Department of Merrell-National Laboratories. The program used was previously described by Allen, *et al.*[6] Parameters chosen were those suggested by Streitwieser.[7]

5-Bromo-1,6-dimethyl-1*H*-imidazo[1,2-*a*]imidazole Hydrobromide Monohydrate (2).—A solution of Br_2 (1.2 g, 0.0074 mol) in $CHCl_3$ (5 ml) was slowly added to **1** (1 g, 0.0074 mol) in $CHCl_3$ (15 ml) maintained at 5°. The solution was stirred for 5 min and evaporated and the crude solid crystallized from $MeNO_2$ to give **2** (1.5 g), mp 132–133° dec. *Anal.* Calcd for $C_7H_{11}Br_2N_3O$: C, 26.86; H, 3.54; N, 13.42. Found: C, 27.07; H, 3.36; N, 13.64.

Reaction of 2 with Piperidine.—A mixture of **2** (3.1 g, 0.01 mol) and piperidine (2.5 g, 0.03 mol) in C_6H_6 (50 ml) was refluxed for 4 hr and cooled. The solution was extracted with H_2O (discarded), and the organic phase was dried ($MgSO_4$) and evaporated. The residue (1.6 g) was not readily purified either as the free base or as a salt; however, the nmr spectrum of the crude material confirmed the structure as 1,6-dimethyl-5-piperidino-1*H*-imidazo[1,2-*a*]imidazole (**3**).

1,6-Dimethyl-5-formyl-1*H*-imidazo[1,2-*a*]imidazole (4).—**1** (50 g, 0.37 mol) in DMF (100 ml) was slowly added to a formylation complex prepared as described by James, *et al.*,[8] from DMF (250 ml) and $POCl_3$ (80 g, 0.52 mol). The solution was stirred 1 hr at 25°, chilled for 16 hr, and then treated with H_2O (300 ml) and sufficient $NaHCO_3$ to bring the pH to 8. The solution was heated to reflux, cooled, and extracted with $CHCl_3$. The organic phase was extracted with 10% HCl which was then basified with 10% NaOH and extracted with $CHCl_3$. The $CHCl_3$ was evaporated to give a crude solid (50 g) which was crystallized from petroleum ether (bp 90–100°) yielding **4** (29 g), mp 130–135° (oxime mp 280° dec). *Anal.* Calcd for $C_8H_9N_3O$: C, 58.88; H, 5.56; N, 25.75. Found: C, 58.82; H, 5.54; N, 25.79.

1,6-Dimethyl-5-nitro-1*H*-imidazo[1,2-*a*]imidazole (5).—To concentrated H_2SO_4 (5 ml) chilled to −10° was slowly added **1** (1.3 g, 0.01 mol). The temperature was lowered to −20° and ethyl nitrate (0.9 g, 0.01 mol) was added dropwise. After stirring 5–10 min, the acid solution was poured on crushed ice and the pH adjusted to 4–5 with aqueous NaOH. The aqueous phase was extracted with $CHCl_3$ which was evaporated to give crude **5** (1.2 g). Crystallization from C_6H_6 gave pure **5**, mp 181–184°. *Anal.* Calcd for $C_7H_8N_4O_2$: C, 46.66; H, 4.47; N, 31.10. Found: C, 46.81; H, 4.44; N, 31.19.

Reduction of 5 in Acetic Anhydride Solution.—A solution of **5** (4 g, 0.02 mol) in Ac_2O (50 ml) was reduced under 1.5 atm of H_2 pressure for 16 hr in the presence of Raney nickel catalyst.[9] The catalyst was filtered off, the Ac_2O was evaporated, and the residue was taken up in $CHCl_3$. After stirring vigorously for several hours with aqueous $NaHCO_3$, the $CHCl_3$ was separated and evaporated to an oil (3.8 g) which crystallized on standing. A tlc showed two components, one predominant. By careful crystallization from EtOAc a small amount of the minor constituent was obtained, mp 133–137°. It was unsuitable for elemental analysis, but was shown by its nmr spectrum to be principally 5-acetamido-1,6-dimethyl-1*H*-imidazo[1,2-*a*]imidazole (**6**). The mother liquors were evaporated and carefully treated with *i*-PrOH–Et_2O to give a white solid, mp 124–127°, which was shown by its elemental analysis and nmr spectrum to be 5-diacetylamino-1,6-dimethyl-1*H*-imidazo[1,2-*a*]imidazole (**7**). *Anal.* Calcd for $C_{11}H_{14}N_4O_2$: C, 56.40; H, 6.02; N, 23.91. Found: C, 56.02; H, 6.10; N, 24.09.

1,6-Dimethyl-2(or 3),5-dinitro-1*H*-imidazo[1,2-*a*]imidazole (8).—In a manner similar to the preparation of **5**, **1** (16.2 g, 0.12 mol) in H_2SO_4 (150 ml) was treated with 1 equiv of ethyl nitrate (10.9 g, 0.12 mol) at −20°. After addition was complete the temperature was adjusted to −15° and a second equivalent of ethyl nitrate was added. The acid solution was stirred at −5° for 20 min and poured on crushed ice. The resulting solution was extracted with $CHCl_3$ which on evaporation gave crude **8**. Recrystallization from H_2O gave pure **8** (3.2 g), mp 190–192°. *Anal.* Calcd for $C_7H_7N_5O_4$: C, 37.34; H, 3.14; N, 31.11. Found: C, 37.41; H, 3.10; N, 31.24.

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Registry No.—**1**, 38739-75-2; **2**, 38739-94-5; **3**, 38739-95-6; **4**, 38739-96-7; **5**, 38739-97-8; **6**, 38739-98-9; **7**, 38739-99-0; **8**, 38740-00-0; piperidine, 110-89-4.

Acknowledgments.—The authors wish to thank Drs. Fred Kaplan and David Lankin of the University of Cincinnati for attempting the NOE determination. We also wish to express our thanks to Dr. Michael Randall for supervising the HMO calculations and Dr. Michael Edwards for his invaluable suggestions and assistance.

Internal Strain in Benzylic Radical Formation. The Effect of Ring Size in the Reaction of Trichloromethyl Radicals with Benzocycloalkenes

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The degree of importance of steric factors in the formation of organic free radicals has not received full elucidation. Part of this is due to the complexity of the situation and the need to assess both intramolecular and intermolecular effects. The former can qualitatively be considered in terms of I strain as originally proposed by Brown.[1] Overberger, in describing the extension of this generalized approach to radical-forming reactions, has equated changes in activation energy with strain changes in cyclic systems.[2] Intermolecular interactions between attacking radicals and substrates can also greatly influence the course and extent of reaction. Such bulky species as the dialkylamino radical cation[3] and the trichloromethyl radical[4] show unexpectedly increased selectivity in hydrogen-abstraction processes because of this form of steric control.

The relation of internal strain to radical formation has been studied by several groups of workers. Relative rates of hydrogen atom abstraction from cycloalkanes in both the liquid and vapor phases have been obtained using chlorine atom,[5] bromine atom,[6] methyl radical,[7] trichloromethyl radical,[8] and trichloromethylsulfonyl radical,[5] among others. It was noted that ring size did, indeed, affect the relative rates of reaction. With few exceptions the order of reactivity was cyclobutane ≪ cyclopentane < cyclohexane < cycloheptane < cyclooctane. This order clearly shows that the ground-state strain of the cycloalkane cannot be the cause of the effect.

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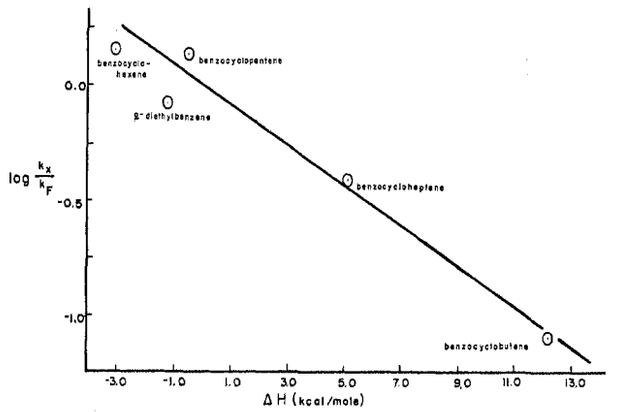

Figure 1.—Correlations of relative reactivities with calculated strain energy changes.

Prior success has been obtained in correlating the reactivity of polycyclic systems with calculated changes in strain energy for both carbonium ion[9] and radical[10] reactions. In hope of extending this approach to the study of the effect of ring size on the ease of hydrogen atom abstraction, a series of benzocycloalkenes was treated with the trichloromethyl radical generated photolytically from bromotrichloromethane at 70°. The trichloromethyl radical was chosen both for its high selectivity and the convenience of operating in a homogeneous medium. The benzannelated cycloalkanes were chosen over their monocyclic counterparts for the following reasons. The annelation of the benzene ring imparts a high degree of rigidity to the hydrocarbon. The effective number of conformers is thereby greatly reduced, thus simplifying all calculations. The presence of the aromatic ring will also cause reaction to take place exclusively in the benzylic position. Table I shows the relative reactivities of

TABLE I

RELATIVE REACTIVITIES OF SOME BENZOCYCLOALKENES TOWARD THE TRICHLOROMETHYL RADICAL AT 70°[a]

Registry no.	System	Relative rate	Average deviation	Number of runs
4026-23-7	Benzocyclobutene	0.076	0.004	5
95-13-6	Benzocyclopentene	1.39	0.08	5
91-20-3	Benzocyclohexene	1.41	0.08	7
264-06-2	Benzocycloheptene	0.42	0.03	5
135-01-3	*o*-Diethylbenzene	0.84	0.06	9

[a] All results given relative to fluorene.

this series of benzocycloalkenes and the electronically equivalent *o*-diethylbenzene. These rates were obtained relative to hydrogen abstraction from fluorene using nmr spectroscopy as the analytical device. It had been originally planned to utilize glc in this capacity; however, the facile dehydrobromination of many of the benzylic halides on the column precluded this approach. The decrease in the nmr signal for benzylic protons was taken as defining the extent of reaction for both the benzocycloalkene and fluorene. These signals are easily separable, being located in distinct areas of the spectrum. All areas were found relative to that of the aliphatic protons in *tert*-butylbenzene. This last compound is suitable as an internal standard owing to its unreactivity under the present conditions.[11]

The strain energies for all species were determined using standard techniques and parameters.[9,10,12] Certain assumptions were of necessity made for the strain associated with the transition states. These structures were assumed to strongly resemble the intermediate radicals.[13] Although cyclic radicals may assume pyramidal structure to relieve potential angle strain,[14-16] it was felt that in the product systems planarity would be maintained in order to maximize the favorable resonance interaction. In Table II are

TABLE II

CALCULATED STRAIN ENERGIES[a]

System	Ground state	Radical	Difference
Benzocyclobutene	116.547	128.637	12.110
Benzocyclopentene	24.797	24.328	−0.469
Benzocyclohexene	17.238	14.195	−3.043
Benzocycloheptene	21.941	27.037	5.096
o-Diethylbenzene	22.627	21.341	−1.286

[a] All results in kcal/mol.

shown the calculated strain energy differences for the present systems. While absolute strain energies, particularly for the cyclobutane derivatives, are strongly exaggerated, the energy differences appear reasonable.

The changes in strain energy may be caused by several factors. In the case of benzocyclobutene the large, unfavorable change in angle strain is the principal factor. This is true to a much lesser extent in benzocyclopentene and is offset by favorable changes in torsional and nonbonded interactions. In benzocyclohexene a favorable change in angle strain is calculated, while in benzocycloheptene changes in angle and torsional strain are both unfavorable. Effects in *o*-diethylbenzene are nearly equivalent in both ground state and radical.

Figure 1 shows a graph of the logarithms of the relative rates plotted against the calculated strain energy changes. Good linearity is obtained. A slope of −0.082 is found with a correlation coefficient of −0.974. This slope is appreciably smaller than the corresponding values of −0.327 and −0.537 found for formation of aliphatic tertiary and secondary radicals.[10] The present small dependence upon strain factors is not, however, surprising in view of the high stability and concomitant ease of formation of benzylic radicals. It is also of interest that *o*-diethylbenzene falls far below the correlation. It is felt that this is due to an intermolecular effect in which one of the ethyl groups may hinder the approach of the large trichloromethyl radical to the benzylic position of the second group. This is much less likely to occur in the more rigid benzocycloalkenes.

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Experimental Section

Materials.—Bromotrichloromethane, benzocyclohexene, benzocyclopentene, and *tert*-butylbenzene were obtained from commercial sources. Benzocyclobutene was kindly donated by Professor Phillip Radlick. Benzocycloheptene was prepared from the Wolff–Kishner reduction of 1-benzosuberone. All materials were purified before use. Purities greater than 99% were determined by glc.

Product Studies.—A mixture of 4.232 g (32.186 mmol) of benzocyclohexene and 36.60 g (184.64 mmol) of bromotrichloromethane were treated under nitrogen for 18 hr at 70° with irradiation by our standard source. After reaction and removal of excess bromotrichloromethane, the reaction mixture was analyzed by gas–liquid chromatography on a 5% SE-30 column. It was shown that about 40% of the tetralin had reacted and one product with a slightly longer retention time than tetralin was formed. The compounds were collected as they eluted from the glc column. An nmr spectrum identified the product as 1,2-dihydronaphthalene. This was formed by probable dehydrohalogenation of the initially formed bromide. The unreacted starting material amounted to 19.311 mmol (2.51 g) and the product to 1.49 g (11.620 mmol). The material balance thus found is 96.1%. Although no attempt was made to isolate the initial bromide, its presence could be readily detected in the reaction mixture by nmr spectroscopy. No elimination product could be detected in the reaction mixture before passage through the SE-30 column.

Kinetic Studies.—Solutions of fluorene, a cycloalkene, bromotrichloromethane, and *tert*-butylbenzene were prepared in the approximate molar ratio of 2:4:20:1. Approximately 0.75 ml of the solution was placed in each of the several ampoules. The ampoules were cooled to Dry Ice–isopropyl alcohol temperature until the solutions solidified. The ampoules were evacuated at 0.5–1.0 mm and flushed with nitrogen several times with three intermediate thawings. The ampoules were sealed under vacuum and one was reserved for the analysis of the unreacted starting materials. The remainder were placed horizontally just below the surface of a mineral oil constant-temperature bath maintained at 70.0 ± 0.5°. The solution was irradiated with ultraviolet light provided by a Sylvania 275-W sun lamp placed 20 cm above the surface of the oil. Reaction times varied from 20 to 40 hr, by which time 30–70% of the total hydrocarbons had reacted. The ampoules were then cooled and opened. Analysis of the mixtures, both before and after the reaction, was carried out *via* nmr spectroscopy. All determinations were run in replicate.

Registry No.—Trichloromethyl radical, 3170-80-7.

Acknowledgments.—We wish to thank the Computer Center of Oregon State University for supplying the requisite funds for these calculations. Deepest gratitude is also expressed to Professor Phillip Radlick of the University of California, Riverside, who generously supplied us with a sample of benzocyclobutene.

Communications

See Editorial, *J. Org. Chem.*, **38**, No. 19, 4A (1972)

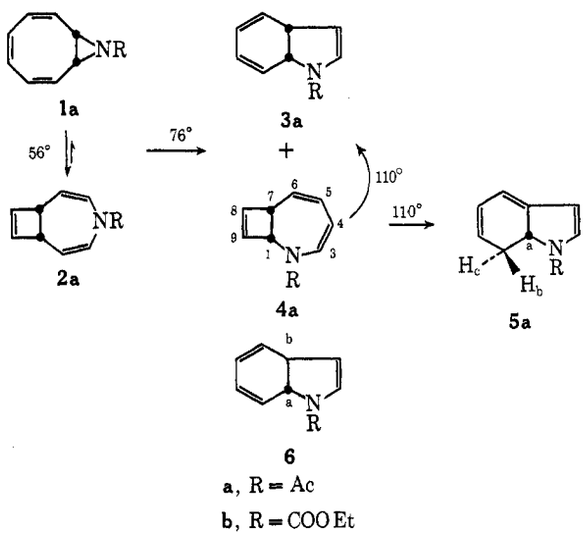
Thermal Reorganization of Select Azabicyclo[*m.n.*0] nonatrienes. Generation of a *cis,cis,trans,cis*-Azonine

Summary: Mild thermal exploration of the C_8H_8NAc energy surface resulted in the discovery of a variety of mechanistically revealing transformations and the detection of a *cis,cis,trans,cis*-azonine.

Sir: Recently, we described the thermal behavior of various *N*-methoxycarbonylazabicyclo[*m.n.*0]nonatrienes.[1] We now report on the thermolysis of the acetamide analogs in terms of (i) product distribution and (ii) cycloadditive trapping.

When warmed to 56° in deaerated (N_2) benzene, **2a**[2] produces a two-component equilibrium consisting (nmr) of ~95% **2a** and 5% **1a** (Scheme I). In turn, when exposed to a higher temperature (76°) this pair undergoes rapid ($t_{1/2}$ ~80 min) and irreversible thermolysis to **3a** and **4a** in the ratio of 1.2:1, respectively (nmr). The thermolysate was separated into its individual components by chromatography at −15° and **3a** was characterized on direct comparison (nmr, ir) with an authentic sample[3] while **4a** was formulated on the basis of its spectra: ν_{CO}^{neat} 1675 cm^{-1}; *m/e* 161 (P^+, 13%);

SCHEME I



$\lambda_{max}^{C_6H_{14}}$ 282 nm (ε 4300), 214 (6000); nmr (100 MHz, benzene-d_6, ~60°) τ 3.92 (1 H, dd, *J* = 2.6, 1.0 Hz, H_8 or H_9), 4.02 (1 H, d, *J* = 8.5 Hz, H_3), 4.1 (1 H, br d, *J* ~ 5 Hz, H_1), 4.30 (1 H, dd, *J* = 11.5, 6.0 Hz, H_6), 4.48 (1 H, dd, *J* = 2.6, 0.7 Hz, H_8 or H_9), 4.51 (1 H, dd, *J* = 11.5, 5.7 Hz, H_5), 4.89 (1 H, dd, *J* = 8.5, 5.7 Hz, H_4), 6.58 (1 H, dd, *J* = 6.0, 4.8 Hz, H_7), 8.28 (3 H, s, methyl).[4] While isomers **3a** and **4a** do not intercon-

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