19-2; **C** (R_1 = TMS, R_2 = CH_3), 87304-30-1; **C** (R_1 = TMS, R_2 = $C_6H_5CH_2$), 87304-31-2; **C** (R_1 = TMS, R_2 = CH_3OCH_2), 87304-32-3; **C** (R_1 = TMS, R_2 = t-BuSi(CH_3)$_2$), 87304-33-4; **C** (R_1 = TMS, R_2 = Si(i-Pr)$_3$), 87304-34-5; **C** (R_1 = TMS, R_2 = t-BuSi(C_6H_5)$_2$), 87304-35-6; **C** (R_1, R_2 = t-Bu-Si(CH_3)$_2$), 87304-36-7; **D** (R_1 = TMS, R_2 = Si(i-Pr)$_3$), 87304-37-8; **E** (R_1 = TMS, R_2 = CH_3), 87304-38-9; **E** (R_1 = TMS, R_2 = $C_6H_5CH_2$), 87304-39-0; **E** (R_1 = TMS, R_2 = CH_3OCH_2), 87304-40-3; **E** (R_1 = TMS, R_2 = t-BuSi(CH_3)$_2$, 87304-41-4; **E** (R_1 = TMS, R_2 = Si(i-Pr)$_3$), 87304-42-5; **E** (R_1 = TMS, R_2 = t-BuSi(C_6H_5)$_2$), 87304-43-6; **E** (R_1, R_2 = t-BuSi(CH_3)$_2$), 87304-44-7; $CH{\equiv}C(CH_2)_4C{\equiv}C(CH_2)_2CH(OH)CH{=}CH_2$, 87226-61-7; $CH_2{=}CHBr$, 593-60-2; CH_3I, 74-88-4; $C_6H_5CH_2Br$, 100-39-0; $ClCH_2OCH_3$, 107-30-2; $(CH_3)_3SiCl$, 75-77-4; t-BuSi(CH_3)$_2$Cl, 18162-48-6; ClSi(i-Pr)$_3$, 13154-24-0; t-BuSi(C_6H_5)$_2$Cl, 58479-61-1; $H_2NC(CH_3)_2CH_2OH$, 124-68-5; CpCo(CO)$_2$, 12078-25-0; 1,7-octadiyne, 871-84-1; 4-methoxybenzoyl chloride, 100-07-2; 2-bromopropene, 557-93-7; propargyl alcohol, 107-19-7; 3-methoxy-1,3,5-(10),8(14),9(11)-estrapentaen-17β-ol, 87226-50-4; 3-methoxy-1,3,5-(10),8(14),9(11)-estrapentaen-17α-ol, 87226-51-5; 4,10-undecadiynal dimethyl acetal, 87226-59-3; 4,10-undecadiynal, 87226-60-6; 1-bromo-3,3-dimethoxypropane, 36255-44-4; 2-(p-methoxyphenyl)-4,4-dimethyl-2-oxazoline, 53416-46-9; 2-(2-methyl-4-methoxy)-4,4-dimethyl-2-oxazoline, 75817-44-6; 6-chloro-4-hexynal ethylene ketal, 87226-62-8; 7-[2-(4,4-dimethyl-2-oxazolin-2-yl)-5-methoxyphenyl]-4-heptynal ethylene ketal, 87226-63-9; 2-[2-(7-hydroxy-8-methylene-3-nonynyl)-4-methoxyphenyl]-4,4-dimethyl-2-oxazoline, 87226-64-0; 1-(7-hydroxy-8-methylene-3-nonynyl)-2-acetyl-5-methoxybenzene, 87226-65-1; 3-bromopropanal ethylene ketal, 18742-02-4; 7-hydroxy-4-hexynal ethylene ketal, 87226-66-2.

Supplementary Material Available: Results of the preparation and cyclization of **2** (22 complexes), ORTEP drawings, details of the X-ray analyses, a listing of positional and thermal parameters, and table of selected bond lengths and bond angles for B [R_1 = Si(CH_3)$_3$, R_2 = CH_3] and C [R_1 = Si(CH_3)$_3$, R_2 = $C_6H_5CH_2$] (13 pages). Ordering information is given on any current masthead page.

Intramolecular Thermal Cyclization Reactions of Diacryloylamines[1]

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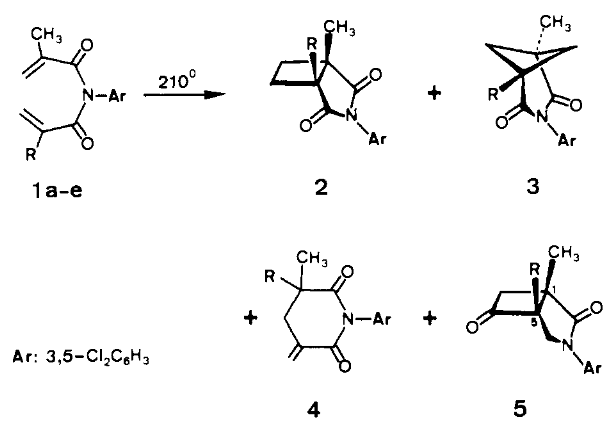
Received May 16, 1983

In the course of screening for antifungal substances against the grey mold fungus on grapes, *Botrytis cinerea*, we have discovered the highly active compound **2b**, which possesses a 3-azabicyclo[3.2.0]heptane skeleton.[2] As an alternative to our photochemical approach[2] to **2b** we envisaged the synthesis of the cyclobutane moiety of **2** by thermal [2 + 2] cyclodimerization of derivatives of methacrylic acid which are known to proceed regiospecifically yielding exclusively 1,2-disubstituted cyclobutanes.[3] However, in all reported cases the necessary 1,2-cis-disubstituted cyclobutane is formed only as the minor component. It was highly tempting to try to enforce the cis mode of head-to-head [2 + 2] cycloaddition by intramolecular fixing of two acrylic units in diacryloyl amines of type **1** whose thermal behavior has not yet been examined.[4]

Scheme I



Scheme II

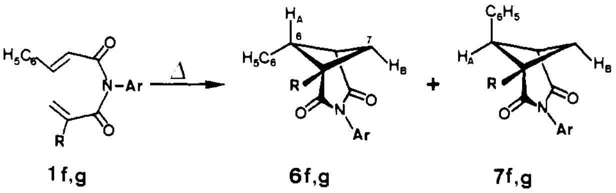


Table I. Substitution Dependence of Product Formation

amide 1	yield, % 2	3	4	5
a, R = H		31	13	6[a]
b, R = CH_3		37	19	7.5
c, R = C_6H_5		50		9
d, R = Si(CH_3)$_3$			21	57[b]
e, R = SCH_3	5[c]	51[c]		

[a] Represents a 1:1 mixture of 5a and the isomer with the position of H and CH_3 exchanged on C(1) and C(5), respectively. [b] Isolation of pure cyclobtanone **5d** (mp 127–128 °C) was achieved by crystallization from the crude reaction mixture after thermolysis of 1d (47% yield). In a separate experiment it was observed that upon chromatography of **5d** on silica gel (25 °C) the angular trimethylsilyl group on C(5) was removed in a remarkably clean reaction to give 5a in quantitative yield. Thus, the yield given represents the yield of isolated **5a** (mp 120–120.5 °C) after treatment of the crude thermolysis mixture with excess of silica gel at room temperature. [c] In this case, **2**e and **3**e were formed even at 170 °C (5 h).

Table II. Cyclization Experiments with Amides 1f and 1g

amide **1**	reaction time, temperature	yield, % 6	7
f, R = CH_3	4 h, 140 °C	45	30
g, R = SCH_3	5 min, 140 °C	46	45
	3 days, 40 °C	51	39

The thermolysis of unsaturated amides **1**[5] was examined in 1,3-dichlorobenzene[10] in sealed tubes (210 °C, 3–16 h). The

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(1) Synthesis and Reactivity of Compounds with Cyclobutane Ring(s). 19. For part 18, see: Alder, A.; Bühler, N.; Bellus, D. *Helv. Chim. Acta* **1982**, *65*, 2405.

(2) Bühler, N.; Baumann, M.; Belluš, D.; Sturm, E. (Ciba-Geigy AG), Eur. Pat. Appl. 17994, 1979. Here the cyclobutane moiety in **2b** was obtained by benzophenone-sensitized [2 + 2] photocycloaddition of ethylene to N-(3,5-dichlorophenyl)dimethylmaleimide at −78 °C.

(3) (a) Seebach, D. "Houben-Weyl, Methoden der Organischen Chemie"; Georg Thieme Verlag: Stuttgart, 1971; Vol. IV/4, p 267 (review). (b) Doering, W. v. E.; Guyton, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 3229. (c) Lingnau, J.; Stickler, M.; Meyerhoff, G. *Eur. Polym. J.* **1980**, *16*, 785.

(4) Examples of thermally induced intramolecular [2 + 2] cycloadditions of molecules having two multiple bonds separated by three atoms to form cyclobutanes or cyclobutenes are rare. Reported to date have been the exclusive head-to-head mode to yield bicyclo[3.2.0]heptane skeletons, cf.: (a) Oppolzer, W.; Loosli, H.-R. *Helv. Chim. Acta* **1974**, *57*, 2605. (b) Klemm, L. H.; Hwang, Y. N.; McGuire, T. M. *J. Org. Chem.* **1976**, *41*, 3813. (c) Doering, W. v. E., personal communication cited in: Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 4417. (d) Shea, K. J.; Wise, S. *Tetrahedron Lett.* **1978**, 2283. (e) Shea, K. J.; Wise, S.; Burke, L. D.; Davis, P. D.; Gilman, J. W.; Greely, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 5708. The exclusive head-to-tail mode to yield bicyclo[3.1.1]heptane skeletons, cf.: (f) ref 4a. (g) Ramamurthy, V.; Liu, R. S. H. *J. Org. Chem.* **1974**, *39*, 3435. as well as mixed modes, cf.: (h) Meinwald, J.; Kapecki, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 6235. (i) Nelsen, S. F.; Gillespie, J. P. *Ibid.* **1972**, *94*, 6238.

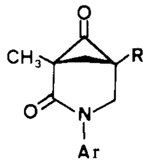
product distribution obtained after flash chromatography of the reaction mixtures (Scheme I) on silica gel was surprising and strongly dependent on the substitution pattern of the acrylic double bond. *For the first time, the thermal head-to-tail mode of* [2 + 2] *cycloaddition of two acrylic units was observed* (e.g., **1** → **3**) accompanied by an unprecedented formation of bicyclic cyclobutanones **5**, which in one case even became the major product (e.g., **1d** → **5d**) (Table I). The expected[3] head-to-head regiochemical orientation was only observed in the thermolysis of **1e** as a minor process.

To establish the structures of **2e** and **3a**, **3c**, and **3e**, we compared their spectroscopic data with those of known bicyclic imides **2b** and **3b**, respectively.[1] For symmetry reasons, ^{13}C NMR spectra of imides **3** show one single triplet for the two bridging methylene carbons (δ (in ppm) for **3a** 39.7, **3b** 45.4, **3c** 44.3, **3e** 45.1), whereas in the ^{13}C NMR spectrum of **2e** two separate triplets for the vicinal methylene carbons appear at 27.5 and 29.3 ppm.[11,12]

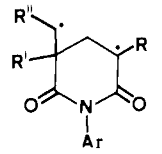
Surprisingly, no [2 + 2] cycloaddition product at all was found upon thermolysis of the α-(trimethylsilyl)acryloyl amide **1d**. It gave predominantly cyclobutanone **5d**, in which the originally terminal methylene sp^2 carbon atom of the α-(trimethylsilyl)-acryloyl appendage is now connected to the lactam nitrogen. Thus, the α-(trimethylsilyl) group alters dramatically the path of the thermal reaction of mixed amides **1**, since analogous cyclobutanones with [3.2.0] bicyclic framework[14] were only minor, although intriguing, components in the thermolyses of **3a–c**.

Upon thermolysis of the mixed amides with cinnamoyl substituents **1f** and **1g**, exclusive formation of the intramolecular head-to-tail cycloadducts was observed as outlined in Scheme II. Thus, heating **1f** in 1,3-dichlorobenzene (140 °C, 4 h) gave the two stereoisomeric cyclobutanes **6f** and **7f** in a ratio of 3:2 in 75% overall yield. The experiment with **1g** showed an enhancing effect of the α-(thiomethyl) substituent on both reaction rate[18] and product yield (see Table II). The [3.1.1] bicyclic imide **7g** bearing a pseudoaxial phenyl group cleanly rearranges thermally (170 °C, 5 h) to the thermodynamically more stable isomer **6g** with a pseudoequatorial phenyl group. The structures of **6** and **7** were established as six-membered imides on the basis of their twin carbonyl stretching IR bands at 1703–1708 cm^{-1} (s) and 1752–1754 cm^{-1} (w), respectively.[12] The stereochemistry at C(6) was clearly elucidated by ^{1}H NMR analysis.[19]

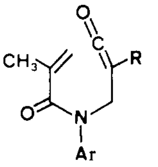
The above observations suggest that the transformation of **1** to **3**, **6**, and **7**, respectively, is a stepwise process with a 1,4-diradical of type B as intermediate. Stabilization of one of the radical sites in B either by captodative substitution[22] (**1e** → **3e**) or by a phenyl group[23] (e.g., **1f** → **6f** + **7f**) results in a considerable lowering of the activation energy for the cycloaddition. Moreover, stabilization of *both* radical sites in B further intensifies this effect, e.g., intramolecular head-to-tail [2 + 2] cycloaddition of amide **1g** already takes place at 40 °C in excellent yield (90%).[24]



A



B



C

Finally, the ene-type reaction products **4**[9] can easily be formed via B by 1,5-hydrogen abstraction from R, if R = CH$_3$. No satisfying reaction mechanism, however, can yet be drawn for the remarkable formation of the 3-azabicyclo[3.2.0]hepta-2,6-diones **5**. A reasonable precursor for **5** might be the ketene C. We are currently studying the possible mechanism of its intramolecular formation in greater depth. Furthermore, studies leading to synthetic exploitation of this attractive new procedure for otherwise difficultly accessible cyclobutane-1,3-dicarboxylic acid derivatives of types **3**, **6** and **7** are in progress.

Acknowledgment. We are grateful to Prof. Dr. H. Fritz, Dr. H.-P. Sauter, and Dr. T. Winkler for the measurement and interpretation of NMR spectra, E. Christen for technical assistance,

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(5) The unsaturated amides **1** were conveniently prepared by the following procedure: (a) Treatment of *N*-(3,5-dichlorophenyl)methacrylamide or cinnamide with 1.0 equiv of PCl$_5$ (25 °C, 1 h) yielded the corresponding imidoyl chlorides,[6] which were used without further purification.[7] (b) Reaction of the sodium salts of α-substituted acrylic acids with 1.0 equiv of the imidoyl chloride in a two-phase system (CH$_2$Cl$_2$/H$_2$O) containing a catalytic amount of tetrabutylammonium bromide (25 °C, 4–24 h) produced the amides **1** in 55–60% overall yields.[8,9]

(6) Bonnett, R. In "The Chemistry of the Carbon-Nitrogen Double Bond"; Patai, S., Ed.; Interscience: New York, 1970; pp 601–606.

(7) In the case of methacrylamide, however, HCl addition to the acrylic double bond was frequently observed. Additional treatment of a toluene solution of the crude products with 1.5 equiv of triethylamine (reflux, 3 h) provided the imidoyl chloride.

(8) The phase-transfer catalyzed reaction of the sodium salts of carboxylic acids with imidoyl chlorides was first reported as a general method for the preparation of diaroyl amides: Rowe, J. E. *Synthesis* **1980**, 114.

(9) All new compounds gave spectroscopic properties (IR, NMR, MS) and elemental analyses consistent with the assigned structures. The complete data will be reported in a forthcoming full paper.

(10) 2,6-Di(*tert*-butyl)-4-methylphenol (2 wt %) was added to the reaction mixtures to prevent polymerization of **1**.

(11) In the ^{13}C NMR spectrum of imide **2a**, prepared along with **3a** in the ratio 3:1 by benzophenone-sensitized intramolecular [2 + 2] photocycloaddition[1] of **1a**, the corresponding cyclobutane carbons appear at 20.1 and 30.2 ppm., respectively.

(12) Furthermore, IR spectra (CH$_2$Cl$_2$) of five-membered imides contain two typical carbonyl stretching bands at 1716–1720 cm^{-1} (s) and 1778–1781 cm^{-1} (w) ($\Delta\nu \sim 60$ cm^{-1}), whereas in the six-membered imides both bands are bathochromically shifted to 1703–1709 cm^{-1} (s) and 1750–1756 cm^{-1} (m), respectively ($\Delta\nu \sim 45$ cm^{-1}).[13] This allows a very convenient distinction between **2** and **3**.

(13) The limited amount of IR data for monocyclic five- and six-membered imides that has been reported (Dolphin, D.; Wick, A. "Tabulation of Infrared Spectral Data"; Wiley-Interscience: New York, 1977; pp 269–277) indicates the same trend.

(14) In the case of **5a**, the ^{1}H NMR spectrum shows coupling of the angular hydrogen (R = H) with both the vicinal methylene hydrogens (J = 2.5 and 8 Hz) as well as cross-ring coupling with the methylene hydrogens of the cyclobutanone ring ($J_{\mathrm{cis}} = J_{\mathrm{trans}} = 2.5$ Hz).[15] For **5b**, the connectivity of the carbon skeleton was independently established by measurement of all carbon–carbon one-bond couplings from noise-decoupled ^{13}C NMR spectra.[16] The existence of $^{1}J_{\mathrm{C(1),C(5)}} = 29.0$ Hz in **5b** unambiguously rules out the alternative isomeric structure A. For **5c** and **5d** corresponding ^{13}C NMR data were found.[17]

(15) The values obtained are in the range of the cross-ring coupling constants reported for cyclobutanone, cf.: Craven, P. G.; Dabbit, O.; McIlwaine, W. R.; Sutcliffe, L. H. *Spectrochim. Acta Part A*, **1980**, *36A*, 245.

(16) (a) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 6021. (b) Wray, V. *Progr. NMR Spectrosc.* **1979**, *13*, 177 and references cited therein.

(17) In addition, the ^{13}C NMR signal of the methylene carbon in the cyclobutanone ring (t × q at 58.7 ppm for **5c** and 59.3 ppm for **5d**) shows a long-range coupling $^{3}J_{\mathrm{C,H}}$ with the hydrogens attached to the angular methyl group at C(1).

(18) A similar rate acceleration effect of an α-thiomethyl group was also observed in the case of **1e** (see Table I).

(19) It was determined that H$_{\mathrm{A}}$ was vicinally coupled to the angular hydrogen by 6 Hz in **6**, whereas in **7** this coupling constant was 0 Hz.[20] The long-range coupling constant ^{4}J between H$_{\mathrm{A}}$ and H$_{\mathrm{B}}$ was 0 Hz for **6** and amounted to 6 Hz in the case of **7** (both hydrogens diequatorial).[21]

(20) Similar coupling constants have been found in other [3.1.1]heptane ring systems containing a conformationally rigid puckered cyclobutane ring: (a) Abraham, R. J.; Cooper, M. A.; Indyk, H.; Siverns, T. M.; Whittaker, D. *Org. Magn. Reson.* **1973**, *5*, 373. (b) Gassmann, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, *104*, 3740.

(21) Representative $^{4}J_{\mathrm{HH}}$W couplings measured in rigid bicyclic systems are compiled: Marchand, A. P. "Methods in Stereochemical Analysis"; Verlag Chemie: Deerfield Beach, FL, 1982; Vol. 1 Table 37.

(22) (a) Viehe, H. G.; Merényi, R.; Stella, L.; Janousek, Z. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917. (b) Crans, D.; Clark, T.; von Ragué-Schleyer, P. *Tetrahedron Lett.* **1980**, 3681. (c) Klessinger, M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 908.

(23) The average radical stabilization energy (RSE) of the phenyl group obtained on the basis of bond dissociation energies as well as from studies of ring-opening reactions of small-ring compounds is 12.2 ± 2.0 kcal/mol: Wehrli, R.; Schmid, H.; Belluš, D.; Hansen, H.-J. *Helv. Chim. Acta* **1977**, *60*, 1325 and references cited therein.

(24) Since α-thioalkyl- and α-thioaryl-substituted acrylonitriles are known to cyclodimerize under very mild conditions (see: (a) Gundermann, K. D.; Röhrl, E. *Justus Liebigs Ann. Chem.* **1974**, 1661. (b) Belluš, D. *Helv. Chim. Acta* **1977**, *60*, 2379), the smooth formation of **2e**, **3e**, and especially of **6g** and **7g** represents the first examples of mixed [2 + 2] cycloadditions of α-thioalkyl-substituted acrylates.

and Dr. J. G. Dingwall for helpful comments regarding the manuscript.

Registry No. **1a**, 87282-40-4; **1b**, 85673-26-3; **1c**, 87282-41-5; **1d**, 87282-42-6; **1e**, 87282-43-7; **1f**, 87282-44-8; **1g**, 87282-45-9; **2e**, 87282-46-0; **3a**, 87282-47-1; **3b**, 85673-30-9; **3c**, 87282-48-2; **3e**, 87282-49-3; **4a**, 87282-50-6; **4b**, 87282-51-7; **4d**, 87282-52-8; **5a**, 87282-53-9; **5b**, 87282-54-0; **5c**, 87282-55-1; **5d**, 87282-56-2; **6f**, 87282-57-3; **6g**, 87282-58-4; **7f**, 87333-74-2; **7g**, 87333-75-3; cis-3-(3,5-dichlorophenyl)-5-methyl-3-azabicyclo[3.2.0]hepta-2,6-dione, 87282-59-5.

Intramolecular [8 + 2] Cycloadditions of Alkenylheptafulvenes

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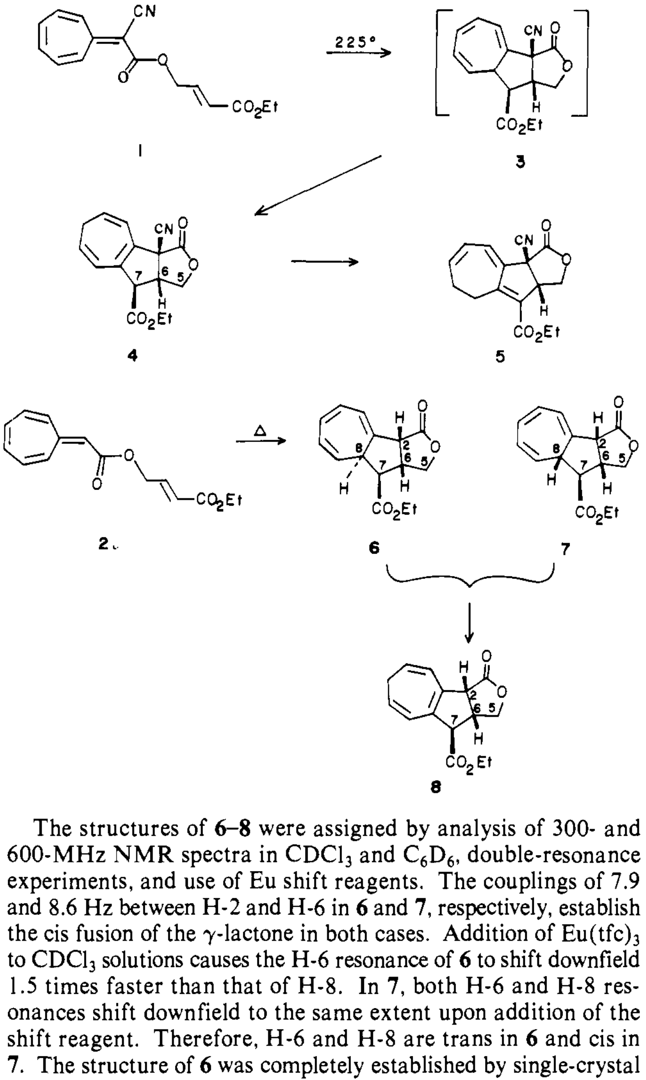
In the course of our investigations of intramolecular cycloadditions involving 10π electrons,[1] we have discovered the first examples of intramolecular [8 + 2] cycloadditions and have devised a computational method that successfully predicted the stereoselectivities of these reactions. This reaction is the prototype of a promising new technique for stereoselective hydroazulene synthesis, and the computational method should be of value of the prediction of stereoselectivities of intramolecular [4 + 2] cycloadditions[2] as well.

The intermolecular [8 + 2] cycloaddition was discovered by Doering and Wiley as a method to trap heptafulvene.[3] Subsequently, many substituted heptafulvenes have been synthesized[4,5] and have been found to undergo [8 + 2] cycloadditions with enamines or electron-deficient "tetraenophiles".[5]

The cyano-substituted compound **1** was prepared by condensation of 3-carbethoxyallyl cyanoacetate with 2 mol of tropylium fluoroborate.[4a] Thermolysis of the ditropyl compound gives cycloheptatriene and orange-red crystalline **1**, mp 106–107 °C, in 20% yield.[6] The synthesis of the heptafulvene **2**, possessing only one stabilizing substituent at C-8, involved reaction of α-tropylacetyl chloride with the 3-carbethoxyallyl alcohol. The resulting monotropyl ester was dehydrogenated with trityl fluoroborate followed by triethylamine[5] to give orange-red **2** (46%), a red oil that polymerizes slowly upon standing in solution and was used without further purification.

Sealed-tube thermolysis of the cyano compound **1** in toluene at 225 °C gave a light yellow crystalline product, **4**, mp 103–106 °C, in 65% yield. Adduct **4** must arise from a 1,5-sigmatropic hydrogen shift of the cycloheptatriene ring[5,7] of **3**. The adduct has characteristic γ-lactone and ester frequencies in the IR spectrum (1780, 1725 cm^{-1}), cycloheptatriene and ethyl resonances in the NMR spectrum, a doublet for H-7 at δ 3.72 (J_{67} = 1 Hz), and a complex ABX pattern at δ 3.95 and 4.77 assigned to the protons at C-5 and C-6. At higher temperatures, **5**, the product of further hydrogen shifts of **4**, was also formed,[6] along with trace amounts of two azulenes, whose structures were not further investigated.

Thermolysis of **2** in toluene at 145 °C gave **6** (mp 147–148 °C), **7**, and **8** (both oils) in 24% yield in a 7:1:1.6 ratio. At 180 °C, **6** and **8** are formed in a ratio of 2.8:1, along with traces of **7**.



The structures of **6**–**8** were assigned by analysis of 300- and 600-MHz NMR spectra in $CDCl_3$ and C_6D_6, double-resonance experiments, and use of Eu shift reagents. The couplings of 7.9 and 8.6 Hz between H-2 and H-6 in **6** and **7**, respectively, establish the cis fusion of the γ-lactone in both cases. Addition of $Eu(tfc)_3$ to $CDCl_3$ solutions causes the H-6 resonance of **6** to shift downfield 1.5 times faster than that of H-8. In **7**, both H-6 and H-8 resonances shift downfield to the same extent upon addition of the shift reagent. Therefore, H-6 and H-8 are trans in **6** and cis in **7**. The structure of **6** was completely established by single-crystal X-ray analysis.[8]

Four diastereomeric [8 + 2] adducts can be formed in these cycloadditions. We have modeled the four diasteromeric transition structures in the following manner. A transition state for the [8 + 2] reaction of heptafulvene with ethylene was approximated, using MNDO calculations[9] to locate the highest energy point on

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[1] Gupta, Y. N.; Doa, M. J.; Houk, K. N. *J. Am. Chem. Soc.*, **1982**, *104*, 7336.

[2] (a) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. (b) Brieger, G.; Bennett, J. M. *Chem. Rev.* **1980**, *80*, 63. (c) Oppolzer, W. *Synthesis* **1978**, 793.

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[8] Crystal data of **6**: $C_{15}H_{16}O_4$, M_r 260.3 orthohombic, $P2_12_12_1$, a = 8.408 (2) Å, b = 10.246 (2) Å, c = 15.657 (4) Å, Z = 4, D_c = 1.282 g cm^{-3}. 614 observations with Mo Kα radiation were used and the structure was refined to an R index of 0.079. There is disorder in the location of the methyl group of the ethyl ester, which prevented further refinement. The fractional atomic corrdinates are available as supplementary material.

0002-7863/83/1505-6714$01.50/0