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Cycloaddition of 1-Azirines with Cyclopentadienones. Formation of 2*H*- and 3*H*-Azepines, and Mechanistic Interpretation[1,2]

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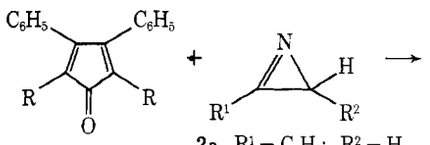
Cyclopentadienones **1** and 1-azirines **2** react in refluxing toluene to afford 3*H*-azepines **3** directly, with loss of CO. Azirines **2** react similarly with 1,3-diphenylinden-2-one (**16**) and phencyclone (**17**) to give 2*H*-azepines **18** and **19**. The phenanthro-2*H*-azepines **19** rearrange under basic or thermolytic conditions to the more stable 3*H* isomers with the ring proton at the 9 position of the phenanthrene nucleus. Analogous cycloadditions of **16** and **17** with 1,2,3-triphenylcyclopropene (**22**) lead to cycloheptatrienes and exo bridging carbonyl compounds. The mechanism of azepine formation is rationalized in terms of an *endo*-2-azatricyclo[3.2.1.$0^{2,4}$]oct-6-en-8-one intermediate (**13**) which extrudes CO with disrotatory ring opening of the aziridine C–N bond, to afford primarily 2*H*-azepines which may or may not then rearrange to the 3*H* isomers. Analysis of the nmr spectra, with particular attention to the conformational preference of the azepine ring, is also recorded.

During the last decade 1-azirines have become readily available and their synthetic utility has been extensively developed.[3] Recently the first cycloadditions of these heterocyclic systems have been reported. These include thermal reactions with ketenes,[4,5] ketenimines,[5] nitrile oxides,[6] cyclopentadienones,[2,7] cyclopentadiene,[8] diphenylisobenzofuran,[9] and diazomethane[10] to yield a variety of products. 1-Azirines also react photochemically (*via* the nitrile ylide) with themselves,[11-13] as well as with various carbon–carbon[14,15] and hetero double bonds.[15,16]

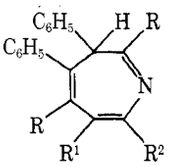
The synthesis and chemistry of azepines has likewise evolved largely during the last decade.[17] Although a number of examples of N-substituted 1*H*-azepines are known,[17] attempts to prepare the unsubstituted system have led to the formation of 3*H*-azepines.[18] 4*H*-Azepines rearrange under thermal or basic conditions to the 3*H* isomers.[19-22] No example of the 2*H*-azepine was known prior to this study.[2] This has led to the generalization[21] that the relative stabilities of the azepine systems are in the order 2*H* < 4*H* < 3*H*. It has also been calculated[23] that for the parent systems, 1*H*-azepine has a resonance energy of −1.80 kcal mol^{-1}, whereas that of the 3*H*-azepine is +0.23.

We report here our detailed findings on the reaction of 1-azirines with a variety of cyclopentadienones to give 2*H*- and 3*H*-azepines.

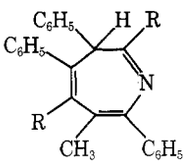


1a, R = C_6H_5
b, R = CH_3
c, R = C_2H_5

2a, $R^1 = C_6H_5$; $R^2 = H$
b, $R^1 = C_6H_5$; $R^2 = CH_3$
c, $R^1 = R^2 = C_6H_5$
d, $R^1 = C_6H_5$; $R^2 = CH_2OH$
e, $R^1 = C_6H_5CH_2$; $R^2 = H$



3a, $R = R^1 = C_6H_5$; $R^2 = H$
b, $R = R^1 = C_6H_5$; $R^2 = CH_3$
c, $R = R^1 = R^2 = C_6H_5$
d, $R = R^1 = C_6H_5$; $R^2 = CH_2OH$
e, $R = C_6H_5$; $R^1 = C_6H_5CH_2$; $R^2 = H$
f, $R = CH_3$; $R^1 = C_6H_5$; $R^2 = H$
g, $R = R^2 = CH_3$; $R^1 = C_6H_5$
h, $R = CH_3$; $R^1 = R^2 = C_6H_5$
i, $R = CH_3$; $R^1 = C_6H_5CH_2$; $R^2 = H$
j, $R = C_2H_5$; $R^1 = C_6H_5$; $R^2 = H$
k, $R = C_2H_5$; $R^1 = C_6H_5$; $R^2 = CH_3$



4a, R = C_6H_5
b, R = CH_3

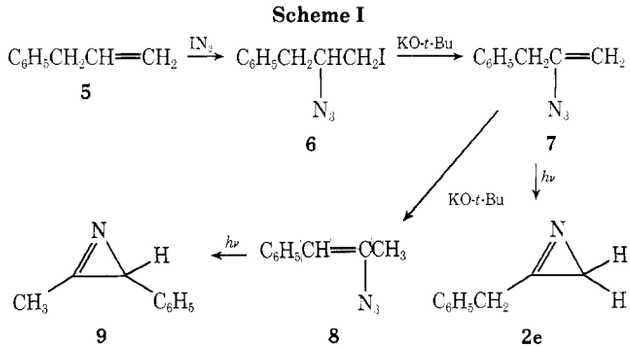
Results and Discussion

Though no reaction occurs between tetracyclone (**1a**) and azirine **2b** in refluxing benzene overnight, clean conversion into an azepine **3b** with loss of CO takes place in refluxing toluene after 4 days.[2] The structural assignment to 3*H*-azepines **3** was facilitated by the use of dimethylcyclone (**1b**) and 2-phenylazirine (**2a**) as substrates. The resulting azepine **3f**, produced in 86% yield, displayed two methyl singlets at τ 8.24 and 7.72, the latter exhibiting

homoallylic coupling[24,25] (J = 0.8 Hz) to the 7-proton (broad singlet at 3.06), absence of NH absorption and absence of the low-field two-proton multiplet characteristic of the PhC=N- system in the tetracyclone adducts. This eliminated positions 1, 2, 5, and 7 (in formula **3**) as the site of attachment for the proton derived from the azirine ring (*e.g.*, **2b**). An nmr singlet for the benzylic protons in **3e** or **3i** derived from 2-benzylazirine (**2e**) left for consideration only the 3*H*-azepine structure **3** or an isomeric 4*H*-azepine. The mass spectral fragmentation pattern of the azepine products showed the major pathway as loss of the RC≡N moiety. When the 2-methyl group was deuterated, this loss was represented by $CD_3C{\equiv}N$, confirming the 3*H*-azepine (**3**) assignment.

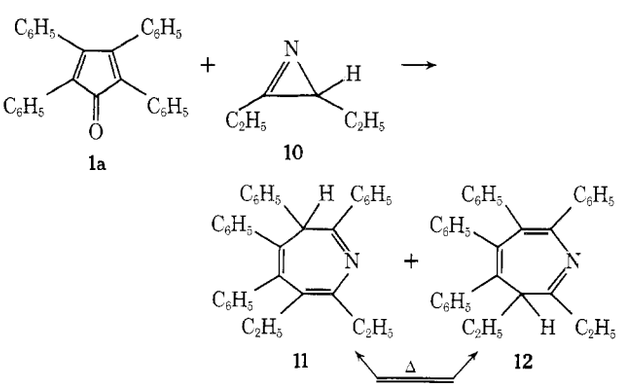
In addition to the isolation of azepine **3i** from the reaction of 2-benzyl-1-azirine (**2e**) and **1a** or **1b**, minor products, shown to be the isomeric **4a** and **4b**, were also obtained. The source of **4a** was not phenyl migration in benzyl azepine **3i**, but the synthetic pathway[26,27] used in the formation of azirine **2e** (Scheme I). We were able to show that vinyl azide **8** was produced by base promoted isomerization of **7** even during the very short (10 min) dehydroiodination of **6** and that its photolysis product **9** reacted with tetracyclone **1a** to afford **4a**.

Scheme I



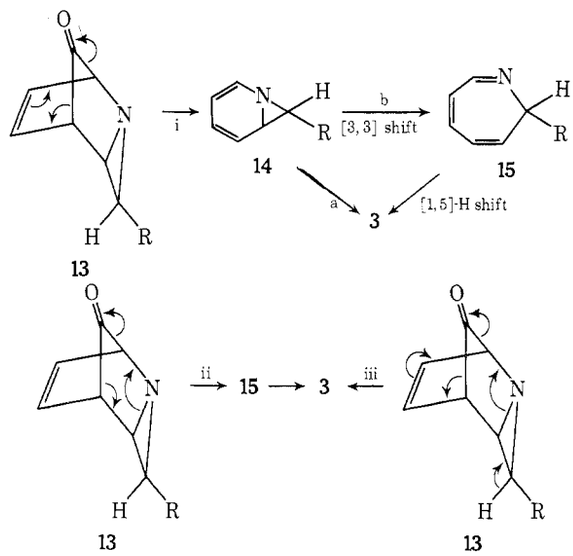
In subsequent preparative procedures 2-aryl-1-azirines could be generated *in situ* from the corresponding vinyl azides. The vinyl azide was first decomposed in refluxing toluene and the dienone then added. This technique removed the task of preparing and handling the obnoxious smelling 1-azirines.

Although no thermally allowed [1,5]-hydrogen shifts were observed on the 3*H*-azepines **3**, such a process was detected on heating **11** or **12** in xylene. The same equilibrium mixture (8:3) was produced on refluxing **10**[27] with **1a** for 10 days. The structure of **12** was obvious from its nmr spectrum which displayed a triplet at τ 5.87 (H-3), and a H_AH_B pattern for the methylene protons of the 2-ethyl group, which underwent slow exchange with D_2O at room temperature.



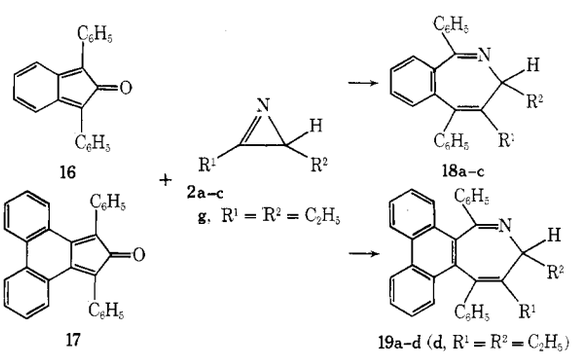
Mechanism. The formation of azepines **3** from azirines **2** and cyclopentadienones, resulting in the 2 and 3 substituents of the azirine being placed at C-6 and C-7, indicated that rupture of the azirine C=N bond had occurred[28] during cycloaddition and one was therefore dealing with a Diels–Alder addition. This is also consistent with the failure of 3,3-dimethyl-2-phenyl-1-azirine[29] and 3-carbomethoxy-2-phenyl-1-azirine[27,30] to react with **1a** or **1b**.

If the assumption is made that 1-azirines and cyclopentadienones first react in a [4 + 2] fashion to give an endo intermediate **13** (see below), then three possible routes are available to account for the subsequent formation of 3*H*-azepines. Mechanism i involves loss of carbon monoxide



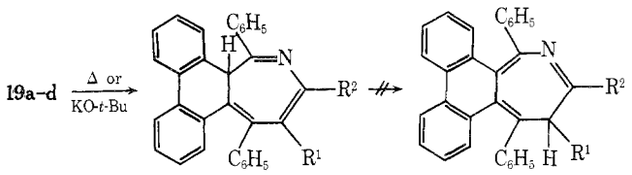
from **13** through involvement of the C=C bond to afford the azanorcaradiene **14**. The latter can either undergo ring opening (path a) to give the 3*H*-azepine **3** or a disrotatory electrocyclic rearrangement (path b) to produce the 2*H*-azepine **15** which rearranges *via* a thermally allowed [1,5]-hydrogen shift to give the thermodynamically more stable **3**. In mechanism ii, CO is lost *via* participation of the aziridine carbon–nitrogen bond to afford **15** which rearranges to **3** as above. Mechanism iii utilizes a concerted hydrogen migration with loss of carbon monoxide from **13** to yield **3** directly. Acceleration for the analogous process in the decarbonylation of tricyclooctenones is well established.[31]

Routes i and iii differ from ii inasmuch as they both require participation of the carbon–carbon double bond of **13** in the primary step for azepine formation. If this double bond were rendered less available (*i.e.*, requiring destruction of aromatic resonance), then route ii should be favored. Indeed, when 1,3-diphenylinden-2-one **16**[32] and phencyclone **17**[32] were chosen as the dienone components, in the reaction with azirines **2a–c** and **2g** in refluxing xy-



lene[33] and toluene, respectively, highly crystalline products **18a–c** and **19a–d** were rapidly formed. The reaction times of **16** and **17** with azirines indicated that phencyclone had comparative reactivity to the dimethylcyclone **1b** (in toluene) and that the indenone **16** was five to six times as reactive as **1b** (in xylene).

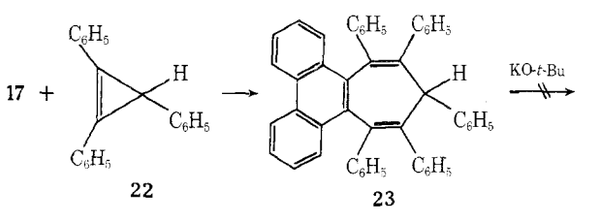
The adducts **19,** which showed the expected low-field [τ ($CDCl_3$) 1.45–1.20] two-proton multiplet attributable to the ortho hydrogens on PhC=N, were found to isomerize in high yield, on treatment with potassium *tert*-butoxide in refluxing dimethoxyethane or upon thermolysis at *ca.* 200°.



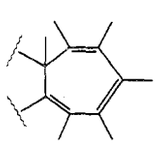
20a-d **21**

The products **20a–d** exhibited a one-proton singlet in the region τ ($CDCl_3$) 4.35–3.67. The isomeric 3*H*-formula **21,** produced by a [1,5]-hydrogen shift of **20,** was eliminated by the absence of coupling of the ring proton of **20d** ($R^1 = R^2 = C_2H_5$) with the ethyl group. Products **20a–d** all displayed a four-proton multiplet at τ ($CDCl_3$) 1.70–0.95, tentatively ascribed to the ortho protons of the 2- and 5-phenyl groups. The latter falls within the deshielding region of the phenanthrene nucleus. Due to the higher resonance energy of a benzene ring (as in **18**) *vs.* the center ring of a phenanthrene (as in **19**), 2*H*-azepines **18** did not undergo rearrangement under similar reaction conditions that effected the transformations **19** → **20.**

For the reaction **19** → **20** to proceed, it is evident that the difference in energy parameters of the 2*H*- and 3*H*-azepines must be greater than the comparable parameters of the center ring of the phenanthrene nucleus. Some support of this proposal is provided by the fact that the cycloheptatriene **23** [prepared from phencyclone **17** and 1,2,3-triphenylcyclopropene (**22**)] did not isomerize to **24** under the basic conditions employed for **19** → **20.** In the acecyclone series[34] the analog of **23** was more stable than that of **24.**



22 **23**

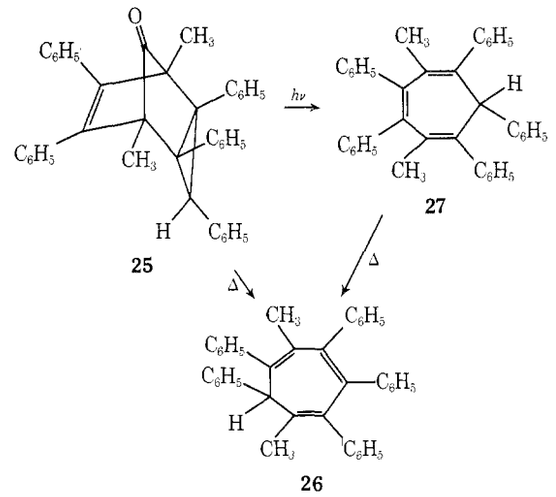


24

Additional evidence to substantiate the mechanism of azepine formation comes from the cycloaddition of cyclopropenes to cyclopentadienones. In analogy with previous studies,[30,35] bridged ketonic intermediate **25** [ν_{max} (KBr) 1760 cm^{-1}] was isolable on heating **22** with **1b** in benzene for 4 hr. The nmr spectrum of **25** displayed equivalent methyl groups at τ 9.11 and a one-proton singlet at 7.13.

When **25** was heated under reflux in toluene or xylene, it smoothly lost CO and the unsymmetrical cycloheptatriene **26** was formed (nonequivalent methyl groups at τ 8.80 and 8.16 and the ring proton at 5.18). The initial interpretation[2a] invoked a mechanism similar to ia, but this was revised[2b] since photochemical decarbonylation of **25** produced the symmetrical cycloheptatriene **27** (equivalent methyl groups at τ 8.25 and the ring proton at 5.00) which rearranged on heating to **26.**

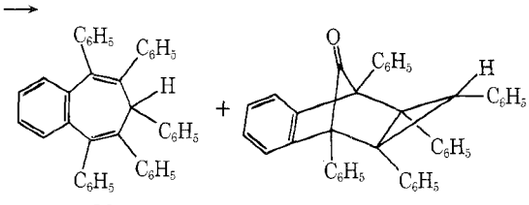
1b + 22 →



25 **27** **26**

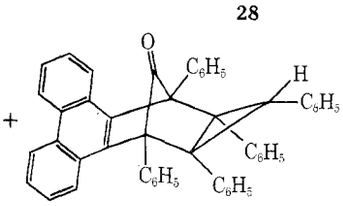
It is well established that the presence of a fused endo cyclopropane ring in the β positions to bridging carbonyl[35] and azo[36] compounds greatly accelerates the extrusion of carbon monoxide and nitrogen from these molecules, due to more efficient orbital overlap in the transition states. Hence, we believe that **13** has the endo configuration and that the electron pair on the aziridine N facilitates the loss of CO. Support for this proposal comes from the isolation of the exo ketones **28** and **29** (ν_{max} 1776 cm^{-1}) in addition to the cycloheptatrienes **30** and **23.** The endo ketones would be expected to decompose readily to afford **30** and **23,** but the exo isomers **28** and **29** were stable up to 300°.

16 + 22 →



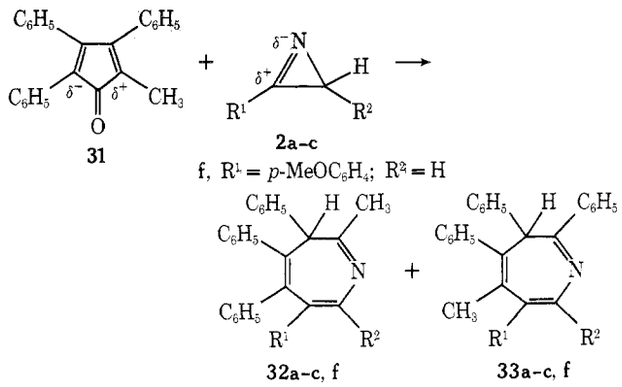
30 **28**

17 + 22 → **23** +



29

Regiochemistry. The regiochemistry of the azirine cycloaddition reaction was also examined, using the unsymmetrical dienone **31.** Formally the 3*H*-azepines **32** and **33** are expected from this reaction, their relative amounts depending on the electronic nature of the azirine carbon–nitrogen double bond and the steric factors involved in the addition. The ratios of **32:33** (see Table I) were determined by nmr integration of the crude reaction mixture and separation was accomplished by fractional crystallization and chromatography. If the azirine double bond and the dienone are polarized as shown, then azepines **32** should be the predominant products (if steric control is unimportant). This is indeed the case when phenylazirine **2a** is employed. The use of *p*-methoxyphenylazirine **2f** causes an increase in the ratio of **32:33** as anticipated. However,



31 2a-c

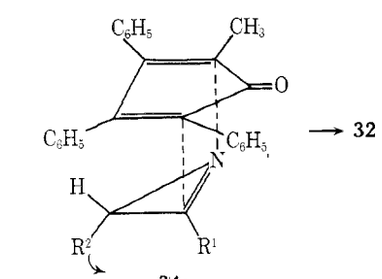
f, $R^1 = p\text{-}MeOC_6H_4$; $R^2 = H$

32a-c, f 33a-c, f

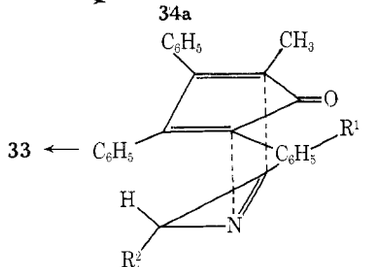
Table I
Ratio of 3*H*-Azepine 32:33 Formed in the Cycloaddition of 30 to 2

	32:33	
a	2	1
b	1	1.4
c	1	6
f	5	1

when the 3-substituted azirines **2b** and **c** were used a reversal of the product ratios occurred. The reasons for this were not immediately apparent since the changes in azirine substituents do not occur at the reactant centers. It may tentatively be ascribed to a "weighting" effect of the azirine ring induced by the 3 substituent, the introduction of which causes a decrease in efficiency of the azirine ring to achieve coplanarity with the dienone in the endo transition states **34a** and **b.** This effect manifests itself by a tilting down-



34a



34b

wards of the azirine ring about the C=N bond, and an increased interaction of the azirine 2-aryl substituent with the 2 and 5 substituents of the dienone. Clearly if this is the case, then **34b** will be favored since it involves an aryl–methyl interaction compared to the aryl–phenyl one of **34a.** The observed results support this hypothesis.

Of interest is the fact that the physical properties of 3*H*-azepine **32c** ($R^1 = R^2 = C_6H_5$) [pale yellow crystals, mp 206°; τ ($CDCl_3$) 7.76 (s, 3 H), 4.36 (s, 1 H), 3.50–2.50 (m, 25 H)] are similar to those of an alleged[7] 4*H*-azepine [pale yellow crystals, mp 198–201°; τ ($CDCl_3$) 7.80 (s, 3 H), 4.39 (s, 1 H), 3.32–2.67 (m, 25 H)] isolated in minor yield from tetracyclone **1a** and 3-methyl-2-phenylazirine (**2b**). It is proposed that the 4*H* structure is incorrect and that this compound is in fact the 3*H*-azepine **32c.** This is conveniently explained by assuming a [1,5]-hydrogen shift of the major product of the reaction, namely the 3*H*-azepine **3b.** As a generalization, it should be noted that the observed *[1,5]-hydrogen shifts in the isomerization of azepines always proceeded in the direction of the C=N rather than in the direction of the N=C bond, e.g.,* **11 ⇄ 12, 19 → 20, 3b → 32c.**

Nmr Spectra. The chemical shifts of the 3*H*-ring proton in the azepines studied reveal some interesting trends. The 3*H* in the tetracyclone derived series (τ 3.6–3.9 in **3a–e, 5a, 11**) is shifted downfield by *ca.* 65 Hz compared to azepines derived from the 2,5-dialkylcyclones **1b,c** with the same azirines (τ 4.7–4.85 in **3f–i, 5b**). This is not taken to indicate a change of conformation of the azepine ring but a deshielding effect of the 2-phenyl group. In a not too dissimilar model system **35,** the benzhydrilic proton is shifted downfield by *ca.* 56 Hz on changing R = CH_3[37] to R = C_6H_5.[38]

$(C_6H_5)_2CHCOR$
35a, R = CH_3
b, R = C_6H_5

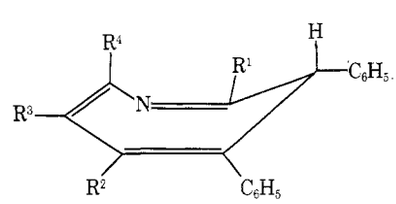
The mean position of the proton in the series derived from the unsymmetrical cyclone **31,** compared to the analogous 2,5-dimethylazepines, experiences a shift downfield of *ca.* 22 Hz for $R^1 = CH_3$ and an upfield shift of *ca.* 13 Hz when $R^1 = C_6H_5$. Consequently, the introduction of a 5-phenyl substituent on the azepine ring increases the deshielding mechanisms experienced by the 3*H* proton. Furthermore the substitution of methyl groups at the 2 and 5 positions by phenyl groups causes a shift downfield of *ca.* 30 Hz of the 7 proton.

Homoallylic coupling, verified by spin decoupling, was observed in **3f** between the 2-CH_3 and the 7-H (J = 0.8 Hz). This coupling disappeared in the 2-CD_3 analog and was found to be general for a 2-alkyl group and a 7 proton. It was interesting that this occurred through the nitrogen atom, since previously observed[39,40] homoallylic coupling in 3*H*-azepines did not involve the nitrogen atom. Examples are known though involving a heteroatom.[24,25] In all 2-phenyl-substituted azepins, the two ortho protons of the PhC=N– system absorb at lower field (*ca.* 0.5 ppm lower) than the other aromatic protons.

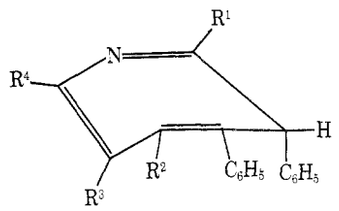
The appearance of the methylene protons of the 2-ethyl group of **12** as an AB pattern is consistent with restricted rotation and proximity to a chiral center (C-3). As expected the 3*H* appeared as a triplet (J = 7.5 Hz). A similar observation has been made for a 2-ethoxy group.[39] An unexpected result was the AB pattern (J = 13 Hz) for the methylene protons of the $-CH_2OH$ group in the 7 position of **3d.** These were broadened by the –OH, but deuterium exchange caused the signals to be well resolved.

Similarly we observed an ABX pattern for the parent azirine **2d** (J_{AB} = 12.5 Hz, J_{AX} = 3.0 Hz, J_{BX} = 4.7 Hz). These results probably indicate a preferred conformation in solution.

Conformations of Azepines. It is reasonable to assume[7] that of the two possible conformations of the 3*H*-azepine ring **36** and **37,** the thermodynamically more stable one, **36,**



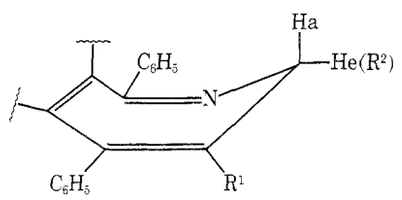
36



37

has the 3*H* proton in the axial position and the 3-phenyl group equatorial.

It is significant that in the benzo- and phenanthro-2*H*-azepines **18a** and **19a**, the ring protons were coupled (J = 10 and 9 Hz, respectively), indicating slow ring inversion on the nmr time scale. The lower field doublets were assigned[41] to the equatorial proton and the higher doublets to the axial proton in conformer **38**. When the 2 position



38

was substituted by a methyl group (**19b** and **20b**), then the higher field signal for the axial ring proton remained at approximately the same chemical shift, indicating that the methyl group occupied the equatorial position. A phenyl group at position 2 would also be expected to be equatorial. When the 2 group was ethyl, then the ring proton exhibited a pattern characteristic for X of an ABX system, indicative of restricted rotation of the 2-ethyl group and its attachment to a chiral center.

The nmr data of the phenanthro-3*H*-azepines **20** display the ring proton at approximately the same position as in the tetracyclone-derived 3*H*-azepines. There is considerable driving force for this proton to occupy the axial position since in this conformation the planarity of the phenanthrene nucleus is maintained, unlike in the other conformation. This substantiates the assumption of **36** as the most stable conformation of the simple 3*H*-azepines.

Experimental Section[42]

General Procedure for the Preparation of 3*H*-Azepines[43] from Cyclones 1a,b,c. The cyclopentadienone (5 mmol) and the azirine (6 mmol) were heated under reflux in toluene (15 ml) in an atmosphere of nitrogen until tlc indicated that all the dienone had reacted. (Times are indicated in the text.) The solvent was removed *in vacuo* and the residue either recrystallized directly or chromatographed over Woelm neutral alumina (activity I), as indicated in the text.

2,3,4,5,6-Pentaphenyl-3*H*-azepine (3a) was isolated from **1a** and **2a** after 4 days, by recrystallization from ethanol as golden yellow crystals (87%): mp 212°; nmr τ 2.48 (4-H), 3.62 (3-H).

Anal. Calcd for $C_{36}H_{27}N$: C, 91.3; H, 5.75. Found: C, 91.4; H, 5.9.

7-Methyl-2,3,4,5,6-pentaphenyl-3*H*-azepine (3b) was isolated directly from **1a** and **2b** after 6 days, by recrystallization from ethanol as yellow hexagonal plates (65%): mp 212°; nmr τ 8.23 (7-CH_3), 3.77 (3-H).

Anal. Calcd for $C_{37}H_{29}N$: C, 91.1; H, 6.0. Found: C, 91.0; H, 6.0.

2,3,4,5,6,7-Hexaphenyl-3*H*-azepine (3c) was obtained from **1a** and **2c** after 12 days, by chromatography using ether–petroleum (1:3) eluent, as pale yellow crystals from ethanol (61%): mp 227°; nmr τ 3.62 (3-H).

Anal. Calcd for $C_{42}H_{31}N$: C, 91.8; H, 5.7. Found: C, 91.5; H, 5.7.

7-Hydroxymethyl-2,3,4,5,6-pentaphenyl-3*H*-azepine (3d) was obtained from **1a** and **2d** after 6 days as lemon yellow granules (55%) from ethanol: mp 213°; nmr τ 7.4 (OH), 3.6 (3-H).

Anal. Calcd for $C_{37}H_{29}NO$: C, 88.2; H, 5.8. Found: C, 88.0; H, 5.7.

Tetracyclone (1a) and 2-Benzyl-1-azirine (2e). After 3 days' reflux, the residue was chromatographed. Elution with dichloromethane–pentane (1:30) afforded 6-methyl-2,3,4,5,7-pentaphenyl-3*H*-azepine (**4a**) (5%) as bright yellow needles: mp 177° from hexane; nmr τ 8.6 (6-CH_3), 3.83 (3-H).

Anal. Calcd for $C_{37}H_{29}N$: C, 91.1; H, 6.0. Found: C, 90.9; H, 6.0.

Continued elution with increasing amounts of dichloromethane in pentane afforded 6-benzyl-2,3,4,5-tetraphenyl-3*H*-azepine (**3e**) (51%) as bright yellow crystals from hexane: mp 161°; nmr τ 6.72 (6-CH_2), 2.74 (4-H), 3.8 (3-H).

Anal. Calcd for $C_{37}H_{29}N$: C, 91.1; H, 6.0. Found: C, 90.9; H, 6.0.

Tetracyclone (1a) and 2,3-Diethylazirine (10). The solvent was removed after 10 days' reflux and the residue chromatographed. Elution with dichloromethane–hexane (1:2) afforded a mixture (85%) of azepines. Two recrystallizations from ethanol afforded 6,7-diethyl-2,3,4,5-tetraphenyl-3*H*-azepine (**11**) as yellow needles: mp 151°; nmr τ 9.68 (t, J = 7.5 Hz, 6-Et), 8.01 (q, J = 7.5 Hz, 6-CH_2), 8.9 (t, J = 7.5 Hz, 7-Et), 7.79 (q, J = 7.5 Hz, 7-CH_2), 3.94 (3-H).

Anal. Calcd for $C_{34}H_{31}N$: C, 90.0; H, 6.9. Found: C, 90.1; H, 7.0.

Two recrystallizations of the combined filtrate material gave 2,3-diethyl-4,5,6,7-tetraphenyl-3*H*-azepine (**12**) as pale yellow flakes: mp 127°; τ ($CDCl_3$) 9.15–8.70 (m, 6 H), 8.70–8.25 (m, 2 H), 8.03–7.54 (m, 2 H), 5.87 (t, J = 7.5 Hz, 1 H), 3.40–2.50 (m, 20 H).

Anal. Calcd for $C_{34}H_{31}N$: C, 90.0; H, 6.9. Found: C, 89.9; H, 7.0.

2,5-Dimethyl-3,4,6-triphenyl-3*H*-azepine (3f) was obtained from **1b** and **1a** after 13 hr by recrystallization from hexane as tan crystals (86%): mp 123°; nmr τ 7.72 (d, J = 0.8 Hz, 2-CH_3), 8.24 (5-CH_3), 3.06 (7-H), 4.71 (3-H).

Anal. Calcd for $C_{26}H_{23}N$: C, 89.4; H, 6.6. Found: C, 89.5; H, 6.7.

In a large-scale preparation the vinyl azide (20.0 g, 0.138 mol) was first decomposed in toluene (250 ml) under reflux for 2 hr. The dienone (30.0 g, 0.115 mol) was added and the mixture heated under reflux for an additional 12 hr. Work-up afforded the azepine (33.9 g, 85%).

2,5,7-Trimethyl-3,4,6-triphenyl-3*H*-azepine (3g) was isolated from **1b** and **2b** as pale yellow flakes (83%) from ethanol: mp 182°; nmr τ 7.79 (2-CH_3), 8.42 (5-CH_3), 8.48 (7-CH_3), 4.82 (3-H).

Anal. Calcd for $C_{27}H_{25}N$: C, 89.2; H, 6.9. Found: C, 89.5; H, 7.0.

The azepine (88%) was also prepared *via* the vinyl azide as for **3f**.

2,5-Dimethyl-3,4,6,7-tetraphenyl-3*H*-azepine (3h) was obtained from **1b** and **2c** after 3.5 days by recrystallization from ethanol as pale yellow needles (63%): mp 189°; nmr τ 7.72 (2-CH_3), 8.36 (5-CH_3), 4.72 (3-H).

Anal. Calcd for $C_{32}H_{27}N$: C, 90.3; H, 6.4. Found: C, 90.6; H, 6.5.

1b and 2-Benzyl-1-azirine (2e). After 2 days' reflux the solvent was removed and the residue chromatographed. Ether–pentane (1:2) eluted 2,5,6-trimethyl-3,4,7-triphenyl-3*H*-azepine (**4b**) as pale yellow crystals (6%) from hexane: mp 181°; nmr τ 7.73 (2-CH_3), 7.99 (5-CH_3), 8.33 (6-CH_3), 4.85 (3-H).

Anal. Calcd for $C_{27}H_{25}N$: C, 89.2; H, 6.9. Found: C, 89.4; H, 6.9.

Elution with increasing amounts of ether in pentane afforded 6-benzyl-2,5-dimethyl-3,4-diphenyl-3*H*-azepine (**3i**) as pale yellow crystals (51%) from hexane: mp 90°; nmr τ 7.79 (2-CH_3), 8.1 (5-CH_3), 6.5 (CH_2), 3.17 (7-H), 4.77 (3-H).

Anal. Calcd for $C_{27}H_{25}N$: C, 89.2; H, 6.9. Found: C, 89.3, H, 6.7.

2,5-Diethyl-3,4,6-triphenyl-3*H*-azepine (3j) was obtained from **1c** and **2a** after 17 hr by chromatography (ether–hexane, 1:3) as a pale yellow oil (90%). The picrate crystallized as bright yellow needles from ethanol: mp 169°; nmr τ 8.8 (t, J = 7.5 Hz, 2-CH_3), 9.3 (t, J = 7.2 Hz, 5-CH_3), 7.35–8.04 (m), 2.96 (7-H), 4.78 (3-H).

Anal. Calcd for $C_{34}H_{30}N_4O_7$: C, 67.3; H, 5.0; N, 9.2. Found: C, 67.3; H, 5.0; N, 9.2.

2,5-Diethyl-7-methyl-3,4,6-triphenyl-3*H*-azepine (3k) was isolated from **1c** and **2b** as pale yellow crystals (66%): mp 113° from ethanol; nmr τ 8.76 (t, J = 7.5 Hz, 2-CH_3), 7.59 (q, J = 7.5 Hz, 2-CH_2).

Anal. Calcd for $C_{29}H_{29}N$: C, 89.0; H, 7.5. Found: C, 89.0; H, 7.5.

Addition of 2-Methyl-3,4,5-triphenylcyclopentadienone (31) to Azirines. The general procedure was used and the times for reflux given in the text.

2-Phenyl-1-azirine (2a) and **31** afforded a 2:1 mixture of **32a**: **33a** after 30 hr. Chromatography with benzene eluent afforded 5-methyl-2,3,4,6-tetraphenyl-3*H*-azepine (**33a**) (28%) as bright yellow granules: mp 170° from ethanol; nmr τ 8.2 (5-CH_3), 3.83 (3-H).

Anal. Calcd for $C_{31}H_{25}N$: C, 90.5; H, 6.1. Found: C, 90.2; H, 6.2.

Continued elution using dichloromethane gave 2-methyl-3,4,5,6-tetraphenyl-3*H*-azepine (**32a**) (59%) as pale yellow needles: mp 174° from ethanol; nmr τ 7.81 (d, J = 0.9 Hz, 2-CH_3), 4.36 (3-H).

Anal. Calcd for $C_{31}H_{25}N$: C, 90.5; H, 6.1. Found: C, 90.6; H, 6.0.

3-Methyl-2-phenyl-1-azirine (2b) and **31** gave a 1:1.4 mixture of **32b:33b** after 4 days. Chromatography using benzene eluent afforded 5,7-dimethyl-2,3,4,6-tetraphenyl-3*H*-azepine (**33b**) (53%) as lemon yellow crystals from chloroform–ethanol: mp 165°; nmr τ 8.38 (5-CH_3), 8.36 (7-CH_3), 3.94 (3-H).

Anal. Calcd for $C_{32}H_{27}N$: C, 90.3; H, 6.4. Found: C, 90.3; H, 6.5.

Elution with chloroform then gave colorless needles from ethanol of 2,7-dimethyl-3,4,5,6-tetraphenyl-3*H*-azepine (**32b**): mp 164°; nmr τ 7.8 (2-CH_3), 8.29 (7-CH_3), 4.49 (3-H).

Anal. Calcd for $C_{32}H_{27}N$: C, 90.3; H, 6.4. Found: C, 90.1; H, 6.6.

2,3-Diphenyl-1-azirine (2c) and **31** afforded a 1:6 mixture of **32c:33c** after 7 days. Two recrystallizations of the residue from ethanol afforded 5-methyl-2,3,4,6,7-pentaphenyl-3*H*-azepine (**33c**) (51%) as pale yellow crystals: mp 187°; nmr τ 8.32 (5-CH_3), 3.83 (3-H).

Anal. Calcd for $C_{37}H_{29}N$: C, 91.1; H, 6.0. Found: C, 90.8; H, 6.2.

Two recrystallizations of the combined filtrate material afforded 2-methyl-3,4,5,6,7-pentaphenyl-3*H*-azepine (**32c**) (8%) as pale yellow crystals: mp 206°; nmr τ 7.76 (2-CH_3), 4.36 (3-H).

Anal. Calcd for $C_{37}H_{29}N$: C, 91.1; H, 6.0. Found: C, 91.3; H, 6.1.

2-*p*-Methoxyphenyl-1-azirine (2f) (prepared *in situ* from the vinyl azide) and **31** afforded a 5:1 mixture of **32f:33f** after 30 hr. Two recrystallizations of the residue from chloroform–ethanol afforded 6-*p*-methoxyphenyl-2-methyl-3,4,5-triphenyl-3*H*-azepine (**32f**) (45%) as pale yellow needles: mp 197°; nmr τ 7.82 (d, J = 0.8 Hz, 2-CH_3), 6.43 (OCH_3), 4.38 (3-H).

Anal. Calcd for $C_{32}H_{27}NO$: C, 87.0; H, 6.2. Found: C, 86.7; H, 6.1.

Preparative layer chromatography (SiO_2, ether–petroleum, 1:2) of the combined filtrate material afforded 6-*p*-methoxyphenyl-5-methyl-2,3,4-triphenyl-3*H*-azepine (**33f**) (9%) as bright yellow needles from chloroform–ethanol: mp 192°; nmr τ 8.2 (5-CH_3), 6.22 (OCH_3), 3.86 (3-H).

Anal. Calcd for $C_{32}H_{27}NO$: C, 87.0; H, 6.2. Found: C, 86.8; H, 6.3.

1,3-Diphenylinden-2-one (16) and Azirines. The dimer of **16** (2 mmol) and the azirine (3 mmol) were heated under reflux in xylene (15 ml). Reaction with azirines **2a** and **2b** required 3 hr, and with azirine **2c** the reaction required 10 hr. The solvent was removed and the residue dissolved in the minimum amount of benzene and then added to a dry column of neutral alumina. Elution with ether–pentane (1:1) directly, afforded the following pure adducts.

3,4,7-Triphenylbenz[*e*]-2*H*-azepine (18a)[43] recrystallized from ethanol as colorless needles (65%): mp 157°; nmr τ 5.06 (d, J = 10 Hz, eq 2-H), 6.4 (d, J = 10 Hz, ax 2-H).

Anal. Calcd for $C_{28}H_{21}N$: C, 90.5; H, 5.7. Found: C, 90.7; H, 5.5.

2-Methyl-3,4,7-triphenylbenz[*e*]-2*H*-azepine (18b) recrystallized from chloroform–ethanol as colorless crystals (68%): mp 201°; nmr τ 8.55 (d, J = 6.5 Hz, 2-CH_3), 6.4 (q, J = 6.5 Hz, 2-H).

Anal. Calcd for $C_{29}H_{23}N$: C, 90.35; H, 6.0. Found: C, 90.3; H, 5.9.

When toluene was used as solvent for the reaction, it required 7 days to reach completion.

2,3,4,7-Tetraphenylbenz[*e*]-2*H*-azepine (18c) recrystallized from chloroform–hexane as pale yellow crystals (63%): mp 185°; nmr τ 5.3 (2-H).

Anal. Calcd for $C_{34}H_{25}N$: C, 91.2; H, 5.6. Found: C, 91.0; H, 5.6.

Phencyclone (17) and azirine cycloadditions were conducted by heating **17** (2.6 mmol) and the azirine (2.8 mmol) in toluene (15 ml) under reflux for 2–3 days. The residue, after removal of the solvent, was dissolved in the minimum volume of chloroform and added to a dry Woelm neutral alumina column. Elution with chloroform afforded the following adducts.

3,4,7-Triphenylphenanthro[9,10-*e*]-2*H*-azepine (19a) crystallized from chloroform–hexane as colorless flocculent crystals (69%): mp 258°; nmr τ 5.09 (d, J = 9 Hz, eq 2-H), 6.4 (d, J = 10 Hz, ax 2-H).

Anal. Calcd for $C_{36}H_{25}N$: C, 91.7; H, 5.3. Found: C, 91.5; H, 5.3.

2-Methyl-3,4,7-triphenylphenanthro[9,10-*e*]-2*H*-azepine (19b) crystallized from chloroform–hexane as colorless flocculent needles (71%): mp 231°; nmr τ 8.55 (d, J = 6.5 Hz, 2-CH_3), 5.91 (q, J = 6.5 Hz, 2-H).

Anal. Calcd for $C_{37}H_{27}N$: C, 91.5; H, 5.60. Found: C, 91.3; H, 5.5.

2,3,4,7-Tetraphenylphenanthro[9,10-*e*]-2*H*-azepine (19c) crystallized from benzene–heptane as pale yellow granules (84%): mp 174°; nmr (C_6D_6) τ 4.57 (2-H).

Anal. Calcd for $C_{42}H_{29}N$: C, 92.1; H, 5.3. Found C, 91.9; H, 5.6.

2,3-Diethyl-4,7-diphenylphenanthro[9,10-*e*]-2*H*-azepine (19d) crystallized from chloroform–ethanol as pale yellow crystals (90%): mp 215°; nmr τ 8.91 (t, J = 7.5 Hz, 3-Et), 8.99 (t, J = 7 Hz, 2-Et), 6.9–8.1 (m, 4), 6.41 (dd, J = 9 and 9 Hz, 2-H).

Anal. Calcd for $C_{34}H_{29}N$: C, 90.4; H, 6.5. Found: C, 90.1; H, 6.6.

Rearrangements of the Phenanthro-2*H*-azepines 19a–d. A general procedure is given for (1) basic and (2) thermal rearrangement.

(1) Basic. The azepine (0.5 mmol) and potassium *tert*-butoxide (0.6 mmol) were heated under reflux in dry dimethoxyethane (5 ml) for 10 hr. The solvent was removed and the residue purified by ptlc on silica.

(2) Thermal. The azepine (0.5 mmol) was either heated neat or in triglyme (5 ml) at *ca.* 200° for 8 hr. Purification was achieved as for (1). The following 3*H*-azepines were obtained using either of these techniques. Yields were 30–90% and chloroform–ethanol was used for recrystallization.

2,5,6-Triphenylphenanthro[9,10-*c*]-3*H*-azepine (20a) crystallized as brilliant yellow crystals: mp 237°; nmr τ 3.67 (3-H).

Anal. Calcd for $C_{36}H_{25}N$: C, 91.7; H, 5.3. Found: C, 91.4; H, 5.6.

7-Methyl-2,5,6-triphenylphenanthro[9,10-*c*]-3*H*-azepine (20b) crystallized as bright yellow crystals: mp 248°; nmr τ 7.87 (2-CH_3), 3.92 (3-H).

Anal. Calcd for $C_{37}H_{27}N$: C, 91.5; H, 5.6. Found: C, 91.4; H, 5.8.

2,5,6,7-Tetraphenylphenanthro[9,10-*c*]-3*H*-azepine (20c) crystallized as pale yellow crystals: mp 264°; nmr τ 3.75 (3-H).

Anal. Calcd for $C_{42}H_{29}N$: C, 92.1; H, 5.3. Found: C, 91.8; H, 5.4.

6,7-Diethyl-2,5-diphenylphenanthro[9,10-*c*]-3*H*-azepine (20d), crystallized as golden needles: mp 211°; nmr τ 8.97 (t, J = 8 Hz, CH_3), 8.85 (t, J = 7 Hz, CH_3).

Anal. Calcd for $C_{34}H_{29}N$: C, 90.4; H, 6.5. Found: C, 90.3; H, 6.6.

1b and 1,2,3-Triphenylcyclopropene (22). The dienone (2.5 g, 9.6 mmol) and the cyclopropene (2.7 g, 10 mmol) were heated under reflux for 4 hr. Removal of the solvent and recrystallization of the residue from chloroform–ethanol afforded colorless needles (4.7 g, 92%) of 1,5-dimethyl-2,3,4,6,7-pentaphenyltricyclo[3.2.-1.^{1,5}0.^{2,4}]oct-6-en-8-one (**25**): mp 202° dec; ν_{max} (KBr) 1760 cm^{-1}; τ ($CDCl_3$) 9.11 (s, 6 H), 7.13 (s, 1 H), 3.80–3.50 (m, 2 H), 3.30–2.70 (m, 23 H).

Anal. Calcd for $C_{40}H_{32}O$: C, 90.9; H, 6.1. Found: C, 91.0; H, 6.0.

Photochemical Decarbonylation of 25. The ketone (1.0 g) was dissolved in dichloromethane (70 ml) and irradiated at 254 nm in a Rayonet photochemical reactor for 4.5 hr. Removal of the solvent gave a colorless solid (0.95 g, 100%). Rapid recrystallization from chloroform–ethanol afforded colorless crystals of 3,6-dimethyl-1,2,4,5,7-pentaphenylcycloheptatriene (**27**): mp 188–192°; τ ($CDCl_3$) 8.25 (s, 6 H), 5.00 (s, 1 H), 3.55–3.20 (m, 4 H), 3.20–2.90 (m, 6 H), 2.90–2.45 (m, 13 H), 2.45–2.15 (m, 2 H).

Anal. Calcd for $C_{39}H_{22}$: C, 93.6; H, 6.4. Found: C, 93.5; H, 6.5.

Thermolysis of the Symmetrical cycloheptatriene 27. The cycloheptatriene (186 mg) was heated under reflux in tetrachloroethylene (5 ml) and the reaction monitored by nmr spectroscopy. The equilibrium did not change much after 5 hr, consisting of about 75% of **26** and minor isomers. The solvent was removed after 17 hr and the residue recrystallized from chloroform–ethanol to give 2,6-dimethyl-1,3,4,5,7-pentaphenylcycloheptatriene (**26**) as colorless crystals: mp 189°; τ ($CDCl_3$) 8.80 (s, 3 H), 8.15 (s, 3 H), 5.18 (s, 1 H), 3.75–3.45 (m, 2 H), 3.25–2.30 (m, 23 H).

Anal. Calcd for $C_{39}H_{32}$: C, 93.6; H, 6.4. Found: C, 93.3; H, 6.5.

Thermolysis of the Ketone 25. The ketone (180 mg) was heated under reflux in xylene (6 ml) for 20 hr. Removal of the solvent and recrystallization of the residue gave pure **26** (110 mg, 64%): mp 189°.

The Indenone 16 and the Cyclopropene 22. The dienone (500 mg, 1.77 mmol) and the cyclopropene (475 mg, 1.77 mmol) were heated under reflux in toluene (15 ml) for 2 days. The solvent was removed and the nmr spectrum of the residue showed it to be a 4:1 mixture of **30:28.** Chromatography on neutral alumina and elution with ether–pentane (1:1) afforded 1,2,3,4,5-pentaphenyl-3*H*-benzocycloheptatriene (**30**) as pale orange needles from chloroform–ethanol: mp 228°; τ ($CDCl_3$) 4.77 (broadish s, 1 H), 3.25–2.20 (m, 29 H).

Anal. Calcd for $C_{41}H_{30}$: C, 94.2; H, 5.8. Found: C, 94.2; H, 5.8.

Elution with ether afforded *exo*-1,2,3,4,5-pentaphenyltricyclo-[3.2.1^{1,5}.0^{2,4}]benzo[*f*]oct-6-en-8-one (**28**) as colorless plates from chloroform–ethanol: mp 249°; ν_{max} (KBr) 1776 cm^{-1}; τ ($CDCl_3$) 6.15 (s, 1 H), 3.55–2.15 (m, 29 H).

Anal. Calcd for $C_{42}H_{30}O$: C, 91.6; H, 5.5. Found: C, 91.5; H, 5.4.

Phencyclone (17) and Cyclopropene 22. The dienone (1.0 g, 2.62 mmol) and the cyclopropene (0.75 g, 2.8 mmol) were heated under reflux in toluene (15 ml) for 10 hr. The mixture was allowed to cool and the solid (1.1 g) filtered off. Fractional recrystallization from chloroform afforded first 1,2,3,4,5-pentaphenylphenanthro-[9,10-*g*]-3*H*-cycloheptatriene (**23**) as colorless crystals: mp 319°.

Anal. Calcd for $C_{49}H_{34}$: C, 94.5; H, 5.5. Found: C, 93.1; H, 5.4.

Secondly, *exo*-1,2,3,4,5-pentaphenylphenanthro[9,10-*f*]tricyclo-[3.2.1^{1,5}.0^{2,4}]oct-6-en-8-one (**29**) crystallized as colorless needles: mp 270°; ν_{max} (KBr) 1776 cm^{-1}.

Anal. Calcd for $C_{50}H_{34}O$: C, 92.3; H, 5.3. Found: C, 91.1; H, 5.2.

Registry No.—**1a,** 479,33-4; **1b,** 26307-17-5; **1c,** 51932-77-5; **2a,** 7654-06-0; **2b,** 16205-14-4; **2c,** 16483-98-0; **2d,** 52124-00-2; **2e,** 18709-44-9; **2f,** 32687-32-4; **3a,** 33070-61-0; **3b,** 33070-63-2; **3c,** 33070-66-5; **3d,** 52124-01-3; **3e,** 33654-83-0; **3f,** 33070-60-9; **3g,** 33070-62-1; **3h,** 33070-65-4; **3i,** 52124-02-4; **3j** picrate, 51932-79-7; **3k,** 52124-03-5; **4a,** 52124-04-6; **5b,** 52124-05-7; **10,** 18709-43-8; **11,** 33654-82-9; **12,** 33654-81-8; **16,** 23414-46-2; **17,** 5660-91-3; **18a,** 39934-14-0; **18b,** 39934-15-1; **18c,** 39934-16-2; **19a,** 39934-03-7; **19b,** 39934-04-8; **19c,** 52124-06-8; **19d,** 52124-07-9; **20a,** 52124-08-0; **20b,** 52124-09-1; **20c,** 52124-10-4; **20d,** 52124-11-5; **22,** 16510-49-9; **23,** 52124-12-6; **25,** 52154-42-4; **26,** 52124-13-7; **27,** 52124-14-8; **28,** 52154-43-5; **29,** 52124-15-9; **30,** 39934-07-1; **31,** 33535-80-7; **32a,** 52124-16-0; **32b,** 52124-17-1; **32c,** 52124-18-2; **32f,** 52124-19-3; **33a,** 52124-20-6; **33b,** 52124-21-7; **33c,** 52124-22-8; **33f,** 52124-23-9.

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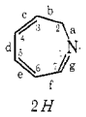
(43) Since the numbering of the azepine system is not completely systematic,[17] the lettering system adopted in this paper follows the numbers

3H



2H

Reactions of 3*H*-Azepines Derived from Cyclopentadienones and 1-Azirines[1]

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Reactions of 3*H*-azepines **3,** available from cycloaddition of 1-azirines with cyclopentadienones, were examined with a view to producing 1*H*-azepine derivatives. Treatment of **3** with benzoyl chloride resulted in 2-alkylidine-*N*-benzoyl- 2,3-dihydro-1-azepines (**7**), which failed to isomerize to the antiaromatic system **5.** Photolysis of **7** led to 1,3 (N to C) benzoyl transfer. Attempted base-catalyzed deuterium exchange underlined the difficulty of isolating an 8-π-electron system. Acid isomerization of 7-unsubstituted azepines **3a–c** produced substituted anilines, presumably *via* unstable 1-azepines, while the 7-methyl substrate **19** afforded cyclohexadienone products.

Recently we have developed[1,2] a procedure for the preparation of 3*H*-azepines **3** by cycloaddition of 1-azirines **1** with cyclopentadienones **2.** Such compounds might provide an entry into the interesting 8-π-electron system,[3] the 1*H*-azepine **5** or **6.** For instance, addition of acid chlorides to the imine double bond of **3** may lead directly or *via* **4** to the N-substituted 1*H*-azepine **5.** Removal of RCO from **5** could give the elusive N-unsubstituted 1*H*-azepine **6,** which in our case should be stabilized by the multiple substitution on the ring carbons. Alternatively, **6** might just revert to **3,** since it has been shown that the 3*H*-azepine is in general the thermodynamically more stable isomer.