Aziridines. XV. The Synthesis and Reactions of 1,3-Diazabicyclo[3.1.0]hex-3-enes

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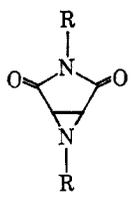
Received December 14, 1966

The synthesis of the previously unknown 1,3-diazabicyclo[3.1.0]hex-3-enes by the reaction of 2-aryl-3-aroylaziridines with aldehydes or ketones and ammonia is described. Some of the 1,3-diazabicyclo[3.1.0]hex-3-enes and their salts are photochromic. Other of the 1,3-diazabicyclo[3.1.0]hex-3-enes undergo rearrangement and oxidation in the presence of base to form pyrimidines. The 1,3-diazabicyclo[3.1.0]hex-3-enes react with acetic acid to form 2-aryl-3-aroylaziridines.

Examples of diazabicyclo compounds in which an aziridine ring is fused to another heterocyclic system are sparse. Only the 2,4-dioxo-3,6-diazabicyclo[3.1.0]-hexanes (**1**)[1,2] and 5-oxo-7-phenyl-1,4-diazabicyclo-[4.1.0]heptane (**2**)[3,4] have been well characterized. We now wish to report on the 1,3-diazabicyclo[3.1.0]-hex-3-enes (**3**) which have been prepared by a slight modification of an existing procedure that leads to 3-imidazolines.[5-7]



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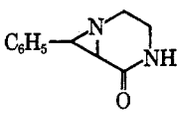

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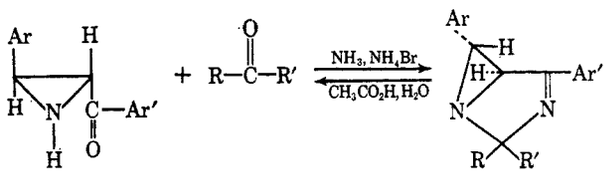
The 1,3-diazabicyclo[3.1.0]hex-3-enes are formed in good yields (Table I) by reaction of *trans*-2-aryl-3-aroylaziridines with aldehydes and ketones in alcoholic solutions saturated with ammonia and containing small quantities of ammonium bromide. In acetic acid the 1,3-diazabicyclo[3.1.0]hex-3-enes revert to *trans*-2-aryl-3-aroylaziridines. Thus, compounds **15**, **18**, **22**, **26**,



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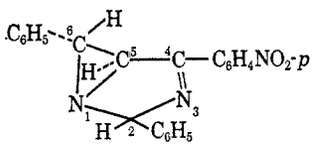
and **29** in moist acetic acid for several days at room temperature give *trans*-2-nitrophenyl-3-benzoylaziridine. Isolation of the starting *trans*-aziridine indicates that the hydrogens at C_5 and C_6 in the 1,3-diazabicyclo-[3.1.0]hex-3-enes were also *trans* to each other and that no epimerization occurred in the synthesis of the bicyclic aziridines. It has been shown that an analogous reaction occurs with the 3-imidazolines which react in acid solution to form α-amino ketones.[5-7]

The nmr spectra of **3** were consistent with the proposed structures; typical coupling constants and chemical shifts characteristic of the 1,3-diazabicyclo[3.1.0]-hex-3-enes in deuteriochloroform are given in Table II. The methine protons of compound **15** exhibit an AB pattern, while those of compounds **5**, **6**, **8**, and **11** show an ABX pattern. The ABX pattern is to be expected for two fused rings with methine protons at C_2, C_5, and C_6. By coincidence, in deuteriochloroform, the peaks for the two methyl groups of compound **15** are both located 1.60 ppm downfield from tetramethylsilane. In benzene, however, the spectrum shows the two methyl groups at 1.42 and 1.50 ppm as would be anticipated for nonequivalent methyl groups.

The nmr spectrum of **11** shows two well-resolved quartets at 2.48 and 3.74 ppm corresponding to the aziridine methine protons. In addition, a poorly resolved quartet of the C_2 proton appears at 6.84 ppm, while a complex pattern of bands extending from 7.2 to about 8.4 ppm characteristic of aromatic protons is apparent. Examination of the Dreiding model of **11**



indicates that the methine proton at C_6 lies above the plane of the imidazoline ring, whereas the methine proton at C_5 is located nearly in the plane of the ring. Therefore, the C_6 proton should be more shielded than the C_5 proton. Because of anisotropy effects as well as the inductive effects of adjacent substituents on the C_5 proton[8] and because the long-range anisotropy effect of the imidazoline ring should exert a diamagnetic shift on the C_6 proton,[9,10] the chemical shifts of 2.48 and 3.74 ppm were assigned for the methine protons at C_6 and C_5, respectively (Table II).

The resonance spectrum of **11** closely approximates that of an ABX system whose coupling constants, based on first-order approximations, were calculated at $J_{AB} = J_{5,6} = 2.2$ cps, $J_{BX} = J_{2,5} = 1.6$ cps, and $J_{AX} = J_{2,6} = 0.9$ cps.[8] Assuming the validity of the Karplus equation which relates J_{HH} to the dihedral angle,[8] the coupling constant for the vicinal C_5 and C_6

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TABLE I

1,3-DIAZABICYCLO[3.1.0]HEX-3-ENES FROM THE REACTION OF 2-ARYL-3-AROYLAZIRIDINES, AMMONIA, AND ALDEHYDES OR KETONES

	ArCHCHNCRR'N=CAr'				Crude yield,			Calcd, %			Found, %		
Compd	Ar	R	R'	Ar'	%	Mp, °C	Formula	C	H	N	C	H	N
4	p-$O_2NC_6H_4$	H	H	C_6H_5	97	179–181	$C_{16}H_{13}N_3O_2$	68.80	4.69	15.04	68.91	5.00	15.12
5	p-$O_2NC_6H_4$	H	CH_3	C_6H_5	74	166–167	$C_{17}H_{15}N_3O_2$	69.62	5.15	14.32	69.54	5.08	14.25
6	p-$O_2NC_6H_4$	H	n-C_3H_7	C_6H_5	59	143–144	$C_{19}H_{19}N_3O_2$	71.00	5.96	13.07	70.78	6.12	13.00
7	p-$O_2NC_6H_4$	H	i-C_3H_7	C_6H_5	46	156–157	$C_{19}H_{19}N_3O_2$	71.00	5.96	13.07	71.19	6.27	12.88
8	p-$O_2NC_6H_4$	H	C_6H_5	C_6H_5	92	175–176	$C_{22}H_{17}N_3O_2$	74.36	4.84	11.83	74.54	4.99	11.91
9	m-$O_2NC_6H_4$	H	C_6H_5	C_6H_5	83	157–158	$C_{22}H_{17}N_3O_2$	74.36	4.84	11.83	74.21	4.86	11.91
10	C_6H_5	H	C_6H_5	C_6H_5	60	153–154	$C_{22}H_{18}N_2$	85.13	5.85	9.03	84.98	5.90	8.87
11	C_6H_5	H	C_6H_5	p-$O_2NC_6H_4$	59	141–142	$C_{22}H_{17}N_3O_2$	74.36	4.84	11.83	73.95	4.74	11.66
12	p-$O_2NC_6H_4$	H	p-$O_2NC_6H_4$	C_6H_5	48	173–174	$C_{22}H_{16}N_4O_4$	65.99	4.02	13.99	66.20	4.07	
13	p-$O_2NC_6H_4$	H	p-MeC_6H_4	C_6H_5	53	154–155	$C_{23}H_{19}N_3O_2$	74.77	5.18	11.37	75.05	5.39	11.37
14	p-$O_2NC_6H_4$	H	o-$MeOC_6H_4$	C_6H_5	78	193–193.5	$C_{23}H_{19}N_3O_3$	71.68	4.97	10.90	71.76	5.34	11.30
15	p-$O_2NC_6H_4$	CH_3	CH_3	C_6H_5	82	182–183	$C_{18}H_{17}N_3O_2$	70.35	5.57	13.67	70.17	5.52	13.87
16	C_6H_5	CH_3	CH_3	p-$O_2NC_6H_4$	90	151–152	$C_{18}H_{17}N_3O_2$	70.35	5.57	13.67	70.14	5.42	13.93
17	p-ClC_6H_4	CH_3	CH_3	C_6H_5	...	96–97	$C_{18}H_{17}ClN_2$	72.84	5.77	9.44	72.89	5.70	8.58
18	p-$O_2NC_6H_4$	CH_3	C_2H_5	C_6H_5	88	146–147	$C_{19}H_{19}N_3O_2$	71.00	5.96	13.07	70.91	6.20	12.99
19	p-$O_2NC_6H_4$	CH_3	n-C_3H_7	C_6H_5	72	149–150	$C_{20}H_{21}N_3O_2$	71.61	6.31	12.82	71.25	6.37	12.57
20	p-$O_2NC_6H_4$	CH_3	t-C_4H_9	C_6H_5	69	128–129	$C_{21}H_{23}N_3O_2$	72.18	6.63	12.02	72.15	6.95	12.30
21	p-$O_2NC_6H_4$	CH_3	C_6H_5	C_6H_5	37	195–197	$C_{23}H_{19}N_3O_2$	74.77	5.18	11.37	74.58	5.38	11.55
22	p-$O_2NC_6H_4$	C_2H_5	C_2H_5	C_6H_5	74	168–169	$C_{20}H_{21}N_3O_2$	71.61	6.31	12.82	71.38	6.61	12.60
23	m-$O_2NC_6H_4$	C_2H_5	C_2H_5	C_6H_5	78	97–98	$C_{20}H_{21}N_3O_2$	71.61	6.31	12.82	71.11	6.33	12.62
24	p-$O_2NC_6H_4$	▷—	▷—	C_6H_5	30	181–183	$C_{22}H_{21}N_3O_2$	73.51	5.90	11.96	73.37	6.06	11.97
25	p-$O_2NC_6H_4$	$-(CH_2)_4-$		C_6H_5	45	170–171	$C_{20}H_{19}N_3O_2$	72.05	5.74	12.60	72.10	5.95	12.77
26	p-$O_2NC_6H_4$	$-(CH_2)_5-$		C_6H_5	94	156–157	$C_{21}H_{21}N_3O_2$	72.59	6.09	12.09	72.75	6.27	12.13
27	p-$O_2NC_6H_4$	$-(CH_2)_6-$		C_6H_5	63	170–171	$C_{22}H_{23}N_3O_2$	73.10	6.41	11.62	72.87	6.54	11.75
28	p-$O_2NC_6H_4$	$-(CH_2)_7-$		C_6H_5	69	177–178	$C_{23}H_{25}N_3O_2$	73.57	6.71	11.19	73.69	6.88	11.17
29	p-$O_2NC_6H_4$	$-(CH_2)_4CH(CH_3)-$		C_6H_5	55	166–167	$C_{22}H_{23}N_3O_2$	73.10	6.41	11.62	73.37	6.60	11.41
30	p-$O_2NC_6H_4$	$-(CH_2)_2CH(CH_2)_2-CH_3$		C_6H_5	69	168–169	$C_{22}H_{23}N_3O_2$	73.10	6.41	11.62	73.36	6.38	11.80
31	p-$O_2NC_6H_4$	C_6H_5	C_6H_5	C_6H_5	40	235–236	$C_{28}H_{21}N_3O_2$	77.94	4.90	9.73	77.42	4.86	

TABLE II

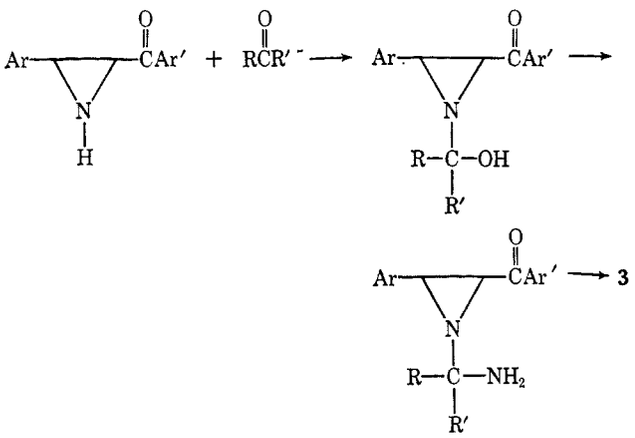
CHEMICAL SHIFTS AND COUPLING CONSTANTS OF 1,3-DIAZABICYCLO[3.1.0]HEX-3-ENES IN DEUTERIOCHLOROFORM

Compd	δ, ppm, from $(CH_3)_4Si$[a] 2-H	5-H	6-H	Cps[b] $J_{2,5}$	$J_{2,6}$	$J_{5,6}$
5[a]	5.70	3.58	2.62	1.2	1.0	1.6
6[a]	5.55	3.60	2.65	1.4	1.0	1.4
8	6.80	3.75	2.49	1.4	0.8	2.0
11	6.84	3.84	2.48	1.6	0.9	2.2
15	...	3.63	2.63	...	...	1.8

[a] The 2-H chemical shift in compounds **5** and **6** show first-order splitting owing to geminal methyl and methylene groups, respectively. [b] Differences in J values could be attributed to factors such as dihedral angle, electronegativity of substituents, bond length, etc., known to affect coupling constants.[8]

protons is consistent with a *trans* configuration. If the protons at C_5 and C_6 were *cis*, a coupling constant larger than 3 cps should have been observed.[8,11,12] This, together with the steric course of the reaction, *i.e.*, that *trans*-aziridinyl ketones are used as starting reagents and that *trans*-aziridinyl ketones are obtained from the hydrolysis of the 1,3-diazabicyclo[3.1.0]hex-3-enes, leaves little doubt that the C_5 and C_6 protons have a *trans* configuration.

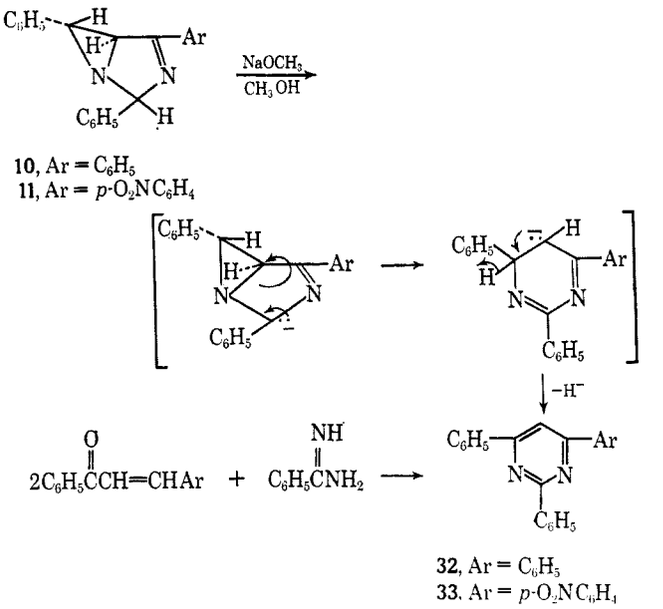
Several mechanisms can be proposed for the formation of the 1,3-diazabicyclo[3.1.0]hex-3-enes. The aziridinyl ketone could react with the aldehyde or ketone to form an aminohydrin which reacts with ammonia to give a diamine that undergoes cyclization to the 1,3-diazabicyclo[3.1.0]hex-3-ene. Alternatively,



the aziridinyl ketone could react with preformed aldimines or ketimines to give intermediates similar to those depicted above. Similar intermediates have been suggested for the formation of 3-imidazolines from α-amino ketones, ketones, and ammonia.[6]

A rearrangement and subsequent oxidation occur when 2,4,6-triphenyl- or 2,6-diphenyl-4-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-enes (**10** and **11**) are treated with methanolic sodium methoxide. The products of these reactions are 2,4,6-triphenyl- and 2,4-diphenyl-6-*p*-nitrophenylpyrimidines (**32** and **33**, respectively). An authentic sample of **33** was prepared by reaction of the chalcone **34** with benzamidine according to the procedure of Dodson and Seyler[13] (Scheme I). Compound **32** has been previously characterized.[13]

SCHEME I



A rapid photochromic change occurs with all the 6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-enes when exposed to sunlight for a few moments. The initially white or cream crystals are converted to deep blue crystals. The blue fades after several days in the dark. Prolonged exposure to ultraviolet light yields a mixture of compounds. The 6-phenyl- or 6-*m*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-enes are not so sensitive to ultraviolet light, although a red coloration is produced which quickly fades in the dark. All of these photochromic changes are currently being investigated.

The hydrochlorides of 2,2-dimethyl- and 2,2-diethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-enes (compounds **15** and **22**) and 2,6-diphenyl-4-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**11**) were easily prepared by passing dry hydrogen chloride through an ethereal solution of the diazabicyclo compounds. The 1,3-diazabicyclo[3.1.0]hex-3-enes can be recovered from their salts by neutralization with sodium methoxide. The site of protonation has not been unequivocally established. It is interesting to note that the salts of the photochromic compounds **15** and **22** are also photochromic and turn bright red instantaneously in sunlight.

Experimental Section

1,3-Diazabicyclo[3.1.0]hex-3-enes (4–31, Table I).—The appropriate *trans*-2-aryl-3-aroylaziridine[14,15] (1 g) was dissolved or suspended in 20 ml of commercial absolute ethanol. A large excess of the aldehyde or ketone (*i.e.*, 3 ml of acetone, benzaldehyde, etc.) was added together with 0.1 g of ammonium bromide and the reaction mixture was saturated with ammonia. The reaction flask was stoppered and kept at room temperature for a minimum of 3 days. The 1,3-diazobicyclo[3.1.0]hex-3-enes which had gradually precipitated during this time were filtered and dried. All of the products were recrystallized from 95% ethanol except compound **31** which was recrystallized from isopropyl alcohol and acetone.

Conversion of 2,6-Diphenyl-4-*p*-nitrophenyl-1,3-diazabicyclo-[3.1.0]hex-3-ene (11) into 2,4-diphenyl-6-*p*-nitrophenylpyrimidine (33).—A solution of 355 mg of **11** was dissolved in 15 ml of 0.13 *M* sodium methoxide in methanol. The reaction mixture was kept at room temperature for 24 hr during which time **33**

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slowly precipitated. The crude **33** (247 mg, 69%) was filtered, dried, and recrystallized four times from 95% ethanol. The recrystallized **33** thus obtained melted at 212–213°.

Anal. Calcd for $C_{22}H_{15}N_3O_2$: C, 74.75; H, 4.27; N, 11.89. Found: C, 74.93; H, 4.42; N, 12.11.

Alternate Synthesis of 33.—Reaction of the chalcone **34** and benzamidine according to the procedure of Dodson and Seyler gave crude **33**. The crude **33** was dissolved in hot acetonitrile and precipitated by the addition of a few drops of water. This crude purification was repeated and the **33** then recrystallized four times from 95% ethanol. The **33** so obtained melted at 212–215° and was identical with the product isolated from the reaction of **11** with sodium methoxide.

Conversion of 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (10) into 2,4,6-triphenylpyrimidine (32) was analogous to the formation of **33** from **11** except that the reaction mixture was refluxed for 24 hr and the solvent evaporated. The residue was washed well with water and recrystallized three times from 95% ethanol. The recrystallized **32** obtained in 30% yield melted at 185–186° (lit.[13] mp 183.5–185°).

Conversion of 2,2-Dimethyl-4-phenyl-6-*p*-nitrophenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (15) into *trans*-2-(*p*-Nitrophenyl)-3-benzoylaziridine.—A mixture of 307 mg of **15** and 10 ml of commercial acetic acid was kept at room temperature for 3 days. The acetic acid was evaporated and the gummy residue treated with 10 ml of methanol. The 2-*p*-nitrophenyl-3-benzoylaziridine (262 mg) was recrystallized twice from 95% ethanol to give material, mp 140–141°, which was identical with an authentic sample of the aziridine. Compounds **18**, **22**, **26**, and **29** reacted analogously to give 2-*p*-nitrophenyl-3-benzoylaziridine in 41, 36, 82, and 74% yields, respectively. Cyclohexanone was also isolated in the form of its 2,4-dinitrophenylhydrazone from the acetolysis of compound **26**.

2,2-Dimethyl-4-phenyl-6-nitrophenyl-1,3-diazabicyclo[3.1.0]-hex-3-ene Hydrochloride.—Dry hydrogen chloride was bubbled through a solution of 500 mg of **15** in 75 ml of dry ether for about 5 min. The red hydrochloride was filtered and washed repeatedly with dry ether. Decomposition of the hydrochloride took place between 185–200°.

Anal. Calcd for $C_{18}H_{18}ClN_3O_2$: Cl, 10.31. Found: Cl, 10.21.

The hydrochlorides of **11** and **22** were also prepared and decomposed at 205–245° and 98–145°, respectively. The chlorine analyses for these two compounds were close to the theoretical.

***trans*-2-Phenyl-3-*p*-nitrobenzoylaziridine** was prepared by suspending 5 g of 4′-nitrochalcone dibromide in a mixture of 50 ml of 95% ethanol and 12–15 ml of concentrated ammonium hydroxide. The mixture was stirred 6.5 hr and filtered. The material was recrystallized from ethanol and melted at 122–122.5°.

Anal. Calcd for $C_{15}H_{12}N_2O_3$: C, 67.15; H, 4.51; N, 10.44. Found: C, 67.12; H, 4.83; N, 10.06.

Registry No.—**4**, 13591-54-3; **5**, 13591-55-4; **6**, 13591-56-5; **7**, 13591-57-6; **8**, 13591-58-7; **9**, 13591-59-8; **10**, 13591-60-1; **11**, 13591-61-2; **11** hydrochloride, 13591-62-3; **12**, 13591-63-4; **13**, 13746-77-5; **14**, 13591-64-5; **15**, 13591-65-6; **15** hydrochloride, 13591-66-7; **16**, 13591-67-8; **17**, 13591-68-9; **18**, 13591-69-0; **19**, 13573-32-5; **20**, 13591-70-3; **21**, 13573-33-6; **22**, 13591-71-4; **22** hydrochloride, 13591-72-5; **23**, 13591-73-6; **24**, 13591-74-7; **25**, 13591-75-8; **26**, 13591-76-9; **27**, 13591-77-0; **28**, 13591-78-1; **29**, 13591-79-2; **30**, 13591-80-5; **31**, 13639-90-2; **33**, 13573-34-7; *trans*-2-phenyl-3-*p*-nitrobenzoylaziridine, 13591-81-6; **34**, 1666-86-0.

Acknowledgment.—Financial assistance for this investigation was provided by Grant CA-10015 from the National Institutes of Health and from Grant DA-ARO-D-31-124-G821, U. S. Army Research Office, Durham, N. C.

Cyclization Reactions of 6-Hepten-2-yl Radicals, 1-Trichloromethyl-6-hepten-2-yl Radicals, and Related Compounds[1]

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Received November 4, 1966

Bromotrichloromethane, carbon tetrachloride, and chloroform all react with 1,6-heptadiene to give cyclization products having a five-membered ring, contrary to published reports. An unusually clean cyclization of 6-iodo-1-heptene to *cis*- and *trans*-1-methyl-2-iodomethylcyclopentanes occurred by heating with azonitrile initiator. Model compounds were used for comparison of their infrared and nmr spectra to confirm the structures of the new compounds. Free-radical reaction of 1-iodoperfluoropropane with 1,6-heptadiyne gave little if any cyclization product, possibly because of the highly strained structure which would have resulted. Addition of carbon tetrachloride to 1,6-heptadiene by the redox–transfer method gave considerably better yield of product than azonitrile initiation.

Cyclization of certain perfluoroalkyl-substituted 6-hepten-2-yl radicals to a five-membered ring product was observed[2] in the free-radical reaction of iodoperfluoroalkane and 1,6-heptadiene. This behavior contrasts with that observed in cyclic polymerization which is reported[3,4] to give six-membered rings, but resembles that recently reported by Walling and Pearson[5] and by Lamb, Ayers, and Toney[6] for the 5-hexen-1-yl radical.[7] Julia and Maumy[8] and Cadogan, Hey, and Hock[9] have obtained both five- and six-membered ring products from free-radical cyclizations. Friedlander and Tiers,[10] in a patent which discloses many related free-radical reactions of 1,6-heptadiene and its analogs with various addenda, describe cyclization products from presumably similar radicals in terms of six-membered ring structures.[11] A detailed report of these reactions has not appeared, and it was felt that, in view of the unexpected nature of our more recent results,[2] a closer examination of this subject would be desirable.

(1) This work was supported by the U. S. Army Research Office, Durham.

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(4) G. B. Butler and R. J. Angelo, *ibid.*, **79**, 3128 (1957).

(5) C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964).

(6) R. C. Lamb, P. W. Ayers, and M. K. Toney, *ibid.*, **85**, 3483 (1963).

(7) It was also noted[5] that the 5-penten-1-yl radical failed to cyclize at all under these conditions; this was attributed to an unfavorable highly strained transition state leading to cyclic product. These results also parallel our finding that 1,5-hexadiene gave no cyclic product in free-radical reactions with iodoperfluoropropane.[2]

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(10) W. S. Friedlander and G. Van Dyke Tiers, German Patent 1,098,942 (Feb 1961) (to Minnesota Mining and Manufacturing Co.).

(11) *Cf.* C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 446.