92%) of **35** as a pale yellow solid, mp 135 °C: ^{1}H NMR (250 MHz, $CDCl_3$) 2.59 (ddd, J = 10.8, 10.8, 8.7 Hz, 1 H), 3.06 (ddd, J = 10.8, 10.9, 3.1 Hz, 1 H), 3.42 (ddd, J = 14.4, 8.7, 3.1 Hz, 1 H), 3.91 (s, 3 H), 3.97 (ddd, J = 14.4, 10.8, 10.9 Hz, 1 H), 7.27–7.54 (m, 15 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 27.8 (t), 41.4 (t), 53.8 (q), 73.7 (s), 83.7 (s), 125.8 (d), 127.9 (d), 128.0 (d), 128.1 (d, 2 C), 128.3 (d), 128.5 (d), 128.7 (d), 128.9 (d), 131.0 (s), 139.0 (s), 139.3 (s), 150.6 (s), 154.3 (s), 155.5 (s), 166.2 (s); IR (neat) 3021, 1724, 1600 cm^{-1}; MS (70 eV) *m/z* 466 (M^+, 4), 407 ($M^+ - CO_2CH_3$, 3), 346 (4), 305 (14), 288 ($M^+ - CO_2CH_3 - C_6H_5 - NCO$), 230 (2), 206 (2), 180 (2), 166 (13), 165 (44), 129 (2), 119 (9), 103 (5), 91 (4), 77 (9), 59 (2); HRMS (70 eV) calcd for $C_{27}H_{22}N_4O_4$ 466.1641, found 466.1642.

General Procedure for the Flash Vacuum Pyrolysis (FVP) of Methyl 2-(Methyleneamino)-1-cyclobutene-1-carboxylates (GP 4). A quartz tube (2.5 cm o.d., 80 cm length) was used for the pyrolyses. The tube was connected to a cold trap cooled by liquid nitrogen. The substances were placed in a 50-mL pear-shaped flask, which was heated by an oven of a Büchi Kugelrohr apparatus. The pyrolysis apparatus was treated with vaporous hexamethyldisilazane (HMDS) before every run. Pyrolyses were then carried out under vacuum at 10^{-3}–10^{-4} mm generated by an oil diffusion pump (Leybold Heraeus DO 30). The temperature of the tube was maintained at 500 ± 5 °C during the pyrolysis of **4a**, **16a**, and **21**. In the case of **16** 550 ± 5 °C was required. The flask was heated at 80–120 °C so that the rate of vaporization was 100–200 mg/h. The cold trap was then allowed to warm to rt. The crude product was collected as an ethereal solution and purified by column chromatography (silica gel, ether/PE 1:3).

3,4-Dihydro-3-[1′-(methoxycarbonyl)vinyl]-1-phenylisoquinoline (39a) was obtained according to GP 4 in 68% yield (136 mg) as a white solid, mp 85 °C, from 200mg of **4a**: ^{1}H NMR (250 MHz, $CDCl_3$) 2.72 (dd, J = 12.4, 15.5 Hz, 1 H), 3.13 (dd, J = 15.5, 5.1 Hz, 1 H), 3.82 (s, 3 H), 4.70 (dd, J = 12.4, 5.1 Hz, 1 H), 6.06 (m, 1 H), 6.41 (d, J = 0.8 Hz, 1 H), 7.23–7.28 (m, 3 H), 7.34–7.47 (m, 4 H), 7.60–7.67 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 32.5 (t), 51.9 (q), 57.2 (d), 126.78 (d), 126.83 (t), 127.7 (d), 127.9 (d), 128.1 (d), 128.7 (s), 129.0 (d), 129.4 (d), 130.9 (d), 138.0 (s), 138.9 (s), 141.7 (s), 167.1 (s), 167.2 (s); IR (neat) 3027, 2951, 1718, 1609 cm^{-1}; MS (70 eV) *m/z* 291 (M^+, 77), 290 ($M^+ - H$, 73), 276 ($M^+ - CH_3$, 48), 260 ($M^+ - OCH_3$, 19), 232 ($M^+ - CO_2CH_3$, 39), 230 (59), 206 ($M^+ - CH_2CCO_2CH_3$, 100), 204 (21), 178 (16), 165 (11), 128 (13), 115 (7), 105 (4), 89 (3), 86 (9), 84 (14), 77 (7), 73 (2), 51 (2). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.28; H, 5.97; N, 4.81.

1-Cyclopropyl-3,4-dihydro-3-[1′-(methoxycarbonyl)vinyl]-isoquinoline (39b) was obtained in 50% yield (56 mg) as a colorless oil from 112 mg of **16a** according to GP 4: ^{1}H NMR (250 MHz, $CDCl_3$) 0.82–1.03 (m, 3 H), 1.10–1.19 (m, 1 H), 2.14 (m, 1

H), 2.47 (dd, J = 12.4, 15.3 Hz, 1 H), 3.03 (dd, J = 15.3, 5.1 Hz, 1 H), 3.79 (s, 3 H), 4.43 (dd, J = 12.4, 5.1 Hz, 1 H), 5.98 (m, 1 H), 6.37 (d, J = 1.5 Hz, 1 H), 7.15-7.22 (m, 1 H), 7.32–7.38 (m, 2 H), 7.76–7.82 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 7.0 (t), 8.6 (t), 14.5 (d), 32.7 (t), 51.8 (q), 55.9 (d), 125.0 (d), 126.4 (t), 127.1 (d), 127.6 (d), 129.9 (s), 130.5 (d), 136.5 (s), 142.5 (s), 167.2 (s), 167.5 (s); IR (neat) 3004, 2951, 1724, 1620 cm^{-1}; MS (70 eV) m/z 255 (M^+, 45), 254 ($M^+ - H$, 74), 240 ($M^+ - CH_3$, 22), 226 (8), 224 ($M^+ - OCH_3$, 4), 196 ($M^+ - CO_2CH_3$, 15), 194 (22), 170 ($M^+ - CH_2CCO_2CH_3$, 100), 168 (26), 167 (14), 149 (17), 128 (7), 115 (7), 105, 97, 85, 77 (3), 71 (6), 57 (6); HRMS (70 eV) calcd for $C_{16}H_{17}NO_2$ 255.1260, found 255.1248.

3,4-Dihydro-3-[1′-methoxycarbonyl)vinyl]-1-(1″-methylcyclopropyl)isoquinoline (39c). According to GP 4, **39c** was obtained in 68% yield (396 mg) as a colorless oil from 582 mg of **16b**: ^{1}H NMR (250 MHz, $CDCl_3$) 0.64 (ddd, J = 4.0, 5.6, 9.5 Hz, 1 H), 0.78 (ddd, J = 4.0, 5.6, 9.5 Hz, 1 H), 0.96 (ddd, J = 4.0, 5.6, 9.5 Hz, 1 H), 1.15 (ddd, J = 4.0, 5.6, 9.5 Hz, 1 H), 1.39 (s, 3 H), 2.56 (dd, J = 11.4, 15.5 Hz, 1 H), 3.01 (dd, J = 15.5, 5.3 Hz, 1 H), 3.77 (s, 3 H), 4.51 (dd, J = 11.4, 5.3 Hz, 1 H), 5.87 (m, 1 H), 6.33 (d, J = 1.2 Hz, 1 H), 7.15–7.20 (m, 1 H), 7.29–7.36 (m, 2 H), 7.82–7.88 (m, 1 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 11.9 (t), 13.6 (t), 21.6 (s), 23.6 (q), 32.0 (t), 51.8 (q), 56.2 (d), 126.3 (t), 126.3 (d), 126.7 (d), 127.8 (s), 127.9 (d), 130.4 (d), 137.3 (s), 141.7 (s), 167.1 (s), 169.7 (s); IR (neat) 3060, 2953, 1718, 1618 cm^{-1}; MS (70 eV) m/z 269 (M^+, 42), 268 ($M^+ - H$, 48), 254 ($M^+ - CH_3$, 24), 240 (7), 222 (8), 210 ($M^+ - CO_2CH_3$, 13), 208 (12), 184 ($M^+ - CH_2CCO_2CH_3$, 100), 182 (41), 168 (21), 157 (21), 128 (26), 115 (11), 101 (5), 91 (4), 80 (3), 67 (5). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.83; H, 7.10; N, 5.16.

(*Z*)-3,4-Dihydro-3-[1′-(methoxycarbonyl)propenyl]-1-phenylisoquinoline (39d). According to GP 4, **39d** was obtained in 53% yield (71 mg) as a yellow oil from 180 mg of a mixture of **20** and **21** (1:2.8): ^{1}H NMR (250 MHz, $CDCl_3$) 2.05 (d, J = 7.2 Hz, 3 H), 2.77 (dd, J = 15.2, 13.4 Hz, 1 H), 3.01 (dd, J = 15.2, 4.9 Hz, 1 H), 3.80 (s, 3 H), 4.57 (dd, J = 13.4, 4.9 Hz, 1 H), 6.56 (q, J = 7.2 Hz, 1 H), 7.23–7.29 (m, 3 H), 7.34–7.46 (m, 4 H), 7.58–7.84 (m, 2 H); ^{13}C NMR (62.9 MHz, $CDCl_3$) 15.9 (q), 33.0 (t), 51.3 (q), 58.9 (d), 126.7 (d), 127.6 (d), 127.9 (d), 128.1 (d), 128.8 (s), 129.0 (d), 129.3 (d), 130.8 (d), 134.6 (s), 138.1 (d), 138.3 (s), 139.0 (s), 166.8 (s), 168.2 (s); IR (neat) 2948, 1748, 1666 cm^{-1}; MS (70 eV) m/z 305 (M^+, 59), 304 ($M^+ - H$, 30), 290 ($M^+ - CH_3$, 49), 246 ($M^+ - CO_2CH_3$, 63), 245 (18), 244 ($M^+ - CO_2CH_3 - H_2$, 54), 230 (18), 206 ($M^+ - CH(CH_3)CCO_2CH_3$, 100), 204 (20), 179 (12), 178 (25), 165 (42), 128 (17), 115 (13), 105 (16), 91 (6), 77 (26), 69 (6), 59 (16). Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.52; H, 6.20; N, 4.59.

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