2-Vinylaziridine (III). The sulfate ester (86.3 g, 0.515 mole) in 100 ml of water was added rapidly to 300 g of a hot 33% sodium hydroxide solution. The reaction was heated sufficiently, during and after completion of addition, to affect distillation. The aqueous distillate was cooled, saturated with potassium hydroxide, extracted with ether, and dried over potassium hydroxide. Distillation through a spinning-band column gave 20.4 g (49% yield) of 2-vinylaziridine, bp 97–99°. Major infrared absorbances appeared at 3.05 (s), 6.10 (s), 10.10 (s), 11.03 (vs), 12.05 (s), and 12.5 (s) μ.

Anal. Calcd for C_4H_7N: C, 69.57; H, 10.14. Found: C, 69.54; H, 10.53.

1-[1,2-Bis(trifluoromethyl)]vinyl-2-vinylaziridine (IV). Hexafluoro-2-butyne (4.06 g, 0.025 mole), was condensed into a glass pressure reactor containing 1.38 g (0.02 mole) of 2-vinylaziridine in 2 ml of Freon 11, at −196°. The reactor was then placed in a −76° bath and kept there, with occasional shaking, for 2 hr. By rapidly stripping off solvent and excess reactant at below room temperature, a >90% yield of 1-[1,2-bis(trifluoromethyl)]vinyl-2-vinylaziridine was realized. Distillation of the aziridine IV by procedures other than a rapid trap–trap distillation on a vacuum line invariably resulted in isomerization of IV. Major infrared absorbances appeared at 6.02 (vs), 6.95 (m), 7.69 (vs), 7.90 (vs), 8.35 (s), 8.60 (s), 10.15 (w), 10.80 (w), and 11.62 (w) μ.

Anal. Calcd for $C_9H_7F_6N$: C, 41.56; N, 6.06. Found: C, 41.61; N, 5.94.

2,3-Bistrifluoromethyl-3,4-dihydro-7H-azepine (V). By allowing the 1,2-divinylaziridine IV to stand overnight at room temperature or for several hours at higher temperatures, there was obtained a pale yellow oil. Rapid vacuum distillation through a short-path still gave 2,3-bistrifluoromethyl-3,4-dihydro-7H-azepine as a water-white liquid, bp 75° (43 mm). Major infrared absorbances appeared at 5.95 (m), 7.0 (m), 7.29 (m), 7.39 (s), 7.65 (s), 7.85 (vs), 8.23–8.95 (vs), 9.30 (s), 10.20 (s), 10.36 (s), 11.00 (w), and 11.65 (w) μ.

Anal. Calcd for $C_9H_7F_6N$: C, 41.56; F, 49.35; N, 6.06. Found: C, 41.70; F, 49.80; N, 6.18.

3-Amino-4-hydroxy-1,5-hexadiene (VI). A mixture 91.3 g (0.95 mole) of 2,3-divinyloxirane, 500 ml of tetrahydrofuran, and 1.3 l. of concentrated ammonium hydroxide was rapidly stirred for 1 week at room temperature and then at reflux temperatures for 4 hr. Removal of the volatile materials on a vacuum stripper left a viscous residue from which 37.2 g (34.8%) of 3-amino-4-hydroxy-1,5-hexadiene, bp 90–92° (11 mm), was isolated. On standing, the amino alcohol partially solidified. Isolation of the solid and recrystallization from benzene gave a white solid, mp 59–61°. No attempt was made to determine the stereochemistry of this solid amino alcohol.

Anal. Calcd for $C_6H_{11}NO$: C, 63.72; N, 12.39. Found: C, 63.20; N, 12.63.

***trans*-2,3-Divinylaziridine (VII).** The reaction of 13.3 g (0.117 mole) of 3-amino-4-hydroxy-1,5-hexadiene in 500 ml of anhydrous ether with 15.0 g (0.129 mole) of chlorosulfonic acid yielded 22.1 g (97%) of the corresponding sulfate ester, mp 178–180° dec.

Anal. Calcd for $C_6H_{11}NO_4S$: C, 37.31; N, 7.25. Found: C, 37.41; N, 7.42.

In the manner previously described, the sulfate ester gave a 28.6% yield of *trans*-2,3-divinylaziridine, bp 55–56° (30 mm). The infrared spectrum of VII showed major absorbances at 3.05 (m), 6.11 (s), 10.12 (s), 10.95 (vs), 11.90 (vs), and 12.30 (m) μ.

Anal. Calcd for C_6H_9NO: C, 75.79; H, 9.47. Found: C, 76.02; H, 9.48.

1-[1,2-Bis(trifluoromethyl)]vinyl-2,3-divinylaziridine (VIII). The preparation of this trivinylaziridine was analogous to that described for the synthesis of IV. Thus, 0.33 g (3.5 mmoles) of 2,3-divinylaziridine in 1 ml of Freon 11 when treated with 1.0 g (6 mmoles) of hexafluorobutyne-2 at −76° for 2 hr yielded VIII quantitatively. The major infrared absorbances appeared at 6.0 (m), 7.88 (vs), 8.31 (s), 8.70 (vs), 10.11 (m), 10.75 (m), and 11.53 (w) μ.

Anal. Calcd for $C_{10}H_9F_6N$: C, 46.69; N, 5.45. Found: C, 46.09; N, 5.14.

2,3-Bis(trifluoromethyl)-7-vinyl-3,4-dihydro-7H-azepine (IX). Heating the trivinylaziridine VIII at 50° for 1–2 hr gave a pale yellow liquid. A trap–trap distillation of the latter on a vacuum line gave IX as a water-white liquid. The infrared spectrum of IX disclosed major absorbances at 6.15 (w), 6.31 (m), 7.10 (w), 7.30 (m), 7.60 (m), 7.85 (vs), 8.2–8.95 (vs), 10.05 (m), 10.60 (m), 10.95 (m), 12.55 (m), and 14.10 (m) μ.

Kinetic Measurements. The progress of the thermal valence isomerization of the 1,2-divinylaziridine was followed by gas chromatographic analysis. Good resolution of the divinylaziridine IV and the generated valence isomeric azepine V was realized with a column of silicone oil on Firebrick maintained at room temperature. Under the conditions of operation, the aziridine had three times the retention time of benzene, and the azepine had twelve times the retention time of benzene. The kinetics were all performed with the internal standard benzene so that the gas chromatographic measured areas could be related to the internal standard.

The Polar Fluorination of Propenylbenzene[1,2]

Richard F. Merritt

Contribution from Gorgas Laboratory, Rohm and Haas Company, Redstone Research Laboratories, Huntsville, Alabama 35807. *Received September 15, 1966*

Abstract: It has been demonstrated that elemental fluorine will add to *cis*- and *trans*-propenylbenzene in a predominately *cis* manner. Fluorination in methanol will produce the diastereoisomeric 1-methoxy-2-fluoropropylbenzenes in addition to the vicinal difluorides; *trans* dehydrofluorination of vicinal difluorides will predominate only in very favorable situations.

The previous investigations[1,3,4] of the direct fluorination of the carbon–carbon double bond have shown that the adducts are of predominately *cis* configuration. Fluorination of 1,1-diphenylethylene produced both direct adduct as well as 1,1-diphenyl-2-fluoroethylene.[1] It was postulated that molecular adducts as well as "open" carbonium ions were involved.

It appeared of interest to study an aliphatic olefin to assess the effect, if any, of sovent polarity and temperature on the stereospecificity of the addition. In this paper we present the results of fluorine addition to *cis*- and *trans*-propenylbenzene.

Results

The identification of the products followed a scheme essentially as outlined in Scheme I. In nonpolar

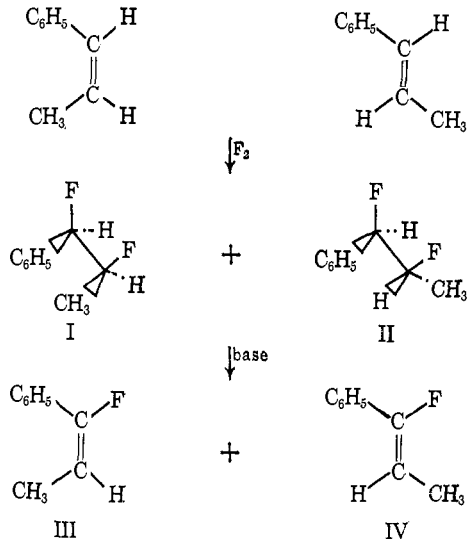
(1) For part III of the low-temperature fluorination series see R. F. Merritt, *J. Org. Chem.*, 31, 3871 (1966).

(2) This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021 AMC-11536(Z).

(3) R. F. Merritt and T. E. Stevens, *J. Am. Chem. Soc.*, **88**, 1822 (1966).

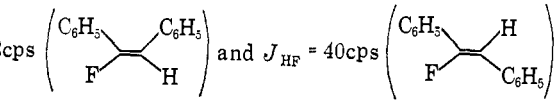
(4) R. F. Merritt, *J. Org. Chem.*, 31, 1859 (1966).

Scheme I



solvents the *dl-erythro* (I) and *dl-threo* (II) difluorides were the major products from *cis*- and *trans*-propenylbenzene, respectively. Table II details the percentage composition found with each change of reaction conditions. Both isomers were separated by preparative vapor phase chromatography and identified by fluorine and proton nmr as well as dehydrofluorination experiments.

The *cis*- (III) and *trans*-1-fluoropropenylbenzenes (IV) arising from the dehydrofluorinations could be readily identified by the relative magnitudes of the vicinal HF coupling constants. The values of 22 and 36 cps were observed for the two isomers and structures were assigned as *cis* III and *trans* IV, respectively. The trend in vicinal HF coupling constants across a double bond has been shown[5,6] to be J_{HF} *trans* > J_{HF} *cis*.



The results of dehydrofluorinations with potassium *t*-butoxide in *t*-butyl alcohol at 75° are given in Table I.

Table I. Dehydrofluorination Product Distribution

Reactant mixture, %		Product mixture, %	
I (*erythro*)	II (*threo*)	III (*cis*)	IV (*trans*)
31	69	12	88
75	25	34	66
100	0	38	62
12	88	5	95

The *cis*/*trans* ratio was determined by both vapor phase chromatography and electronic integration of the fluorine nmr spectra of the mixtures. An internal standard (cumene) was used to monitor material balance. There is no evidence to rule out the possibility of a III to II isomerization during the elimination reaction. However, such an isomerization was not observed with *t*-butoxide dehydrochlorinations of the chlorine adducts of propenylbenzene.[7]

(5) *Cf.* ref 4.
(6) H. M. McConnell, C. A. Reilly, and A. D. McLean, *J. Chem. Phys.*, **24**, 479 (1956).
(7) R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1967).

It becomes apparent upon inspection of the data presented in Table I that *trans* elimination is favored exclusively with the *threo* isomer, which is also the most reactive. With the *erythro* isomer, the alternative mode of *cis* dehydrofluorination becomes comparable with the more hindered requirements for *trans* elimination.

Previous work[8] on the steric requirements of dehydrofluorination has not been definitive enough to suggest the quite similar energy requirements for *trans vs. cis* elimination. The entire picture is internally consistent as *cis* adducts would be expected to predominate, as has been amply shown by previous work.[3,4]

Fluorinations in methanol resulted in the formation of *dl-erythro*- (V) and *dl-threo*- (VI) 1-methoxy-1-phenyl-2-fluoropropanes as well as difluorides I and II. These mixtures (V and VI) were not completely resolved by vapor phase chromatography but were identified by their nmr (H^1 and F^{19}) spectra and elemental analysis. As the amounts of the two diastereoisomers were nearly equal in every case, they were not separated and characterized independently. Table II lists the various solvents and conditions used for both the *cis* and *trans* isomers. The difluorides I and II were treated with methanol containing a trace of HF for periods exceeding those of the fluorinations. No indication (vpc) of ethers V and VI could be found, which would eliminate methanolysis of the benzilic fluorine atom as the source of V and VI.

Table II

Solvent	Temp, °C	Product composition, % (I) *erythro*	(II) *threo*	V + VI
	trans-1-Phenylpropene			
CCl_3F	−78	31	69	..
CCl_3F	−126	27	73	..
CCl_2F_2	−145	29	71	..
CH_3OH	−78	7.0	44	49
	cis-1-Phenylpropene			
CCl_3F	−78	78	22	..
CCl_2F_2	−145	79	21	..
CH_3OH	−78	38	12	50

In all the fluorinations the olefin was completely soluble except for the run at −145° (CCl_2F_2). The apparent heterogeneity of this run did not appear to vary the product composition appreciably. Small amounts (~1 g) of 5A Molecular Sieve[9] were used to scavenge traces of HF found in the fluorine and produced in the reaction. Omission of the Molecular Sieve caused no change in the product composition. Addition of equivalent amounts of HF to the solution before fluorination caused no variation in either product distribution or yield. Experiments conducted with 50% of 1 equiv of fluorine produced the same isomeric mixture of difluorides indicative of kinetic control of the product distribution. No isomerization was noted of the recovered propenylbenzenes. The difluorides were found to be unreactive to fluorine under the usual fluorination conditions, and the composition was unchanged upon exposure of up to equivalent

(8) D. E. M. Evans, W. J. Feast, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 4848 (1967), and additional citations included therein.
(9) Trademark of Union Carbide Corp.

amounts of HF. The addition is apparently diffusion controlled as no detectable difference in absorption rates of fluorine was noted throughout the temperature range studied. No olefin examined to data has been sufficiently unreactive to allow measurements of absorption (addition) rates.

Discussion

It is apparent from Table II that the products are similar to those found in ionic chlorinations[7] but that fluorination appears to be more stereospecific. The same product mixture is not obtained from *cis*- and *trans*-1-phenylpropene, which implies that a common intermediate is not formed and really should not be expected.

The nonpolar solvents employed along with low temperatures tend to make molecular complexes such as VII attractive. Collapse of such a complex will produce the *cis* adducts. It is expected[10] that fluorine will not be as effective a bridge as bromine and chlorine so that the participation of "fluoronium ions" will be of lesser importance than "bromonium" or "chloronium ions." The role of the "open" carbonium ion VIII is, there-

VII VIII

fore, necessary to account for both the observations of *trans* addition and placement of the methoxy group exclusively at the benzylic carbon atom.

Fluorinations in methanol lead to an apparent *greater* degree of stereospecificity and *cis* addition predominates by a factor of about 6:1 for *trans*-propenylbenzene and only 3:1 for the *cis* olefin. This increased stereospecificity is contrary to previous observations with chlorination.[7] Aqueous or alcoholic halogenations usually produce *low* yields (<15%) of dihalide and predominately halo ether.[7,11] The high yields of difluoride, coupled with high *cis* stereospecificity, supports the existence of complex VII and also implies that it is more impervious to nucleophilic solvents than "similar" olefin complexes with chlorine or bromine. It is also possible that the increased stereospecificity is due in part to the preferential methanolysis of the open carbonium ion VIII which serves as the precursor for *trans* adduct. The fluoro ethers V and VI were formed in essentially equal amounts for both the *cis*- and *trans*-propenylbenzenes. This observation will favor the methanolysis of an open carbonium ion VIII rather than a displacement from a complex such as VII. The latter process would require a "back-side" and "front-side" displacement to occur with equal probability to account for the observed isomer ratios.

In each fluorination a small amount (<3%) of a trifluoride identified as 1-phenyl-1,2,2-trifluoropropane ($C_6H_5CHFCF_2CH_3$) was formed. As the difluorides were stable to fluorination, its precursor is likely to be the fluoroolefin 1-phenyl-2-fluoropropene ($C_6H_5CH{=}CFCH_3$). This product will arise *via* proton loss from the open carbonium ion VIII. The very favorable situation for this process is in the fluorination of 1,1-diphenylethylene[1] wherein the major product is the fluoroolefin 1,1-diphenyl-2-fluoroethylene.

A reasonable interpretation of the current information on low-temperature addition of fluorine is that it behaves in an ionic manner similar to the other halogens. However, molecular adducts caused by the very high electronegativity of the fluorine play an important role in determining product stereochemistry. Work is currently in progress to explore various Wagner–Meerwein type rearrangements which will arise *via* participation of the "open" carbonium ion formed in conjunction with (or after) the molecular complex.

Experimental Section

Materials. The *cis*- and *trans* 1-phenylpropenes were obtained from the Chemical Samples Co. in purities of 97.5 and 99%, respectively. The fluorine was obtained from Allied Chemical Corp. and passed through a NaF-filled HF scrubber just prior to use. It was used *without* a diluent. Its purity was routinely checked by iodometry and mass spectra, and the only detectable impurity appeared to be oxygen at <0.5%. All solvents were of the highest commercial purity and were thoroughly degassed before use.

Apparatus. The apparatus and general operation thereof has been described previously.[1] *Extreme care* must be taken to ensure that the fluorine-handling system be well ventilated as leaks inevitably occur caused by valve and connector corrosion. Personnel operating the fluorination apparatus should be shielded to avoid direct contact with the undiluted fluorine. Explosions have never occurred but most olefins will burn if the fluorine is admitted too rapidly. The stopcock grease (Kel-F No. 90[12]) must be free of hydrocarbon impurities or the stopcocks and ground joints will burn through.

Fluorination of *cis*- and *trans*-Propenylbenzene. The olefin (2.6 g, 22 mmoles) was dissolved in 50 ml of the solvent and placed in the reactor along with 1.0 g of No. 5A Molecular Sieve.[9] The solution was cooled to the required temperature by means of an appropriate slush bath [−78° = CO_2–acetone; −126° = methylcyclohexane–N_2 (l); and −145° = methylcyclopentane–N_2 (l)]. The mixture was then stirred vigorously and degassed at ~1 mm for 10 min. The fluorine (22 mmoles) was introduced above the solution at a rate such that the pressure in the reactor portion never exceeded 5 mm. Approximately 2 hr was required for complete stoichiometric consumption of the fluorine. The mixture was warmed to 25° under nitrogen; 50 ml of ether was added, and the entire solution was washed with 50 ml of 1% NaOH solution. After drying (magnesium sulfate), the colorless solution was concentrated to *ca.* 5 ml with a 50-cm Vigreux column. Vacuum distillation of the adducts was unsuccessful as decomposition and polymerization occurred very rapidly. Cumene was added to this concentrated solution as an internal standard and the entire solution was analyzed by vapor phase chromatography [0.25 cm. × 7 ft dioctyl phthalate–Chromosorb G (AW) at 139° Aerograph A-90-P]. Separation and purification of all products was achieved with this column. Yields (80–90% total) were calculated in relation to a known weight of cumene. Response factors to cumene were determined for each class of product. The retention times relative to cumene were 2.42 (I), 2.79 (II), and 3.59, 3.89 (V and VI). The distribution is given in Table I and the product data are listed below.

1-Phenyl-1,2-difluoropropane (I and II). The infrared spectra were consistent with the structures with C–F bands at 9.3, 9.6, 9.9, and 10.12 μ. The fluorine and proton nmr spectra for the two diastereoisomers are outlined in Table III. *Anal.* Calcd for $C_9H_{10}F_2$: C, 69.21; H, 6.46; F, 24.33. Found for *erythro:* C, 70.01; H, 6.51; F, 23.7. Found for *threo:* C, 69.83; H, 6.60; F, 23.8.

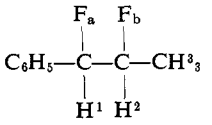
1-Phenyl-1-methoxy-2-fluoropropane (V and VI). The infrared spectra contained both methoxy (9.0 μ) and C–F (9.25, 9.4) bands. The fluorine and proton spectra are given in Table IV. *Anal.* Calcd for $C_{10}H_{13}FO$: C, 71.40; H, 7.99. Found: C, 70.97; H, 8.20.

(10) P. E. Peterson and R. J. Bopp, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p S-003.

(11) P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, **58**, 466 (1936).

(12) Trademark of the Minnesota Mining and Manufacturing Co.

Table III.[a] Nmr Data

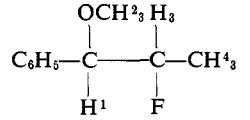


	(I) *erythro*	(II) *threo*
$J_{F_aH^1}$	48 cps	48 cps
$J_{F_aF_b}$	~15–16 cps	~15 cps
$J_{F_aH^2}$	~15–16 cps	~15 cps
$J_{F_bH^1}$	~14 cps	~14 cps
$J_{F_bH^3}$	~23 cps	~23 cps
$J_{F_aH^3}$	~1.6 cps	<0.5 cps
$J_{H^2H^3}$	~6.5 cps	6.5 cps
δ_{F_a}	ϕ +193.5	ϕ +186.8
δ_{F_b}	ϕ +182.5	ϕ +183.8
δ_{H^1}	−326 cps	−317 cps
δ_{H^2}	−290 cps	−270 cps
δ_{H^3}	−70 cps	−71 cps

[a] Fluorine nmr spectra are reported in units of ϕ = ppm from CCl_3F as internal standard. Proton spectra are reported in cps from tetramethylsilane as internal standard. All spectra were run in CCl_4 as 20% solutions unless otherwise indicated. A Varian HR-40 was used for fluorine spectra and a Varian A-60 for proton spectra.

Dehydrofluorination of I and II. The difluorides (0.1–0.2 g) were treated with 1.0 equiv of potassium *t*-butoxide in *t*-butyl alcohol (~2 ml). The mixture was heated to 75° for 1 hr and then ice–water (1.0 ml) was added. After extraction, washing, drying, and concentration to *ca.* 1 ml, the solution was analyzed by vapor phase chromatography (0.25 in. × 4 ft didecyl phthalate, 129°) and F^{19} nmr. Cumene was added before the reaction to monitor the material balance (usually ~97%). The two isomers were separated by preparative gas phase chromatography for characterization. The fluorine and proton nmr spectra are given in Table V. The infrared spectra are consistent with the assigned structures. *Anal.* Calcd for C_9H_9F: C, 79.39; H, 6.66. Found for *cis:* C, 79.04; H, 6.55. Found for *trans:* C, 79.30; H, 6.75.

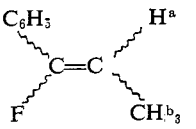
Table IV. Nmr Data[a]



J_{FH^1}	8 cps	δ_F	ϕ +178.5
J_{FH^2}	<0.5 cps	δ_{H^4}	−78, −62 cps
J_{FH^3}	47 cps	δ_{H^3}	−284 cps
J_{FH^4}	24 cps	δ_{H^1}	−242 cps
		δ_{H^2}	−193, −194 cps

[a] See footnote *a*, Table III.

Table V. Nmr Data[a]



	cis	*trans*
J_{FH^a}	22 cps	36 cps
J_{FH^b}	2.2 cps	2.5 cps
$\delta_{H^aH^b}$	7.5 cps	7.0 cps
J_F	ϕ +102.6	ϕ +121.0
δ_{H^a}	−324 cps	−319 cps
δ_{H^b}	−105 cps	−107 cps

[a] See footnote *a*, Table III.

Acknowledgment. I am grateful to Mrs. Carolyn Haney for infrared and nmr spectra and to Mr. Morris Howard for technical assistance.

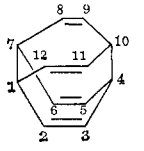
Pyrolysis of Some Bridged Homotropilidene Systems[1]

John N. Labows, Jr.,[2] Jerrold Meinwald, Herbert Röttele, and Gerhard Schröder

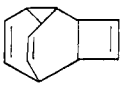
Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850, and the Institut für Organische Chemie, Technische Hochschule Karlsruhe, Karlsruhe, Germany. *Received August 29, 1966.*

Abstract: A new $(CH)_{12}$ hydrocarbon, obtained by pyrolysis of tetracyclo[5.3.2.$0^{2,5}$.$0^{6,8}$]dodeca-3,9,11-triene (**2**), is shown to be tricyclo[5.3.2.$0^{4,8}$]dodeca-2,5,9,11-tetraene (**5**). Its nmr spectrum is similar to that of bicyclo[3.3.2]-deca-2,7,9-triene (**10**), characterized as the pyrolysis product of dihydrobullvalene (**14**). Possible pathways for these thermal rearrangements are discussed.

We have been interested in the possibility of synthesizing the theoretically interesting $(CH)_{12}$ hydrocarbon tricyclo[5.5.0.$0^{4,10}$]dodeca-2,5,8,11-tetraene (**1**). In connection with another problem, it had been noted that the readily accessible isomeric $(CH)_{12}$ hydrocarbon, tetracyclo[5.3.2.$0^{2,5}$.$0^{6,8}$]dodeca-3,9,11-triene (**2**),[3] undergoes a thermal rearrangement to give a new, crystalline $C_{12}H_{12}$ product, A, of unknown structure.[4] Because of the possibility that this unknown might be the desired **1**, and because of the current interest in related thermal rearrangements, we have examined this reaction in greater detail.



1



2

(1) Partial support of this study by a National Science Foundation research grant (GP 4128) is acknowledged with pleasure. We are grateful to Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

(2) National Institutes of Health Predoctoral Fellow, 1964–1967.

(3) G. Schröder, *Chem. Ber.*, 97, 3131 (1964).

(4) H. Röttele, Diplomarbeit, Technische Hochschule Karlsruhe, Jan 1965.