protective groups (CBZ, formyl, and acetyl), including the easily removable ones; and (iii) various amino acid derivatives including both L- and D-isomers and dipeptides were utilized as nucleophiles.

In summary, a radically altered stereospecificity of subtilisin in organic solvents affords facile enzymatic preparation, impossible in water, of diverse peptides containing D-amino acids, thus providing a new synthetic route to bioactive peptides.

Thermal Generation and Dimerization of [4]Metacyclophane

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The field of cyclophanes with very short bridges continues to bring forth intriguing results.¹ While [5] metacyclophane (1977)² and [5]paracyclophane (1985)³ have already been synthesized, attempts to bridge a benzene ring with four atoms have not yet vielded an isolable compound. [4] Paracyclophane, predicted by Schaefer et al. "on statistical grounds" to be synthesized in 1992,4 has recently been generated photochemically at low temperatures, intercepted with alcohols,^{5,6} and identified by its UV spectrum.⁶ [4] Metacyclophane (2a) is expected to be less strained and more stable than its para isomer and thus appears to be overdue in this series.

Our previous attempts⁷ to obtain 2a by irradiation of its Dewar isomer 1a⁸ were unsuccessful because 1a furnished the prismane isomer in a quantitative escape reaction. In the course of those studies, we observed on GCMS small quantities of compounds with double mass. An investigation of the dimer formation has now furnished good evidence for the involvement of 2a and has revealed some fascinating reactions and products.

Depending on the thermolysis conditions, 1 yielded different product mixtures (see Scheme I and Table I). Compounds 3 and 12^9 were known. The structures of 10 and 11 could be assigned



from their spectral data and from those of deuteriated derivatives.¹⁰

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The dehydrogenated dimer 4 was not further characterized. Unfortunately, 8, 9, and probably three other dimers formed in comparable amounts turned out to be so similar in their physical properties that we have not yet been able to separate them by HPLC or by preparative GC; the latter technique suffers from the additional disadvantage that some decomposition occurred at the high injector temperatures required due to the low volatilities of the products. Therefore, their structural assignment is tentative; it is based on GCMS and a few typical ¹H NMR signals,¹⁰ and on their thermal behavior.

When 1 was injected into the gas chromatograph (injector temperature 300 °C, Table I, entry 1), 10a was the main component of the product mixture. Heating la at 200 °C in a KOH-conditioned¹¹ sealed ampoule gave, besides much polymer, the same substances, but with drastically changed product ratios, and 12a as the main component (77%; entry 2). Mechanistically revealing were the ampoule experiments at lower temperatures (entries 3 and 4); here, according to GCMS and NMR analysis, a mixture of at least five dimers, including 8a and 9a, was obtained.

⁽¹⁾ For a recent review; see: Cyclophanes; Keehn, P. M.; Rosenfeld, S.

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⁽¹¹⁾ Reactions in unconditioned ampoules gave variable results; in most cases, large amounts of 3 (up to 60%) were obtained. In a run with 2 mol % p-toluenesulfonic acid, the yield of 3 rose to 90%.

	conditions			products ^a							
entry		1a (mg)	T (°C)	t (min)	3a	4 a	8a + 9a + isomers	10a	11a	12a	recoveryb
1	GC	7	300 ^c		5	1		89	4	1	50 ^d
2	ampoule	5	200 ^e	5	<1	4	<1	13	6	77	ca. 20 ^d
3	ampoule	5	1 75 °	5	2		>95			1	ca. 100 ^f
4	ampoule	5	150°	5	<1		>90				g
5	ampoule	h	200	5	1	8		2	10	54	ca. 20/

Table I. Products from the Thermolysis of 1a

^a In percent of total recovery; furthermore, <1% of methylindanes was present in many runs. ^b In percent of 1a. ^c Injector: 300 °C; oven: 200 °C; 1.5 m 15% SE-30 on Chromosorb W; 60 mL H₂/min. ^d Isolated yield (preparative GC). ^eA KOH-pretreated Pyrex ampoule of 0.5-mL contents was used. / Determined from ¹H NMR with C_6H_6 as internal standard. *Not determined; 6% of 1a was present. *The product mixture (8a, 9a + isomers) from entry 3 was used.

When this mixture was heated separately to 200 °C (entry 5), it lead to extensive formation of polymer (broad signals in the ¹H NMR spectrum) and a ratio of **11a:12a** similar to that in entry 2; this indicates that 8a and 9a are intermediates for 11a and 12a.

The most unexpected aspect of these reactions is the rather clean transformation of the "meta"-bridged 1a to the paracyclophane 12a; this is all but straightforward and signals deepseated rearrangements. Remarkable also is the formation of (substituted) arene cage dimers¹²⁻¹⁴ like **8a–10a** in a single operation. While the parent benzene dimer corresponding to 10a, which has C_2 symmetry, is known,¹² the D_{2h} benzene dimer corresponding to 8a and 9a has not been reported to our knowledge.

A rationalization of our results is given in Scheme I. The essential postulate is the thermal isomerization of 1a to 2a. This step is presumably slightly endothermic (MNDO: $\Delta H_{\rm f}^{\circ}$ (1a) = 74.6 kcal·mol⁻¹; $\Delta H_{\rm f}^{\circ}$ (2a) = 77.1 kcal·mol⁻¹)¹⁵ and rate determining; the high aromatization temperature required for a short-bridged Dewar benzene has precedent.¹⁶ The ensuing transformation of 2a to 11a (or to 12a, respectively) involves four remarkable [4 + 2] reactions (Scheme I). The first two are Diels-Alder reactions and proceed via 5a to 8a (or, for a different orientation of the two bridges, via 6a to 9a).¹⁷ The ease of these unprecedented benzene dimerizations stems from the high-energy content of 2a (e.g., MNDO: $\Delta H (2 \times 2a \rightarrow 9a) = -59.5$ kcal·mol⁻¹). The two following steps from 8a to 11a (or from 9a to 12a), are retro versions of the first two [4 + 2] reactions. While $2a \rightarrow 8a$ involves the formation of the four vertical bonds of the cage, the indicated four horizontal bonds are cleaved for $8a \rightarrow$ 11a. This latter process is thermodynamically favorable because it furnishes two unstrained benzene rings.¹⁸ Note that the initially unexpected para substitution pattern of 12a follows naturally from the proposed mechanism.

Support for Scheme I comes from deuterium-labeling experiments: 1b gave 11b and 12b; 1c gave 11c and 12c, which is identical with 12b. The position of the label in 11b,c was unambiguously deduced from the ¹H NMR spectra.¹⁰ Also, 1c furnished 8c and 9c with the predicted changes of the assignable ¹H NMR signals (e.g., collapse of the olefinic doublets at $\delta = 6.09$ and 6.12 ppm to (br) singlets).

The genesis of 10a is less obvious. It may proceed as depicted by a [4 + 2] dimerization of **2a** to yield **7a**. An intramolecular Diels-Alder reaction of 7a (corresponding to that of 5a or 6a) is prohibited by bridge strain; instead, a formal [2 + 2] addition may get a chance to furnish 10a. Again, deuterium labeling¹⁰ supports this course of events.

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Supplementary Material Available: Listing of spectral, GCMS, and HRMS data (4 pages). Ordering information is given on any current masthead page.

N-Substituted Organo(silyliminomethyl)stannanes: Synthetic Equivalent to Organosilylcarbonyl Anion and **Carbonyl Dianion**

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Acylmetals are often involved as important intermediates in transition-metal-catalyzed reaction with carbon monoxide. Synthetic utilities of some acylmetal compounds such as acylferrate anions1 and related organometallic compounds2 have been demonstrated. However, acylmetals, which are readily available and widely utilizable as synthetic reagents for nucleophilic introduction of acyl group have been so far limited. Recently, we have reported³ a new synthesis of N-substituted organo(silyliminomethyl)stannanes by palladium(0)-catalyzed reaction of isocyanide with organosilylstannanes. Herein we wish to report that ((2,6-xylylimino)(trialkylsilyl)methyl)stannane is selectively transmetallated at -78 °C with *n*-butyllithium to generate in situ ((2,6-xylylimino)(trialkylsilyl)methyl)lithium, which serves as a versatile acylmetal equivalent reacting with various electrophiles. Of special interest is that the reaction of ((2,6-xylylimino)(trialkylsilyl)methyl)lithium with carbonyl compounds makes it possible to introduce successively a second electrophile on the imino carbon with concurrent Brook-type migration of the trialkylsilyl group from imino carbon to oxygen.

A dark brown solution of ((2,6-xylylimino)(trialkylsilyl)methyl)lithium 2, which is prepared in THF at -78 °C by treatment of ((2,6-xylylimino)(trialkylsilyl)methyl)trialkylstannane 1 with *n*-butyllithium (Scheme I), reacted immediately with a variety of electrophiles (MeOH, Me₃SiCl, EtBr, n-BuBr) to give

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