There was no evidence to support the alternate course of cyclization resulting in the formation of a six-membered ring compound (VII) containing primary and secondary difluoramino groups.

The observed cyclization has an analogy to the mechanism proposed for the formation of certain intermediates and cyclic structures in the intra–intermolecular polymerization of various diallyl compounds;[4] however, only six membered ring structures have been reported in these instances. Julia[5] has reported the cyclization of appropriately substituted 5-hexen-1-yl radicals to both five- and six-membered rings, while others[6,7] found that similar radicals gave predominately five-membered ring compounds. Brace[8] has reported that the azobisisobutyronitrile-initiated reaction of perfluoroalkyl iodides with heptadiene and diallyl ether yielded only the cyclopentane derivatives as cyclic products, and proposed a mechanism as presented above for their formation. This latter work likely represents the first example of the cyclization of 1,6-dienes *via* radical attack to give simple cyclic products, and hence, the presently reported work is another case of a similar type reaction.

Other 1,6-dienes investigated were N,N-diallyl acetamide and acrylic anhydride. A bis(difluoramino) derivative of N,N-diallyl acetamide was obtained which was believed to be a cyclic five-membered ring product; however, the compound was not purified sufficiently for conclusive structural determination. The reaction with acrylic anhydride resulted in its polymerization and no attempt was made toward the structural characterization of this polymeric material.

Experimental Section

Tetrafluorohydrazine–Diallyl Ether Reaction.—To a thick-walled glass container (Fischer-Porter Aerosol tube) of 100-cc capacity was introduced a mixture of 5.0 g (0.51 mole) of diallyl ether in 30 ml of carbon tetrachloride. The Aerosol tube was connected to a high-pressure manifold and the entire system was flushed three times with dry nitrogen. The system was degassed and then precharged with tetrafluorohydrazine until no further pressure drop was observed (200 psi). The system was heated by an externally placed oil bath to a temperature of 80° and this temperature was maintained over a period of 3 hr. During this time the N_2F_4 pressure was maintained between 420 and 160 psi by frequently recharging as necessary. Heating was continued until no further pressure drop was observed. After cooling, the mixture was degassed by first venting the excess N_2F_4 and flushing several times with dry nitrogen. The reaction mixture was transferred to a RB flask and the solvent removed at reduced pressure on a rotary evaporator to give 12.4 g of liquid residue. Examination of the residue by gas chromatography indicated a mixture of three components in the ratio 2:1:1 based on gc retention times and peak areas. Distillation of the mixture through an 18-in. Holtzman column gave two fractions, bp 60–65° (4 mm) and 76–78° (4 mm), but was ineffective in giving complete separation of the three components. A small quantity of each was separated by gc.[9] Each product was characterized by its nmr spectra and elemental analysis.

Anal. Calcd for $C_6H_{10}F_8N_4O$: C, 23.53; H, 3.27; F, 49.67; N, 18.30. Found (I): C, 23.71; H, 3.17; F, 49.88; N, 18.62. Calcd for $C_6H_{10}F_4N_2O$: C, 35.64; H, 4.95; F, 37.62; N, 13.86. Found (II): C, 35.76; H, 4.82; F, 37.70; N, 14.25. Found (III): C, 35.78; H, 5.08; F, 37.41; N, 14.17.

Registry No.—I, 13673-71-7; II, 13673-72-8; III, 13673-73-9; tetrafluorohydrazine, 10036-47-4; diallyl ether, 557-40-4.

Acknowledgment.—The encouragement and support of Dr. R. C. Petry, the technical support of Mr. Hollis H. Hill, and the interpretation of the nmr spectra by Dr. F. A. Johnson and Mrs. Carolyn Haney are gratefully acknowledged.

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A Photochemical Cycloaddition of Thiobenzophenone to α-Phellandrene

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An extensive study of the ultraviolet irradiation of thiobenzophenone in alcoholic solvents was reported by Oster and co-workers.[1] The photolytic products from thiobenzophenone were benzhydryl mercaptan, dibenzhydryl disulfide, and tribenzhydryl tetrasulfide, whereas that from benzophenone was dibenzopinacol.[2]

Although the photochemical cycloaddition of carbonyl compounds to carbon–carbon double bonds to form oxetanes is well known,[3–10] very few studies on the photoreaction of thioketones with olefinic compounds have been found in the literature. Dobashi and co-workers[11] observed the formation of 3,3,4,4-tetraphenyl-2,5-dithiabicyclo[4,4,0]decane or 3,3,4,4-tetraphenyl-7-oxa-2,5-dithiabicyclo[4,4,0]decane by the photoaddition of thiobenzophenone to cyclohexene or 2,3-dihydropyran, respectively. Kaiser and Wulfers[12] have also reported the novel photolytic reaction of the mixture of thiobenzophenone and ethylene derivatives to form 1,1-diphenylethylene derivatives. A four-membered ring containing a sulfur atom (thietane) was postulated as a possible intermediate for this photolytic reaction.

When an equimolar mixture of thiobenzophenone and α-phellandrene was irradiated with a Pyrex, filtered, ultraviolet light, we observed the gradual de-

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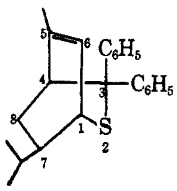
crease of the thiobenzophenone absorbance at 595 mμ, which was accompanied by the disappearance of its blue color. After 70 hr, thiobenzophenone had completely reacted. Thin layer chromatography of the irradiation mixture gave five spots of new products. They were separated by chromatography on silica gel into A (yield of 6.0% based on thiobenzophenone), B (1.9%), C (1.5%), D (1.1%), and E (17.9%). Compounds A and B were identified as dibenzhydryl disulfide and tetraphenylethylene, respectively, from their melting points (A, 152°; B, 220°)[1,13] and nmr spectra. From the elemental analyses and the molecular weight determinations, C, D, and E were found to have the same molecular formula as $C_{23}H_{26}S$, which is equal to that of a one to one adduct of thiobenzophenone with α-phellandrene. C, D, and E melted at 181, 141, and 87°, respectively, with decomposition into blue materials. They were oxidized by peracetic acid to the corresponding sulfones.

In each nmr spectra of C, D, and E, we observed only one vinyl proton. This fact suggested the following six structures (I, II, III, IV, V, VI). Compounds V and VI are addition products of thiobenzophenone and 1-isopropyl-4-methyl-hexa-1,3,5-triene. The latter is a photoisomer[14] of α-phellandrene. The nmr spectrum of C has a doublet which is centered at τ 9.00 (3 H) and coupled with a vinyl proton. This doublet indicates a methyl group. The nmr spectrum of D shows a doublet centered at τ 8.87 (3 H), which is also assignable to a methyl group. The methyl group of E was indicated by a doublet centered at τ 8.28 (3 H). The peaks at τ 9.00 and 8.87 in C and D are in an abnormally high field for the allyl methyl protons. This phenomenon is explained by the fact that the methyl group of C or D lies just above the plane of the benzene ring and that their protons are shielded by the interatomic diamagnetic effect. Among the possible structures I–VI, only I and II are influenced by this shielding effect. However, as the methyl group of I receives a greater shielding effect from the phenyl group than that of II because of its greater proximity, the methyl protons of I appeared in a higher field than those of II. Thus, the structures for C and D were suggested to be those of I and II, respectively.



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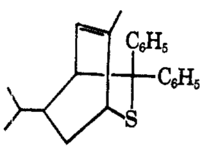

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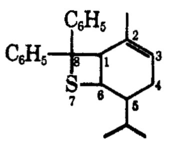

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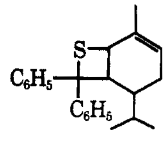

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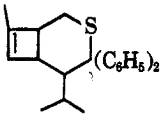
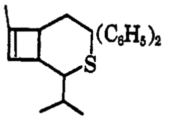
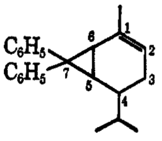


V

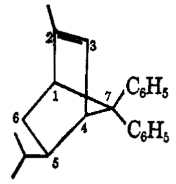


VI

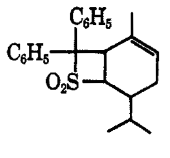
The structure of E also was proved by its nmr spectrum as follows. Compound E had a doublet centered at τ 6.49 (1 H) and a multiplet centered at 6.83 (1 H). As the doublet at this region (τ 6.49) is not reasonable for the structures of V and VI, they are precluded as possible structures of E. Accordingly, there remained only two possible structures, III or IV. Furthermore, the doublet and the multiplet must be assigned to a methyne proton on C-1 and C-6, respectively. If E had a structure of IV, the two methyne protons on C-1 and C-6 would have to show considerably different chemical shifts. But actually, the two methyne protons appeared at nearly the same field strength. Although the isopropyl group of IV would be expected to be under the influence of the ring current of the phenyl group, in actuality, the isopropyl group of E appeared at approximately the same field strength as that of C or D, *i.e.*, two doublets appeared at τ 9.20 and 9.25 in C, at 9.20 and 9.23 in D, and at 9.20 and 9.30 in E. From this fact, we can conclude that the isopropyl group of E is not under the influence of the phenyl group and that the structure of E was proved definitely to be that of III. When we tested the structures of I, II, and III by the following chemical reactions, the above conclusions about the structures were supported.



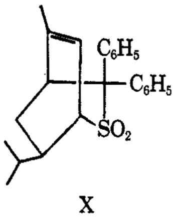
VII



VIII



IX



X

When E was reduced by Raney nickel, 1-methyl-4-isopropyl-7,7-diphenylbicyclo[4,1,0]hept-1-ene (VII) was produced. However, when C or D was reduced by Raney nickel, 2-methyl-5-isopropyl-7,7-diphenylbicyclo[2,2,1]hept-2-ene (VIII) was obtained in each case. Since the starting material *dl*-α-phellandrene was used, the photoproducts C, D, and E must be the racemates. Consequently, the reduction products from C and D would be expected to be similar. This expectation was confirmed by the fact that the reduction products from C and D were actually equal. Compounds I and II are the Diels-Alder adducts. The formation of these compounds suggested to us that the same compounds might be produced under the effect of heat. In fact, by heating an equimolar mixture of thiobenzophenone and α-phellandrene at 100°, we obtained the compounds I and II in yields of 3.6 and 7.7%, respectively. Simultaneously, III and dibenzhydryl disulfide were obtained in yields of 8.8 and 4.6%, respectively. It is concluded, therefore, that 1,4 adducts are formed more easily under the effect of heat than by ultraviolet light, and the 1,2 adduct is formed more easily by the latter than by the former. We are also led to believe that thiobenzophenone may be a useful dienophile for the Diels-Alder reaction and may be available for the syntheses of the

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six-membered heterocyclic compounds containing the sulfur atom.

Experimental Section

Irradiation of the Mixture of Thiobenzophenone and α-Phellandrene.—A mixture of 2.96 g of thiobenzophenone and 2.04 g of *dl*-α-phellandrene was sealed in a Pyrex tube containing nitrogen and was irradiated with the high-pressure mercury lamp for 70 hr. The blue color of thiobenzophenone gradually disappeared with time and after the 70-hr period complete decolorization was observed.

Separation of Photoproducts.—In a solution of 5:1 *n*-hexane-benzene the irradiation mixture was chromatographed first on 170 g of activated alumina, and then on 50 g of silica gel. By this procedure the mixture was separated into the following fractions: R_f 0.65, 0.58, 0.48, 0.38, and 0.33. These values were determined by thin layer chromatography (silica gel, *n*-hexene-benzene, 5:1). From the fraction R_f 0.65, a crystalline material was obtained which was recrystallized from ethanol to give 45 mg of tetraphenylethylene, colorless prisms, mp 220°. Its nmr spectrum in $CDCl_3$ showed a singlet at τ 2.92.

Anal. Calcd for $C_{20}H_{26}$: C, 93.94; H, 6.06; mol wt, 332.42. Found: C, 93.68; H, 6.26; mol wt, 323 (Rast).

From the fraction R_f 0.58, a crystalline material was obtained which was recrystallized from ethanol to give 76 mg of 3,3-diphenyl-5-methyl-7-isopropyl-2-thiabicyclo[2,2,2]oct-5-ene (I), colorless silky needles, mp 181°. The infrared spectrum showed $\nu_{\mathrm{CH}}^{\mathrm{KBr}}$ 2925, 2850, $\nu_{\mathrm{C=C}}^{\mathrm{KBr}}$ 1600, 1490, and $\delta_{\mathrm{CH}}^{\mathrm{KBr}}$ 1440, 750, 705 cm^{-1}; the ultraviolet spectrum showed $\lambda_{\max}^{\mathrm{EtOH}}$ 255 (ϵ 963), 261 (ϵ 915), 266 (ϵ 814), and 273 mμ (ϵ 541); the nmr spectrum in CS_2 gave peaks at τ 2.60–3.20 (10 H, aromatic), 3.98 (1 H, q, J_1 = 7.0, J_2 = 2.0 cps, vinyl), 6.64 (1 H, quartet, J_1 = 7.0, J_2 = 1.6 cps, C-1), 6.80 (1 H, multiplet, C-4), 8.25–8.95 (4 H, C-7, C-8, isopropylmethyne), 9.00 (3 H, doublet, J = 2.0 cps, C-5 methyl), 9.20 and 9.25 (6 H, two doublets, J = 6.0 cps, C-7 isopropyl).

Anal. Calcd for $C_{23}H_{26}S$: C, 82.58; H, 7.80; mol wt, 334.50. Found: C, 82.46; H, 7.71; mol wt, 338.

The fraction of R_f 0.48 was treated in the same manner as described above to give 55 mg of 3,3-diphenyl-6-methyl-8-isopropyl-2-thiabicyclo[2,2,2]oct-5-ene (II), colorless silky needles, mp 141°. The infrared spectrum showed $\nu_{\mathrm{CH}}^{\mathrm{KBr}}$ 2925, 2850, $\nu_{\mathrm{C=C}}^{\mathrm{KBr}}$ 1600, 1490, and $\delta_{\mathrm{CH}}^{\mathrm{KBr}}$ 1440, 745, 700 cm^{-1}; the ultraviolet spectrum showed $\lambda_{\max}^{\mathrm{EtOH}}$ 255 (ϵ 1090), 261 (ϵ 1040), 266 (ϵ 930), and 273 mμ (ϵ 647); the nmr spectrum in CS_2 gave peaks at τ 2.60–3.20 (10 H, aromatic), 4.10 (1 H, quartet, J_1 = 6.0, J_2 = 2.0 cps, vinyl), 6.55 (1 H, quartet, J_1 = 7.0, J_2 = 2.1 cps, C-1), 6.72 (1 H, quartet, J_1 = 6.0, J_2 = 1.7 cps, C-4), 7.70–9.00 (4 H, C-7, C-8, isopropylmethyne), 8.87 (3 H, doublet, J = 2.0 cps, C-6 methyl), 9.20 and 9.23 (6 H, two doublets, J = 6.0 cps, C-8 isopropyl).

Anal. Calcd for $C_{23}H_{26}S$: C, 82.58; H, 7.80; mol wt, 334.50. Found: C, 82.46; H, 7.78; mol wt, 328.

The fraction of R_f 0.38 afforded 2-methyl-5-isopropyl-8,8-diphenyl-7-thiabicyclo[4,2,0]oct-2-ene (III), which was recrystallized from methanol to give 893 mg of colorless prisms, mp 87°. The infrared spectrum showed $\nu_{\mathrm{CH}}^{\mathrm{KBr}}$ 2925, 2850, $\nu_{\mathrm{C=C}}^{\mathrm{KBr}}$ 1600, 1490, and $\delta_{\mathrm{CH}}^{\mathrm{KBr}}$ 1440, 755, 700 cm^{-1}; the ultraviolet spectrum showed $\lambda_{\max}^{\mathrm{EtOH}}$ 221 (ϵ 10,400) (shoulder), 256 (ϵ 1040), 262 (ϵ 969), 268 (ϵ 815), and 273 mμ (ϵ 645); the nmr spectrum in CS_2 showed peaks at τ 2.50–3.10 (10 H, aromatic), 4.57 (1 H, multiplet, vinyl), 6.49 (1 H, doublet, J = 7.4 cps, C-1), 6.83 (1 H, multiplet, C-6), 7.70–9.00 (4 H, C-4, C-5, isopropyl methyne), 8.28 (3 H, doublet, J = 2.0 cps, C-2 methyl), and 9.20 and 9.30 (6 H, two doublets, J = 7.5 cps, C-5 isopropyl).

Anal. Calcd for $C_{23}H_{26}S$: C, 82.58; H, 7.80; mol wt, 334.50. Found: C, 82.75; H, 7.84; mol wt, 336.

The fraction of R_f 0.33 yielded dibenzhydryl disulfide, which was recrystallized from ethanol to give 178 mg of colorless needles, mp 152°. The nmr spectrum in CCl_4 showed the singlets at τ 5.30 (2 H) and 2.89 (20 H).

Anal. Calcd for $C_{26}H_{22}S_2$: C, 78.32; H, 5.58; mol wt, 398.56. Found: C, 78.31; H, 5.70; mol wt, 387.

Thermoreaction of Thiobenzophenone with α-Phellandrene.—The mixture of 2.96 g of thiobenzophenone and 2.04 g of *dl*-α-phellandrene was heated at 100° for 29 hr in a sealed tube containing nitrogen. The reaction mixture showed four spots on thin layer chromatography (R_f 0.58, 0.48, 0.38, and 0.33). This reaction product was separated by the same method as were the photoproducts to give 180 mg of I, 383 mg of II, 441 mg of III, and 230 mg of dibenzhydryl disulfide.

Reduction of 2-Methyl-5-isopropyl-8,8-diphenyl-7-thiabicyclo[4,2,0]oct-2-ene (III) with Raney Nickel.—A mixture of a 20-ml ethanol solution of 200 mg of III and 2 g of Raney nickel was refluxed for 1 hr. The residual oil obtained from the filtrate was chromatographed on 25 g of silica gel using *n*-hexene as the eluent. After evaporation of the solvent, 140 mg of colorless liquid, bp 53° (10^{-3}–10^{-4} mm), bath temperature, was obtained. This liquid was proved to be 1-methyl-4-isopropyl-7,7-diphenylbicyclo[4,1,0]hept-1-ene (VII) by the following spectral and analytical data. The nmr spectrum in CCl_4 showed a singlet at τ 8.00, which is assignable to a methyl group. This lower value is explained by the influence of the ring current of the benzene ring. The other peaks of nmr spectrum were at τ 2.85 (5 H, singlet, aromatic), 2.96 (5 H, singlet, aromatic), 4.91 (1 H, multiplet, vinyl), 8.10–8.85 (5 H, C-3, C-4, C-6, isopropyl methyne), 9.05 and 9.09 (6 H, two doublets, J = 6.0 cps, isopropyl), and 9.25 (1 H, singlet, C-5); the infrared spectrum showed ν_{CH} 2970, 2900, $\nu_{\mathrm{C=C}}$ 1600, 1490, and δ_{CH} 1445, 805, 745, 700 cm^{-1}; the ultraviolet spectrum showed $\lambda_{\max}^{\mathrm{EtOH}}$ 210 (ϵ 12,300) (shoulder), 261 (ϵ 2080), 270 (ϵ 1275), and 277 mμ (ϵ 739).

Anal. Calcd for $C_{23}H_{26}$: C, 91.33; H, 8.67. Found: C, 91.16; H, 8.81.

Reduction of 3,3-Diphenyl-6-methyl-8-isopropyl-2-thiabicyclo[2,2,2]oct-5-ene (II) with Raney Nickel.—A mixture of a 12-ml ethanol solution of 120 mg of II and 1.2 g of Raney nickel was refluxed for 1 hr. The residual oil obtained from the filtrate gave 86 mg of colorless liquid, bp 60° (10^{-3}-10^{-4} mm), bath temperature, by the same procedure as described above. This substance proved to be 2-methyl-5-isopropyl-7,7-diphenylbicyclo[2,2,1]hept-2-ene (VIII) by the physical data. The nmr spectrum in CCl_4 showed a singlet at τ 9.01 (3 H), which is assignable to a methyl group. This higher value is explained by the influence of the ring current of the benzene ring. The other peaks were at τ 2.60–3.10 (10 H, aromatic), 4.07 (1 H, vinyl), 7.90–8.25 (2 H, multiplet, C-1, C-4), 8.25–8.90 (4 H, multiplet, C-5, C-6, isopropyl methyne), and 9.30 (6 H, doublet, J = 6.9 cps, isopropyl); the infrared spectrum showed ν_{CH} 2950, 2875, $\nu_{\mathrm{C=C}}$ 1600, 1490, and δ_{CH} 1440, 745, 700 cm^{-1}.

Anal. Calcd for $C_{23}H_{26}$: C, 91.33; H, 8.67. Found: C, 91.30; H, 8.83.

Reduction of 3,3-Diphenyl-5-methyl-7-isopropyl-2-thiabicyclo[2,2,2]oct-5-ene (I) with Raney Nickel.—A mixture of a 10-ml ethanol solution of 95 mg of I and 1 g of Raney nickel was refluxed for 1 hr. By the same procedure as described above, 73 mg of colorless liquid was obtained. It showed the same infrared and nmr spectra as those of a substance which was formed by the reduction of II. Thus, it was identified as VIII.

Oxidation of 2-Methyl-5-isopropyl-8,8-diphenyl-7-thiabicyclo[4,2,0]oct-5-ene (III).—To a solution of 140 mg of III in 8 ml of acetone, 2 ml of acetic acid and 1 ml of 30% aqueous hydrogen peroxide were added. After standing for 2 hr at room temperature, 4 ml of water was added, and the mixture was evaporated to dryness. The residual solid was refluxed with 30 ml of *n*-hexene for 0.5 hr. Evaporation of the filtrate from the undissolved solid afforded a crystalline material, which was recrystallized from *n*-hexene to give the corresponding sulfone IX as colorless needles, mp 133°. The infrared spectrum shows $\nu_{\mathrm{CH}}^{\mathrm{KBr}}$ 2950, 2875, $\nu_{\mathrm{C=C}}^{\mathrm{KBr}}$ 1600, 1490, $\delta_{\mathrm{CH}}^{\mathrm{KBr}}$ 1440, 700, and $\nu_{\mathrm{SO_2}}^{\mathrm{KBr}}$ 1290, 1150 cm^{-1}; the ultraviolet spectrum showed $\lambda_{\max}^{\mathrm{EtOH}}$ 255 (ϵ 693), 261 (ϵ 637), 267 (ϵ 560), and 273 mμ (ϵ 389). The nmr spectrum in CCl_4 showed peaks at τ 2.50–3.10 (10 H, aromatic), 4.26 (1 H, multiplet, vinyl), 6.42 (1 H, doublet, J = 6.9 cps, C-1), 6.55 (1 H, multiplet, C-6), 7.20–7.90 (2 H, C-4), 8.05 (3 H, doublet, J = 2.0 cps, methyl), 8.20–8.90 (2 H, C-5, isopropylmethyne), and 9.15 (6 H, triplet, J = 6.8 cps, isopropyl).

Anal. Calcd for $C_{23}H_{26}SO_2$: C, 75.37; H, 7.15. Found: C, 75.06; H, 7.04.

Oxidation of 3,3-Diphenyl-5-methyl-7-isopropyl-2-thiabicyclo[2,2,2]oct-5-ene (I).—By the same procedure as described above, 100 mg of I gave 30 mg of the corresponding sulfone X as colorless needles, mp 243–244°. The infrared spectrum showed $\nu_{\mathrm{CH}}^{\mathrm{KBr}}$ 2950, 2860, $\nu_{\mathrm{C=C}}^{\mathrm{KBr}}$ 1600, 1490, $\delta_{\mathrm{CH}}^{\mathrm{KBr}}$ 1440, 745, 705, and $\nu_{\mathrm{SO_2}}^{\mathrm{KBr}}$ 1290, 1120 cm^{-1}; the ultraviolet spectrum showed $\lambda_{\max}^{\mathrm{EtOH}}$ 255 (ϵ 488), 261 (ϵ 553), 267 (ϵ 488), and 272 mμ (ϵ 399).

Anal. Calcd for $C_{23}H_{26}SO_2$: C, 75.37; H, 7.15. Found: C, 75.38; H, 7.17.

Registry No.—I, 13952-45-9; II, 13810-95-2; III, 13810-96-3; VII, 13810-97-4; VIII, 13810-98-5; IX, 13810-99-6; X, 13811-00-2; thiobenzophenone, 1450-31-3; α-phellandrene, 13811-01-3; tetraphenylethylene, 632-51-9; dibenzhydryl disulfide, 1726-02-9.

6-Azabicyclo[3.2.1]octanes

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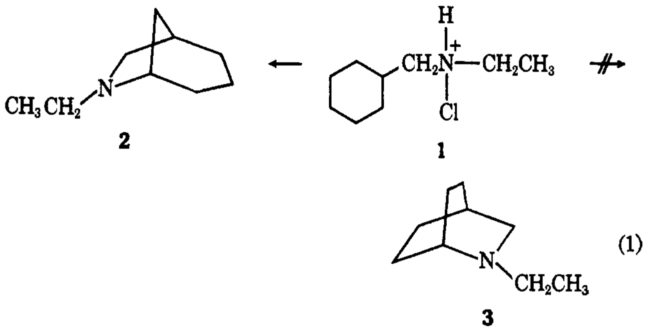
As part of our study of the rearrangements of azabicyclics *via* nitrenium ions,[2,3] we became interested in various synthetic routes to azabicycloalkanes. Prominent among the various synthetic methods for the preparation of azabicycloalkanes is the classical Hofmann–Löffler–Freytag reaction of monocyclic N-chloroamines.[4-7] It is generally accepted that this reaction involves homolytic cleavage of the N–Cl bond of the protonated N-chloroamine to yield an intermediate aminium radical which subsequently abstracts either a δ or ε hydrogen, producing, *via* a chain reaction, either a δ- or ε-chloroalkylamine acid salt. Basification and steam distillation then result in an intramolecular displacement of chloride ion to yield either a five- or six-membered heterocyclic ring.

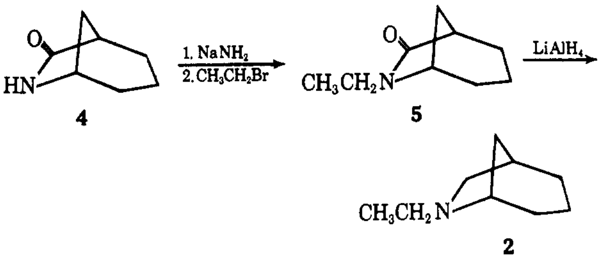
It has been suggested[6,7] that the relative ease of δ- *vs.* ε-hydrogen abstraction is governed by the ability of the N–H–C angle to be close to 180° in the transition state, as well as by the tendency to minimize bond angle strain and steric repulsions in the transition state. However, when an apparent duality of reaction pathways exists, steric factors favoring one route, linearity of hydrogen transfer another, the relative importance of these two effects is difficult to predict *a priori*.[4,7] One such case which interested us owing to our involvement in azabicyclics was the reaction of N-chloro-N-ethylcyclohexanemethylamine (**1**).

The synthesis of **1** was accomplished by reaction of the commercially available cyclohexanecarbonyl chloride with ethylamine and reduction of the resultant amide with lithium aluminum hydride to the corresponding amine, which was then converted into **1** *via* reaction with N-chlorosuccinimide (NCS).

The Hofmann–Löffler–Freytag reaction was carried out by irradiation of a solution of **1** in 85% sulfuric acid for 55 hr with a bank of ten 15-w Sylvania Blacklite fluorescent lamps. Subsequent basification, steam distillation, and Hinsberg separation gave a 10% yield of tertiary amines consisting of 95% of a major component, with two minor impurities constituting the remaining 5%. The major component was shown to be 6-ethyl-6-azabicyclo[3.2.1]octane (**2**) (eq 1) by comparison with an authentic sample of **2** prepared as shown in eq 2 from the known[8] 6-azabicyclo[3.2.1]-octan-7-one (**4**). Comparison of vpc retention times of the minor components of the Hofmann–Löffler–Freytag reaction products with that of an authentic sample[9] of 2-ethyl-2-azabicyclo[2.2.2]octane (**3**) demonstrated the complete absence of **3**.



(1)



(2)

Two rationalizations may be considered in accounting for the absence of **3** in the reaction mixture. If ε-hydrogen abstraction had occurred, subsequent stereospecific incorporation of chlorine might have proceeded to yield exclusively N-ethyl-*cis*-4-chlorocyclohexanemethylamine which would not be able to ring close *via* an intramolecular displacement. This rationale appears unsatisfactory since both *cis*- and *trans*-4-*t*-butylcyclohexyl halides are formed from various sources of 4-*t*-butylcyclohexyl radicals in the presence of halide-transfer agents.[10-12] A more logical explanation is that ε-hydrogen abstraction fails to occur owing to unfavorable nonbonded interactions which would destabilize the requisite transition state.

Since the linearity of hydrogen transfer is a major factor in determining which hydrogen is abstracted, a detailed examination was made of models of the appropriate transition states for δ- and ε-hydrogen abstraction. The transition state for ε-hydrogen abstraction would provide for a C–H· · ·N angle of about 180°, but this transition state would require the boat conformation of cyclohexane. By comparison, the transition state for δ-hydrogen abstraction would have a C–H· · ·N angle of approximately 145°; however, this transfer would proceed through the preferred cyclohexane chair conformation. Apparently, for the cyclohexane–methylaminium radical, nonbonded interactions are more important than linearity of hydrogen transfer in determining whether a δ or ε hydrogen is transferred. This can be compared with the cyclo-

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