a 300-W high-pressure Hg-arc lamp gave reaction products. After removal of the solvent, isolation of the residue by column chromatography on silica gel gave 2-methyl-1,4-naphthoquinone (**20**, 85 mg, 49%) and benzophenone (**22g**, 62 ng 32%) together with 9,9′-bixanthenyl.

Photoproduct **20:** yellow needles from ethanol; mp 107 °C; IR (KBr) 1650 (C=O), 1618 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.2 (d, 3 H, CH_3), 6.84 (d, 1 H, CH), 7.64–7.84 (m, 2 H, aromatic H), 7.96–8.16 (m, 2 H, aromatic H).

Photoproduct **22 g:** colorless crystals; mp 49–50 °C, confirmed by mixture-melting-point method compared with an authentic sample.

Reaction of 1h with Xanthene. Under completely deaerated conditions, irradiation of a mixture of **1h** and xanthene dissolved in benzene gave no photoproduct. However, under aerated conditions, irradiation of **1h** (200 mg) and xanthene (400 mg) dissolved in benzene (30 ml) for 40 h gave 2-methyl-1,4-naphthoquinone (**20**, 63 mg, 67%) and fluorenone (**22h**, 4 mg, 45%). Photoproduct **22n** was assigned to fluorenone by comparing with an authentic sample.

Registry No.—**2**, 64044-74-2; **3**, 64044-75-3; **8c**, 64044-76-4; **8d**, 64044-77-5; **9c**, 64069-99-4; **9d**, 64070-00-4; **10c**, 54034-10-5; **10d**, 64044-78-6; **12c**, 64044-79-7; **20**, 58-27-5; **22g**, 119-61-9; 9,9′-bixanthenyl, 4381-14-0; xanthene, 92-83-1.

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Pericyclic Synthesis and Exploratory Photochemistry of Potentially Direct Progenitors of the Unrestricted Hetero[11]annulene System

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The procedure of α-pyrone C_4H_4 homologation was applied to the synthesis of the heterotricycles shown in **5, 6, 9,** and **18,** which were judged to be useful, potentially direct, synthetic precursors for the construction of "unrestricted" hetero[11]annulenes. Compounds **6, 9,** and **18** readily fragment under the influence of heat or light to produce benzene and the corresponding five-membered heterocycle. On the other hand, exploratory photochemical work with **5** has revealed the system's propensity to undergo dimerization on sensitized illumination and multidirectional bond relocation, to **20** and **21** and **22,** on direct irradiation.

The tactical use of pericyclic transformations offers a unique means of gaining entry into potentially labile unrestricted[1] π-excessive frames such as the hetero[9]-,[2] hetero[13]-,[2b,3] and hetero[17]annulenes.[3] One notable common characteristic of these monocyclic substances is that they were all prepared by synthetic procedures utilizing cyclooctatetraene as the basic synthon and are thus associated with a $(4n + 1)$-membered periphery containing a total of $(4n + 2)$ π electrons. In other words, the pericyclic synthetic schemes developed here[2] and elsewhere[3] are strictly designed for the construction of potentially aromatic heterocycles. In theory, extension of this useful procedure to the preparation of potentially antiaromatic π-excessive heterocycles, i.e., molecules incorporating a $(4n - 1)$-membered periphery and a total of $4n$ π electrons, may be realized simply by changing the basic hydrocarbon building unit from cyclooctatetraene to benzene. We have examined the practical aspects of such a modification to the original synthetic design and wish to present in this report a description of our experiences in this connection, relating to the construction of a variety of potentially direct synthetic progenitors of the unrestricted hetero[11]annulene system.

Multicyclic Valence Tautomers of the Aza[11]annulene System

Since N-substituted azepines are known to undergo thermal cycloaddition[4-6] with a variety of reactive dienes yielding symmetrically bridged 1:1 adducts of general structure **1,** our initial attempts in this project concentrated on the possible application of the α-pyrone-induced C_4H_4 homologation procedure we previously devised[7,8] for converting an aza[9]annulene (azonine) to the 13-membered counterpart. All effort along these lines, however, was effectively frustrated by the failure of the azepine **2**[9] to react with α-pyrone (**3**) on prolonged contact and over a wide temperature range (70–110 °C). Our failure to effect cycloadditive coupling between **2** and **3** was not entirely unexpected insofar as the homologation process as initially designed calls for cycloadditive trapping of a skeletally uncomfortable trans double bond, i.e., a reactive functionality not present in **2.** Therefore, it became necessary to utilize in the basic homologation scheme a C_6H_6NR synthon with more reactive double bonds than are present in **2.** With this in mind we directed our attention to the readily available [3.2.0] photoisomer of **2,** shown as **4**[10] in Scheme I. This molecule does indeed react with a benzene solution of **3** at 65 °C to produce a mixture of cycloadducts (A, Scheme I) in ca. 62% yield. A, in turn, readily extrudes CO_2 upon heating at 140–145 °C in vacuo (ca. 0.05 mm) to yield a thermolysate consisting of the three nonvolatiles **5** (^1H NMR, IR, UV, MS), **6** (^1H NMR, IR, UV, MS), and **7** (^1H NMR, IR) in a molar ratio of 1:1.2:1.8 (60% yield). The assignment of anti stereochemistry to **5** follows from the small value of $J_{8,9}$ (2 Hz) which is more consistently accommodated by the dihedral angle estimated (Dreiding models) for a trans H–H disposition (~100°) than

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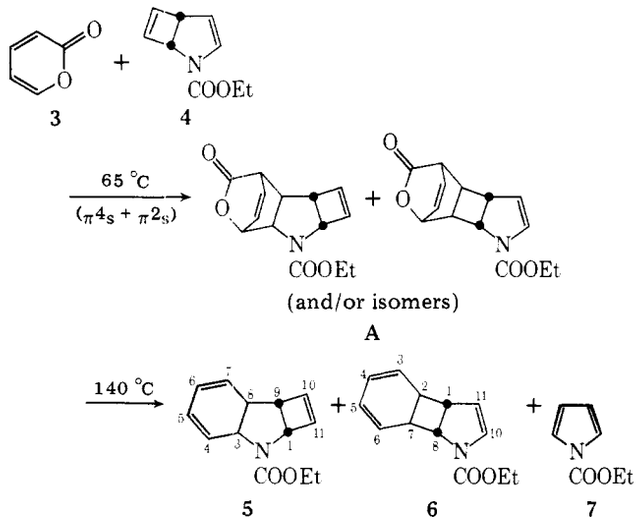
Scheme I

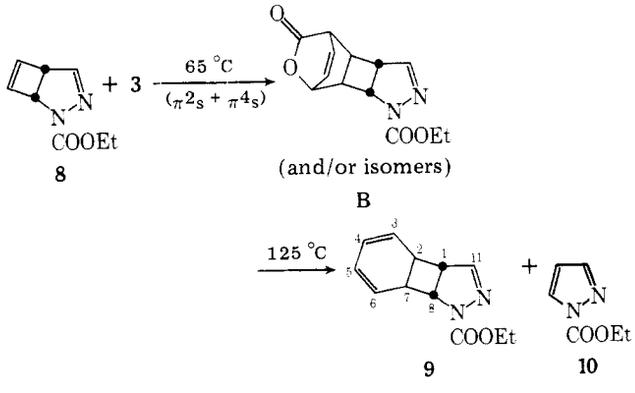


for the cis alternative (~0°) (cf. ^{1}H NMR of **22** (vide infra)). Similar reasoning allows one to assign an anti disposition to **6** ($J_{1,2}$ = 3.5 Hz) as well.

1 2

In related experiments designed for the preparation of one or more multicyclic isomers of an aza[11]annulene incorporating a nitrogen in place of an sp^2 C–H unit, the diazabicycle depicted in **8** (reaction 1) was exposed to **3** at 65 °C, leading to cycloadduct(s) B in ca. 64% yield. Thermally induced (125 °C, 0.05 mm) loss of CO_2 produced a two-component mixture of nonvolatiles consisting of **9** (^{1}H NMR, IR, UV, MS) ($J_{7,8}$ = 3.5 Hz) and pyrazole **10**[12] (^{1}H NMR, MS) in a molar ratio of 1:1.5 (55% yield).[13]

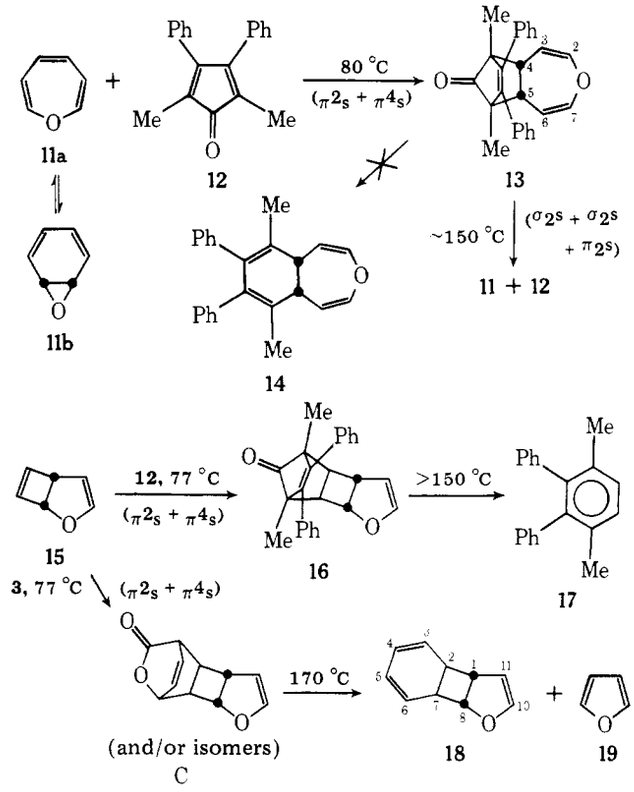
The presence of pyrrole **7** and pyrazole **10** in the pyrolysates of A and B is best accounted for by the respective fragmentation of **6** (and/or its syn isomer) and **9** (and/or its syn counterpart) via a retro-($_\pi$2$_s$ + $_\pi$2$_s$) process whose formal "forbiddenness" is largely lifted because of the developing aromaticity of its six-membered moiety, i.e., as a result of benzene extrusion. Gratifyingly, one finds tricycles **6** and **9** to fragment to **7** + benzene ($k_{109.6°}$ = 3.29 ± 0.23 × 10^{-4} s^{-1}, $\Delta G^{\ddagger}$ = 28.7 kcal/mol) and **10** + benzene ($k_{109.7°C}$ = 3.69 ± 0.20 × 10^{-4} s^{-1}, $\Delta G^{\ddagger}$ = 28.6 kcal/mol), respectively.



Multicyclic Valence Tautomers of the Oxa[11]annulene System

A survey of prior art relating to the response of oxepin (**11**, Scheme II) to thermal cycloaddition[14] reveals it to be strictly limited to dienophilic reagents which invariably single out the

Scheme II



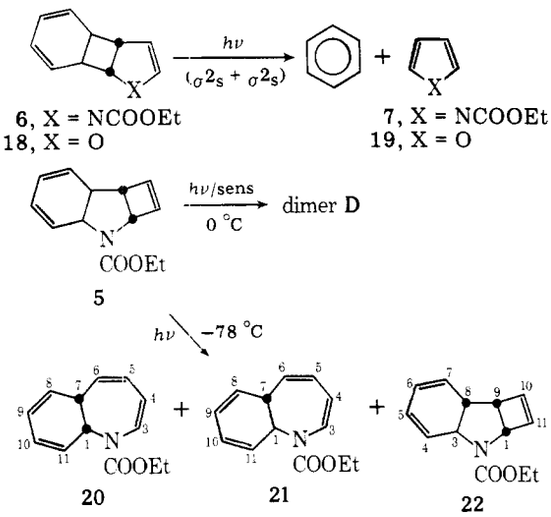
bicyclic oxanorcaradiene form of the molecule, i.e., **11b**, for cycloadditive union.[15] Consequently, it was encouraging to discover that dienone **12** adds cleanly to the remote double bond of oxepin itself, i.e., **11a**. Specifically, we find that prolonged (48 h) exposure of oxepin to **12** in boiling benzene leads to the formation of oxatricycle **13** (mp 164–165 °C; ^{1}H NMR, IR, UV, MS) in 65% yield. The proposed structure clearly follows from the spectroscopic data which require that the molecule possess a pair of magnetically equivalent enol ether functions ($\Delta\tau_{\alpha,\beta}$ = 1.66 ppm) and a highly strained ketonic bridge (ν_{CO} = 1760 cm^{-1}) flanked by a pair of symmetrically disposed methyl groups (6H singlet of τ 8.60). Disappointingly, all attempts at thermally decarbonylating **13** to the desired oxabicycle **14** were frustrated by the molecule's readiness to undergo thermal cycloreversion to **12** and oxepin in benzene solution (110–192 °C) or in the molten state.

Contrasting the rather sluggish response of **11** to cycloaddition with **12**, its bicyclic photoisomer **15**[14,16] undergoes rapid cycloadditive coupling with **12** in hot benzene (77 °C) to produce adduct **16** (mp 142–143 °C; ^{1}H NMR, IR, UV, MS) in essentially quantitative yield. Our preference for an anti disposition of the two rings flanking the cyclobutane unit of **16** follows from the large observed difference between $J_{1,7}$ (2.0 Hz) and $J_{1,5}$ (7.0 Hz), which requires that dihedral angles H^1–H^7 and H^1–H^5 also be widely different; cursory examination of Dreiding models reveals that the key dihedral angles are equal in the syn counterpart of **16** and, as required by the observed coupling constants, distinctly different ($H_{1,5}$ ~5°, $H_{1,7}$ ~110°) in **16**.

Cycloadduct **16** does undergo overall thermal decarbonylation when heated above 150 °C in benzene, but the molecule's basic skeleton is labile at these elevated temperatures so that the only nonvolatile product one isolates under these conditions is the tetrasubstituted benzene **17**. The overall fragmentation of **16** to **17** was monitored by ^{1}H NMR at 163 °C ($t_{1/2}$ ~4.5 h) and 192 °C ($t_{1/2}$ ~18 min) without indication of any intermediates.

Exposure of **15** to α-pyrone (**3**) instead of dienone **12** produced cycloadduct(s) C which, in turn, readily extrudes CO_2

Scheme III



upon heating at 170 °C in vacuo (ca. 0.05 mm) to afford oxatricycle **18** (^{1}H NMR, IR, UV, MS) in 21% overall yield. The assignment of anti stereochemistry to this substance follows from the distinctly different magnitudes of key coupling constants $J_{1,8}$ (7.5 Hz) and $J_{7,8}$ (4.0 Hz) and is further supported by its unquestionable dissimilarity (IR, ^{1}H NMR) from the recently described product of photoinduced coupling between benzene and furan formulated as the syn counterpart of **18**.[17]

Chemically, the general structural features depicted in **18** are supported by the compound's affinity to undergo thermally induced fragmentation ($k_{110.4°C} = 4.49 \pm 0.39 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger} = 28.5$ kcal/mol) to benzene and furan.

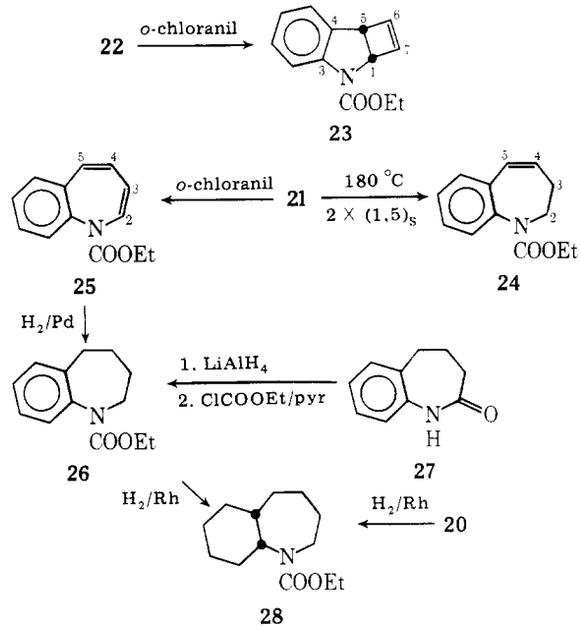
Exploratory Photochemistry

Once the various substances described earlier became available, we turned our attention to exploring their possible usefulness as photoprogenitors of the hitherto unknown hetero[11]annulene frame.

To begin with, we examined the structurally related molecules **6, 9,** and **18** and were disappointed to discover that exposure of this general tricyclic skeleton to either direct or sensitized illumination readily triggers fragmentation to benzene and the expected π-excessive heterocycle (Scheme III). This, of course, is not an unexpected result for it is difficult to conceive of a process such as valence isomerization or dimerization which would effectively compete energetically with the symmetry-allowed genesis of benzene.

Next we turned our attention to the alternate tricyclic arrangement prepared in this study, i.e., **5,** which is structurally incapable of readily extruding an aromatically stabilized fragment. While this is in fact the case, i.e., **5** does effectively resist photofragmentation, exposure of this substance to the type of sensitized irradiation and subsequent workup conditions which proved successful in our recent generation and isolation of an aza[13]annulene[8] resulted in the formation of a dimer (mp 134–137 °C; ^{1}H NMR, IR, UV, MS) as the only tractable product (16% yield). Since this dimeric product is of no direct use to the primary goal set by this study, no serious effort was expended toward its characterization, although it is evident from certain key spectroscopic characteristics that the substance possesses twofold symmetry (^{1}H NMR) and, further, that it lacks a conjugated diene chromophore (UV). Sharply contrasting its response to sensitized irradiation, brief unfiltered exposure of **5** to direct illumination with a low-pressure mercury coil at ca. −78 °C effected clean 50% conversion to three photoisomers characterized as **20** (^{1}H NMR, IR, UV, MS), **21** (^{1}H NMR, IR, UV, MS), and **22** (^{1}H NMR, IR, UV, MS) and isolated in the respective ratio of 2:1:1.

Scheme IV



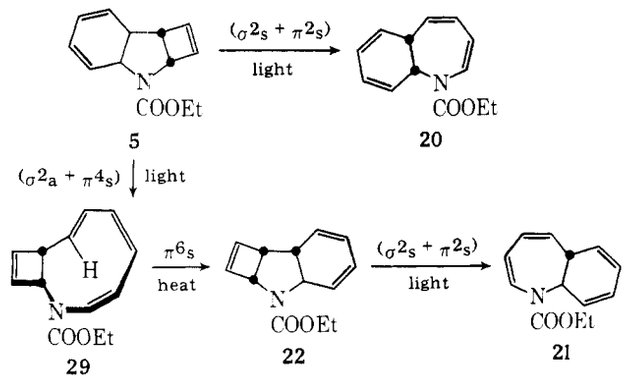
Ring-juncture stereochemical assignments follow in each case from an assessment of pertinent coupling constants. Specifically, one measures $J_{1,7} \sim 7$ Hz for **20**, $J_{1,7} = 17$ Hz for **21**, and $J_{1,9} = 3.5$, $J_{8,9} = 7.5$, and $J_{3,8} = 18.0$ Hz for **22**.

Chemically, the structural assignments of **20, 21,** and **22** received added confirmation from the following transformations: compound **22** was oxidized to **23** (^{1}H NMR, IR, UV, MS) on exposure to *o*-chloranil, and **21** was (i) thermolyzed (GLC injection port, 180 °C) to **24** (^{1}H NMR, IR, UV, MS) and (ii) oxidized to the rare[18,19] 2,3-benzazepine frame depicted in **25** (^{1}H NMR, IR, UV, MS) on treatment with *o*-chloranil. Further, the presence of the same basic [5.4.0] frame in **20** and **21** was securely established through partial hydrogenation (Pd/C) of **25** to **26** (^{1}H NMR, IR, UV, MS), followed by exhaustive saturation (Rh/C) of this substance to **28** (^{1}H NMR, IR, UV, MS), which was shown to be spectroscopically (^{1}H NMR, IR) indistinguishable from a synthetic sample prepared from catalytic hydrogenation (Rh/C) of **20.**

As already stressed in this section's title, the photoinduced transformations described here are largely exploratory, our primary emphasis being directed at deciding whether any of the available tricyclic isomers of the hetero[11]annulene system might be considered synthetically promising. For obvious operational reasons, tricycles **6, 9,** and **18** do not hold much promise in this regard. On the other hand, the multidirectional response of **5** to direct illumination is deemed synthetically encouraging insofar as it may be considered implicative of one or more monocyclic intermediates. It must be remembered, of course, that the overall photoisomerization of **5** to **20, 21,** and **22** may be accounted for equally well via sequential bond relocation as exemplified by the combination of symmetry-permitted steps collected in Scheme V.

To conclude, it might be noted that given the current state of preparative development of **5,** any studies directed at assessing its synthetic utility in relation to the desired monocyclic analogue would undoubtedly be hampered by the molecule's limited availability (ca. 10% yield from **4**). As a result of this complication, it now appears necessary to concentrate one's immediate effort chiefly to the development of such conditions as are required to maximize the source of **5** in the mixture of cycloadducts (A) in Scheme I. It is hoped that, once realized, the increased availability of **5** would allow one to conduct a methodical study aimed at the possible detection and eventual isolation of the desired heteroannulene.

Scheme V



Experimental Section

Preparation of *N*-Carbethoxy-2-azabicyclo[3.2.0]hepta-2,4-diene (4).[21] A solution of *N*-carbethoxyazepine (**2**)[9] (4 g, 0.024 mol) in deaerated (N_2) ethyl ether (650 mL) was irradiated at ambient temperature under a nitrogen atmosphere through a Pyrex filter with a Hanovia 450-W lamp for a period of 20 h. The solution was then concentrated at the water aspirator at ambient temperature, and the resulting crude yellow oil was distilled at a head temperature of 40–45 °C and 0.05 mm to afford pure *N*-carbethoxy-2-azabicyclo[3.2.0]-hepta-2,4-diene (**4**) (3.4 g, 85%) as a colorless oil (^{1}H NMR, IR).

Reaction of *N*-Carbethoxy-2-azabicyclo[3.2.0]hepta-2,4-diene (4) with α-Pyrone (3): Formation of A. A deaerated (N_2) solution of *N*-carbethoxy-2-azabicyclo[3.2.0]hepta-2,4-diene (**4**) (3.4 g, 0.021 mol) and α-pyrone (**3**) (17.0 g, 0.21 mol) in benzene (20 mL) was heated at 60–65 °C under nitrogen for 40 h. The solution was concentrated at the water aspirator, and unreacted α-pyrone was then removed at a bath temperature of 50–55 °C and 0.1 mm to yield a dark residue. This residue was dissolved in a minimum amount of ethyl ether and the resulting solution placed on a 630 × 15 mm jacketed column wet packed (petroleum ether) with activity III Woelm neutral alumina (55 g) and maintained at ca. −15 °C. Elution with petroleum ether/ethyl ether (1:1 v/v, 300 mL) removed the impurities so that subsequent elution with petroleum ether/ethyl ether (1:3 v/v, 300 mL) afforded A (3.4 g, 62%) as a white foamy residue.

Pyrolysis of A: Formation of *N*-Carbethoxy-2-aza-*cis*^{1,9},*trans*^{8,9},*cis*^{3,8}-tricyclo[7.2.0.0^{3,8}]undeca-4,6,10-triene (5), *N*-Carbethoxy-9-aza-*cis*^{1,8},*trans*^{1,2},*cis*^{2,7},*trans*^{7,8}-tricyclo-[6.3.0.0^{2,7}]undeca-3,5,10-triene (6), and *N*-Carbethoxypyrrole (7). A sample of A (3.4 g, 0.013 mol) was pyrolyzed dry under vacuum (0.05 mm) at a bath temperature of 150–165 °C in a short-path distillation unit. Gas evolution was observed, and the distillate was collected in a flask immersed in dry ice/acetone (ca. −70 °C). The resulting colorless oil was then placed on a 760 × 15 mm jacketed column wet packed (petroleum ether) with activity III Woelm neutral alumina (60 g) and maintained at ca. −15 °C. Elution with petroleum ether/ethyl ether (49:1 v/v, 200 mL) afforded *N*-carbethoxypyrrole (**7**) (488 mg, 27%): ^{1}H NMR (60 MHz, $CDCl_3$) τ 2.70 (2H, t, J = 2 Hz), 3.76 (2H, t, J = 2 Hz), 5.60 (2H, q, ethyl), 8.60 (3H, t, ethyl); IR (neat), prominent maxima at 2980, 1750, 1460, 1400 cm^{-1}. Continued elution with petroleum ether/ethyl ether (9:1 v/v, 100 mL) afforded **6** (508 mg, 18%). Distillation at a bath temperature of 45–50 °C and 0.025 mm produced a pure sample of **6** as a colorless oil: IR (neat) prominent maxima at 1710, 1610, 1420, 1335, 1130, 905, 765, 720, 685 cm^{-1}; UV (C_6H_{14}) max 282 (ε 1740), 238 nm (18 900); ^{1}H NMR (100 MHz, $CDCl_3$, +55 °C)[22] τ 3.33 (1H, d, H^{10}, J = 4.25 Hz), 4.1–4.5 (4H, m, H^3 + H^4 + H^5 + H^6), 4.72 (1H, dd, H^{11}, J = 4.25, 3 Hz), 5.39 (1H, dd, H^8, $J_{8,1}$ = 8.5, $J_{8,7}$ = 4 Hz), 5.80 (2H, q, CH_2, J = 7 Hz), 6.4 (1H, m, H^1), 6.71 (1H, ddd, H^7, $J_{7,2}$ = 12, $J_{7,8}$ = 4, $J_{7,6}$ = 3.5 Hz), 6.98 (1H, ddd, H^2, $J_{2,7}$ = 12, $J_{2,1}$ = 3.5, $J_{2,3}$ ~ 4 Hz), 8.71 (3H, t, CH_3, J = 7 Hz); MS *m/e* 139 (P^+ − C_6H_6, 38), 78 (100).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.80; H, 6.98; N, 6.47.

Further elution with the same solvent mixture (150 mL) afforded **5** (423 mg, 15%). Distillation at an oil bath temperature of ca. 45 °C and 0.025 mm afforded a pure sample of **5** as a colorless oil: IR (neat) prominent maxima at 1700, 1400, 1370, 1340, 1310, 1270, 1110, 782 cm^{-1}; UV (C_6H_{14}) max 271 (sh) (ε 2644), 261 (sh) (3830), 251 (4250), 244 nm (4360); ^{1}H NMR (100 MHz, $CDCl_3$)[22] τ 3.68 (1H, dd, H^{11}, $J_{11,10}$ ~ 2, $J_{11,1}$ ~ 2 Hz), 3.7–4.6 (5H, m, H^{10} + H^4 + H^5 + H^6 + H^7), 5.46 (1H, dd, H^1, $J_{1,9}$ = 3.5, $J_{1,11}$ ~ 2 Hz), 5.55 (1H, dd, H^3, $J_{3,8}$ = 9.5, $J_{3,4}$ = 5 Hz), 5.94 (2H, q, CH_2, J = 7 Hz), 6.66 (1H, dd, H^9, $J_{9,1}$ = 3.5, $J_{9,8}$ ~ 2 Hz), 7.21 (1H, dm, H^8, $J_{8,3}$ = 9.5 Hz), 8.83 (3H, t, CH_3, J = 7 Hz); MS *m/e* 217 (P^+, 61), 144 (100).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.70; H, 6.97; N, 6.55.

Thermolysis of 6: Formation of *N*-Carbethoxypyrrole (7) and Benzene. A vacuum-sealed (ca. 0.005 mm) medium-wall NMR tube containing a degassed solution of **6** (75 mg, 0.346 mmol) in acetonitrile-d_3 (ca. 0.4 mL) was heated in a bath of boiling toluene (109.6 °C), and the consumption of the reactant was quantitatively monitored by ^{1}H NMR spectroscopy at ambient temperature to yield k = 3.29 ± 0.23 × 10^{-4} s^{-1} ($\Delta G^{\ddagger}$ = 28.7 kcal/mol). Heating was continued for a total of 7 h, at which time ^{1}H NMR analysis showed only **7** and benzene. Evaporation of all volatiles at the water aspirator afforded *N*-carbethoxypyrrole (**7**) (45 mg, 93.5%) (IR, ^{1}H NMR).

Direct Irradiation of 6 at −78 °C: Formation of *N*-Carbethoxypyrrole. A solution of **6** (100 mg, 0.46 mmol) in deaerated (N_2) petroleum ether (45 mL) was irradiated under nitrogen with a Hanovia low-pressure mercury lamp at −78 °C (dry ice/acetone) for 1 h. The solution was then, in turn, filtered and concentrated at ca. 0 °C at the water aspirator, and the resulting residue was placed on a 300 × 12 mm jacketed column wet packed (petroleum ether) with activity III Woelm neutral alumina (20 g) and maintained at ca. −15 °C. Elution with petroleum ether/ethyl ether (49:1 v/v, 100 mL) afforded *N*-carbethoxypyrrole (**7**) (32 mg, 50%), and continued elution with petroleum ether/ethyl ether (8:2 v/v, 100 mL) produced what is believed to be 3-carbethoxypyrrole (26.5 mg, 41%), which was purified by recrystallization from petroleum ether (white solid): mp 38–39 °C; IR (KBr) prominent maxima at 3300, 1695, 1410, 1310, 1180, 1160, 955, 745 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) τ 3.12 (2H, m), 3.78 (1H, m), 5.74 (2H, q, ethyl), 8.73 (3H, t, ethyl); MS *m/e* 139 (P^+, 63.9), 94 (100).

Direct and Sensitized Irradiation of 6: Formation of *N*-Carbethoxypyrrole (7). A 125 × 15 mm quartz test tube containing a solution of **6** (100 mg, 0.46 mmol) in deaerated (N_2) ethyl ether (12 mL) was capped tightly under nitrogen and placed in an ice bath and its contents irradiated with a 450-W Hanovia mercury arc along the external surface of a quartz immersion well fitted with a Vycor filter and containing the lamp. After a total irradiation time of 80 min, the ether was removed at the water aspirator and the residue separated into *N*-carbethoxypyrrole (**7**) (^{1}H NMR, IR) (60%) and 3-carbethoxypyrrole (^{1}H NMR, IR) (30%) by column chromatography on activity III Woelm neutral alumina at ca. −15 °C (vide supra). Under similar conditions, Pyrex-filtered irradiation of **6** for 1 h in ethyl ether or 80 min in acetone containing Michler's ketone yielded a photolysate consisting (^{1}H NMR, IR) primarily (95%) of *N*-carbethoxypyrrole (**7**).

Irradiation of *N*-Carbethoxypyrrole: Formation of 3-Carbethoxypyrrole. Into each of two quartz test tubes (125 × 15 mm) was placed a solution of *N*-carbethoxypyrrole (**7**) (200 mg, 1.44 mmol) in deaerated (N_2) ethyl ether (12 mL). The tubes were then capped under nitrogen, suspended along the outside surface of a photochemical immersion well fitted with a Vycor filter, and irradiated with a Hanovia 450-W mercury lamp at ca. 0 °C (ice bath) for 2 h. The contents of the tubes were then combined and concentrated at the water aspirator at ca. 0 °C to yield a crude oil which was placed on a 300 × 12 mm jacketed column wet packed (petroleum ether) with activity III Woelm neutral alumina (20 g) and maintained at ca. −15 °C. Elution with petroleum ether/ethyl ether (49:1 v/v, 100 mL) afforded unreacted *N*-carbethoxypyrrole (140 mg, 70%), and subsequent elution with petroleum ether/ethyl ether (8:2 v/v, 100 mL) produced 3-carbethoxypyrrole (50 mg, 25%), which was purified by recrystallization from petroleum ether (IR, ^{1}H NMR).

Sensitized Irradiation of 5: Formation of Dimer D. A solution of **5** (100 mg, 0.46 mmol) and Michler's ketone (100 mg) in deaerated (N_2) acetone (125 mL) was transferred to a photochemical reaction flask fitted with a photochemical immersion well and irradiated through a Pyrex filter with a Hanovia 450-W mercury arc under nitrogen at ca. 0 °C for 1 h. The contents were then concentrated at the water aspirator at ca. 0 °C, and the yellow residue was treated with ethyl ether (25 mL). The resulting precipitate (Michler's ketone) was removed by pressure filtration under nitrogen, and the filtrate was concentrated at the water aspirator at ca. 0 °C to afford a yellow oil which was placed on a 300 × 12 mm jacketed column maintained at ca. −15 °C and wet packed (petroleum ether) with activity III Woelm neutral alumina (20 g). Elution with petroleum ether/ethyl ether (9:1 v/v, 200 mL) removed the impurities so that subsequent elution with petroleum ether/ethyl ether (3:1 v/v, 75 mL) yielded D (32 mg, 16%). Recrystallization from ethyl ether provided a pure sample of this substance: mp 134–138 °C; IR prominent maxima at 1690, 1380, 1275, 1120, 680 cm^{-1}; UV (C_6H_{14}) end absorption; ^{1}H NMR (100 MHz,

$CDCl_3$) τ 3.73 (2H, dd, J = 3.2 Hz), 3.93 (2H, d, J = 3 Hz), 4.10 (2H, dm, J = 10 Hz), 4.62 (2H, broad d, J = 10 Hz), 5.23 (2H, dd, J = 3.5, 2 Hz), 5.7–6.1 (6H, m), 6.35 (2H, broad d, J = 6 Hz), 6.81 (2H, d, J = 3.5 Hz), 7.16 (2H, m), 7.67 (2H, broad s), 8.78 (3H, t); MS *m/e* 434 (P^+, 5.2), 217 (100).

Anal. Calcd for $C_{26}H_{30}N_2O_4$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.75; H, 7.00; N, 6.39.

Direct Irradiation of 5 at −78 °C: Formation of *N*-Carbethoxy-2-aza-*cis*-bicyclo[5.4.0]undeca-3,5,8,10-tetraene (20), *N*-Carbethoxy-2-aza-*trans*-bicyclo[5.4.0]undeca-3,5,8,10-tetraene (21), and *N*-Carbethoxy-2-aza-*cis*^{1,9},*trans*^{3,8},*cis*^{8,9}-[7.2.0.0^{3,8}]undeca-4,6,10-triene (22). A solution of **5** (480 mg, 2.21 mmol) in deaerated (N_2) petroleum ether (45 mL) was irradiated under nitrogen with a Hanovia low-pressure coil at ca. −78 °C (dry ice/acetone) for 1.5 h. The solution was then filtered and concentrated at ca. 0 °C and 0.1 mm, yielding a yellow oil which was placed on a 760 × 15 mm jacketed column maintained at ca. −15 °C and wet packed (petroleum ether) with activity III Woelm neutral alumina (60 g). Elution with petroleum ether (100 mL) and then petroleum ether/ethyl ether (19:1 v/v, 150 mL) afforded **20** (75.8 mg, 16%) as a colorless oil. Vacuum distillation (0.025 mm) at a bath temperature of 35–40 °C afforded pure **20** as a colorless liquid: IR (neat) prominent maxima at 1715, 1260, 770, 675 cm^{-1}; UV (C_6H_{14}) max 267 (sh) (ϵ 16 380), 248 nm (20 340); ^1H NMR (100 MHz, $CDCl_3$)[22] τ 3.29 (1H, d, H^3, $J_{3,4}$ = 9 Hz), 3.8–4.4 (5H, m), 4.4–5.1 (3H, m), 5.74 (2H, d, ethyl), 6.89 (1H, broad d, H^7, $J_{1,7} \sim 7$ Hz), 8.67 (3H, t, ethyl); MS *m/e* 217 (P^+, 59.2), 144 (100).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.85; H, 6.93; N, 6.50.

Continued elution with the same solvent mixture (200 mL) afforded a mixture of products (105 mg) consisting of **20** (25%), **21** (35%), and **22** (40%). Continued elution with petroleum ether/ethyl ether (9:1 v/v, 200 mL) produced unreacted **5** (270 mg, 56%) (^1H NMR).

The three-component fraction was placed on a 760 × 15 mm jacketed column wet packed (petroleum ether) with activity III Woelm neutral alumina (60 g) and maintained at ca. −15 °C. Elution with petroleum ether/ethyl ether (19:1 v/v, 100 mL) followed by the same solvent mixture (50 mL) afforded **20** (25 mg) (^1H NMR, IR). Continued elution with this solvent mixture (100 mL) afforded **21** (30 mg). Vacuum distillation (0.005 mm) at an oil bath temperature of 40–45 °C produced pure **21** as a colorless oil: IR (neat) prominent maxima at 1710, 1255, 710 cm^{-1}; UV (C_6H_{14}) max 270 (sh) (ϵ 7700), 258 nm (17 000); ^1H NMR (100 MHz, acetone-d_6) τ 3.23 (1H, d, H^3, $J_{3,4}$ = 8.5 Hz), 4.0–4.4 (6H, m), 4.5–4.7 (1H, m, H^4), 5.7–6.0 (3H, m, H^1 + ethyl), 6.38 (1H, broad d, H^7, $J_{7,1}$ = 17 Hz), 8.75 (3H, t, ethyl); MS *m/e* 217 (P^+, 100).

Further elution with petroleum ether/ethyl ether (19:1 v/v, 50 mL) yielded an equimolar mixture (20 mg) of **21** and **22**, and final elution with this solvent mixture (50 mL) produced **22** (30 mg). Vacuum distillation (0.005 mm) at an oil bath temperature of 40–45 °C yielded pure **22** as a colorless oil: IR (neat) prominent maxima at 1700, 1275, 685 cm^{-1}; UV (C_6H_{14}) max 254 (ϵ 2450), 227 nm (2480); ^1H NMR[22] (100 MHz, $CDCl_3$) τ 2.98 (1H, broad d, H^4, $J_{4,5}$ = 9.0 Hz), 3.4–4.2 (5H, m), 5.18 (1H, dd, H^1, $J_{1,11}$ = 2.5, $J_{1,9}$ = 3.5 Hz), 5.6–6.1 (3H, m, H^3 + ethyl), 6.47 (1H, dd, H^9, $J_{9,1}$ = 3.5, $J_{8,9}$ = 7.5 Hz), 7.54 (1H, dd, H^8, $J_{8,3}$ = 18, $J_{8,9}$ = 7.5 Hz), 8.70 (3H, t, ethyl); MS *m/e* 217 (P^+, 42), 144 (100).

Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.83; H, 6.89; N, 6.48.

Preparation of *N*-Carbethoxy-2,3,4,5-tetrahydro-1-benzazepine (26). To a cold (ca. 0 °C) deaerated (N_2) solution of 2,3,4,5-tetrahydro-1-benzazepine[23] (809 mg, 5.5 mmol) and pyridine (632 mg, 8 mmol) in dry ethyl ether (20 mL) was rapidly added, under nitrogen, ethyl chloroformate (756 mg, 7 mmol) in dry ethyl ether (10 mL), and the resulting suspension was allowed to stir under these conditions for an additional hour. The mixture was then pressure-filtered under nitrogen, and the resulting filtrate was concentrated at ca. 0 °C, first at water aspirator pressure and then at ca. 0.05 mm and a bath temperature of 70–75 °C, to yield pure *N*-carbethoxy-2,3,4,5-tetrahydro-1-benzazepine (**26**) (638 mg, 53%) as a colorless oil; GLPC analysis (conditions A[20]) indicated the presence of a single component (11 min, 30 s). Preparative GLPC furnished a pure sample of **26** as a colorless oil: IR (neat) prominent maxima at 2870, 1700, 1410, 1310, 1280, 1262, 1182, 1050, 1038, 772, 765 cm^{-1}; UV (C_6H_{14}) max 261 (ϵ 327), 229 (3860), 204 nm (14 910); ^1H NMR (60 MHz, $CDCl_3$) τ 2.9 (4H, s), 5.6–6.7 (4H, m), 7.1–7.4 (2H, m), 7.9–9.1 (7H, m); MS *m/e* 219 (P^+, 74.3), 146 (100).

Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.01; H, 7.91; N, 6.27.

Catalytic Hydrogenation of *N*-Carbethoxy-2,3,4,5-tetrahydro-1-benzazepine (26) to *N*-Carbethoxy-2-aza-*cis*-bicyclo[5.4.0]undecane (28). A mixture of *N*-carbethoxy-2,3,4,5-tetrahydro-1-benzazepine (**26**) (100 mg, 0.46 mmol) and 5% rhodium-on-charcoal catalyst (300 mg) in dry, freshly distilled tetrahydrofuran (20 mL) was treated with hydrogen at ca. 0 °C and atmospheric pressure. Uptake was complete after 24 h. The mixture was then pressure-filtered (N_2) and the filtrate concentrated at the water aspirator to a colorless oil (113 mg, ~ 100%). GLPC analysis (conditions A) revealed the presence of two components, A (80%, 17 min, 20 s) and B (20%, 13 min, 20 s). Collection of the major component (A) yielded a pure sample of *N*-carbethoxy-2-aza-*cis*-bicyclo[5.4.0]undecane (**28**) as a colorless oil: IR (neat) prominent maxima at 2850, 1670, 1410, 1110, 1081 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) τ 5.6–6.6 (4H, m), 6.7–7.3 (1H, m), 7.8–9.1 (18H, m); MS *m/e* 225 (P^+, 36.6), 182 (100).

Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.49; H, 10.30; N, 6.41.

Catalytic Hydrogenation of 20 to *N*-Carbethoxy-2-aza-*cis*-bicyclo[5.4.0]undecane (28). A mixture of **20** (128 mg, 0.59 mmol) and 5% rhodium-on-charcoal catalyst (300 mg) in dry, freshly distilled tetrahydrofuran (200 mL) was treated with hydrogen at ca. 0 °C and atmospheric pressure. Uptake was complete after 24 h. The suspension was then pressure-filtered (N_2) and the resulting filtrate concentrated at the water aspirator to a colorless oil (132 mg, 99%). GLPC analysis (conditions A) revealed the presence of a single component (17 min, 20 s) which was collected to yield a pure sample of *N*-carbethoxy-2-aza-*cis*-bicyclo[5.4.0]undecane (**28**) (IR, ^1H NMR).

Dehydrogenation of 21 to *N*-Carbethoxy-1-benzazepine (25). To a stirring solution of **21** (43 mg, 0.198 mmol) in benzene (5 mL) maintained under nitrogen was added at ambient temperature a solution of *o*-chloranil (49.2 mg, 0.198 mmol) in benzene (2 mL), and the ensuing red solution was allowed to stir under these conditions for an additional 12 h. The resulting orange solution was then concentrated at the water aspirator, the ensuing red-brown residue was dissolved in a minimum amount of ethyl ether, and the solution was placed on a 300 × 12 mm jacketed column wet packed (petroleum ether) with activity III Woelm neutral alumina (20 g) and maintained at ca. −15 °C. Elution with petroleum ether (100 mL) removed all the impurities so that subsequent elution with petroleum ether/ethyl ether (3:1 v/v, 100 mL) afforded *N*-carbethoxy-1-benzazepine (**25**) (27.2 mg, 64%) as a colorless oil. GLPC analysis (conditions B[20]) revealed the presence of a single component (21 min, 45 s) which was collected to yield a pure sample of **25** as a colorless oil: IR (neat) prominent maxima at 1700, 1380, 1330, 1295, 1060, 1040, 770, 760, 710 cm^{-1}; UV (C_6H_{14}) max 306 (sh) (ϵ 1540), 289 (1720), 245 (sh) (9370), 241 (10 570), 228 (11 800), 204 nm (23 500); ^1H NMR (100 MHz, $CDCl_3$) τ 2.5–2.9 (4H, m), 3.14 (1H, d, J = 11.0 Hz), 3.64 (1H, d, J = 7.0 Hz), 3.76 (1H, dd, J = 11.0, 6.0 Hz), 4.19 (1H, dd, $J \sim 7,6$ Hz), 5.77 (2H, q), 8.74 (3H, t); MS *m/e* 215 (P^+, 29.7), 142 (100).

Catalytic Hydrogenation of *N*-Carbethoxy-1-benzazepine (25) to *N*-Carbethoxy-2,3,4,5-tetrahydro-1-benzazepine (26). A mixture of **25** (25 mg, 0.12 mmol) and 5% palladium-on-charcoal catalyst (100 mg) in dry, freshly distilled tetrahydrofuran (20 mL) was treated with hydrogen at ca. 0 °C and atmospheric pressure. After uptake was complete (~24 h), the suspension was pressure-filtered (N_2) and the resulting filtrate concentrated at the water aspirator to a colorless oil (~40 mg). GLPC analysis (conditions A) revealed the presence of a single component (11 min, 30 s) which was collected and shown to be *N*-carbethoxy-2,3,4,5-tetrahydrobenzazepine (**26**), identical (IR, ^1H NMR, GLC) with a synthetic specimen (vide supra).

Thermolysis of *N*-Carbethoxy-2-aza-*trans*-bicyclo[5.4.0]-3,5,8,10-tetraene (21): Formation of Dihydrobenzazepine 24. A sample of **21** (15 mg, 0.07 mmol) was dissolved in ethyl ether (0.5 mL), and the resulting solution was injected into a gas chromatograph (conditions B) in 50-μL portions. The single component observed (21 min, 5 s) was collected at 0 °C as a colorless oil, shown to be the dihydrobenzazepine **24**: IR (neat) prominent maxima at 1705, 1400, 1310, 782, 760 cm^{-1}; UV (C_6H_{14}) max 294 (sh) (ϵ 680), 285 (930), 252 (9070), 227 nm (22 700); ^1H NMR (100 MHz, $CDCl_3$) τ 2.6–2.9 (4H, m), 3.60 (1H, d, H^5, $J_{5,4}$ = 12.5 Hz), 4.05 (1H, dm, H^4, $J_{4,5}$ = 12.5 Hz), 5.81 (2H, q, ethyl), 6.3 (2H, broad m, H^2), 7.4 (2H, broad m, H^3), 8.76 (3H, t, ethyl); MS *m/e* 217 (P^+, 100).

Dehydrogenation of *N*-Carbethoxy-2-aza-*cis*^{1,9},*trans*^{3,8},-*cis*^{8,9}-tricyclo[7.2.0.0^{3,8}]undeca-4,6,10-triene (22) to 23. To a stirring solution of **22** (135 mg, 0.62 mmol) in benzene (5 mL) maintained under nitrogen was added at ambient temperature a solution of *o*-chloranil (152 mg, 0.62 mmol) in benzene (3 mL), and the resulting red solution was allowed to stir under these conditions for ca. 12 h. The ensuing orange solution was then concentrated at the water

aspirator, and the red-orange residue thus obtained was dissolved in a minimum amount of ethyl ether and the solution placed on a 300 × 12 mm jacketed column wet packed (petroleum ether) with activity III Woelm neutral alumina (20 g). Elution with petroleum ether (100 mL) removed the impurities so that subsequent elution with petroleum ether/ethyl ether (3:1 v/v, 100 mL) produced **23** (81 mg, 53%). GLPC analysis (conditions A) indicated the presence of a single component (16 min, 15 s) which was collected to furnish a pure sample of **23** as a colorless oil: IR (neat) prominent maxima at 1700, 1480, 1405, 1380, 1280, 1200, 1150, 1070, 770, 760 cm^{-1}; UV (C_6H_{14}) max 292 (ϵ 2710), 283 (2540), 278 (sh) (2018), 255 (sh) (9660), 247 (11 970), 243 (sh) (11 240), 212 (sh) (26 820), 208 nm (31 150); ^1H NMR (100 MHz, $CDCl_3$) τ 2.15 (1H, broad s), 2.7–3.2 (3H, m), 3.58 (1H, dd, H^7, $J_{7,8}$ = 3, $J_{7,1}$ = 1.5 Hz), 3.82 (1H, d, H^6, $J_{6,7}$ = 3Hz), 4.82 (1H, dd, H^1, $J_{1,5}$ = 4, $J_{1,7}$ = 1.5 Hz), 5.5–5.9 (3H, m, H^6 + ethyl), 8.64 (3H, t, ethyl); MS *m/e* 215 (P^+, 39.7), 142 (100).

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.52; H, 6.09; N, 6.51. Found: C, 72.64; H, 6.20; N, 6.69.

Preparation of *N*-Carbethoxy-2,3-diazabicyclo[3.2.0]hepta-3,6-diene (8).[24] A solution of *N*-carbethoxy-1,2-diazepine[25] (1.0 g, 0.006 mol) in deaerated (N_2) ethyl ether (200 mL) was irradiated at ambient temperature under a nitrogen atmosphere through a Pyrex filter with a Hanovia 450-W lamp for a period of 6 days. The solution was then concentrated at the water aspirator at ambient temperature and the resulting yellow oil placed on a 400 × 20 mm column wet packed (petroleum ether) with activity III Woelm neutral alumina (40 g). Elution with petroleum ether (100 mL) removed residual reactant so that subsequent elution with petroleum ether (150 mL) produced pure *N*-carbethoxy-2,3-diazabicyclo[3.2.0]hepta-3,6-diene (**8**) (0.9 g, 90%) as a pale yellow liquid (^1H NMR, IR).[11]

Reaction of *N*-Carbethoxy-2,3-diazabicyclo[3.2.0]hepta-3,6-diene (8) with α-Pyrone (3): Formation of B. A deaerated (N_2) solution of *N*-carbethoxy-2,3-diazabicyclo[3.2.0]hepta-3,6-diene (**8**) (2.0 g, 0.012 mol) and α-pyrone (**3**) (6.0 g, 0.063 mol) in benzene (6 mL) was heated at 65 °C under nitrogen for 40 h. The solution was concentrated at the water aspirator, and unreacted α-pyrone was then removed at a bath temperature of 50–55 °C and 0.1 mm to yield a dark residue. This residue was dissolved in a minimum amount of ethyl ether and the resulting solution placed on a 300 × 12 mm jacketed column wet packed (petroleum ether) with activity III Woelm neutral alumina (20 g) and maintained at ca. −10 °C. Elution with ethyl ether (300 mL) removed the impurities so that subsequent elution with chloroform (200 mL) afforded B (2.1 g, 64%) as a colorless oil.

Pyrolysis of B: Formation of 9-Carbethoxy-9,10-diaza-*cis*^{1,9},*cis*^{2,7},*trans*^{1,2},*trans*^{7,8}-tricyclo[6.3.0.0^{2,7}]undeca-3,5,10-triene (9), 9-Carbethoxy-9,10-diaza-*cis*^{1,8},*cis*^{2,7},*cis*^{1,2},*cis*^{7,8}-tricyclo[6.3.0.0^{2,7}]undeca-3,5,10-triene (9),[13] and *N*-Carbethoxypyrazole (10). A sample of **8** (2.0 g, 0.008 mol) was pyrolyzed dry under vacuum (0.05 mm) at a bath temperature of 125 °C in a short-path distillation unit in four equal portions. Gas evolution was observed, and the distillate was collected in a flask maintained at −78 °C (dry ice/acetone). The resulting colorless oil was then placed on a 600 × 17 mm jacketed column wet packed (petroleum ether) with activity III Woelm neutral alumina (60 g) and maintained at ca. −15 °C. Elution with petroleum either/ethyl ether (1:5 v/v, 150 mL) afforded *N*-carbethoxypyrazole (**10**)[12] (340 mg, 32%); ^1H NMR (60 MHz, $CDCl_3$) τ 1.82 (1H, d, H^5, $J_{5,4}$ = 3.0 Hz), 2.23 (1H, m, H^3), 3.56 (1H, dd, H^4, $J_{4,3}$ = 1, $J_{4,5}$ = 3.0 Hz), 5.45 (2H, q), 8.54 (3H, t); MS *m/e* 140 (P^+, 16). Continued elution with the same solvent mixture (120 mL) afforded **9** (370 mg, 22.5%). Distillation of this material at a bath temperature of 60–65 °C and 0.02 mm produced a pure sample of **9** as a colorless oil: IR (neat) prominent maxima at 2900, 1730, 1700, 1580, 1420 cm^{-1}; UV (CH_3CN) max 280 (sh) (ϵ 1940), 246 nm (10 140); ^1H NMR (60 MHz, $CDCl_3$) τ 2.93 (1H, d, H^{11}, $J_{11,1}$ = 2.0 Hz), 4.0–4.7 (4H, m, H^3 + H^4 + H^5 + H^6), 5.38 (1H, dd, H^8, $J_{8,1}$ = 8.5, $J_{8,7}$ = 3 Hz), 5.71 (2H, q, ethyl), 6.18 (1H, ddd, H^1, $J_{1,8}$ = 8.5, $J_{1,11}$ = 2.0, $J_{1,2}$ = 3.3 Hz), 6.6–6.9 (2H, m, H^2 + H^7), 8.67 (3H, t, ethyl); MS *m/e* 140 (pyrazole **10**, 12), 78 (100).

Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.04; H, 6.46; N, 12.84. Found: C, 65.97; H, 6.36; N, 12.98.

Further elution with the same solvent combination (50 mL) afforded an equimolar mixture of **9** and what is presumed to be the syn isomer **9′**[13] (40 mg), while final elution with petroleum ether/ethyl ether (1:5 v/v, 100 mL) afforded a pure sample of the presumed isomer **9′** (58 mg, 3.5%) as a colorless liquid: ^1H NMR (60 MHz, $CDCl_3$) τ 3.10 (1H, d, H^{11}, $J_{11,1}$ = 2.0 Hz), 4.0–4.8 (4H, m, H^3 + H^4 + H^5 + H^6), 4.8–5.2 (1H, m, H^8), 5.73 (2H, q, ethyl), 5.7–6.6 (3H, m, H^1 + H^2 + H^7), 8.66 (3H, t, ethyl).

Thermolysis of 9: Formation of *N*-Carbethoxypyrazole (10) and Benzene. A vacuum-sealed (ca. 0.005 mm) medium-wall NMR tube containing a degassed solution of **9** (75 mg, 0.344 mmol) in acetonitrile-d_3 (ca. 0.4 mL) was heated in a bath of boiling toluene (109.7 °C), and the consumption of the reactant was quantitatively monitored by ^1H NMR spectroscopy at ambient temperature to yield k = 3.69 ± 0.20 × 10^{-4} s^{-1} ($\Delta G^{\ddagger}$ = 28.6 kcal/mol). Heating was continued for a total of 7 h, at which time ^1H NMR analysis showed only **10** and benzene.

Under a similar set of thermolysis conditions, a sample of what is presumed to be **9′** produced a clean two-component mixture consisting (^1H NMR) of benzene and **10**.

Direct Irradiation of 9 at −78 °C: Formation of *N*-Carbethoxypyrazole (10). A solution of **9** (50 mg, 0.229 mmol) in deaerated (N_2) ethyl ether/petroleum ether (1:5 v/v, 50 mL) was irradiated under nitrogen with a Hanovia low-pressure mercury lamp at −78 °C (dry ice/acetone) for 1 h. Concentration at ca. 0 °C at the water aspirator afforded *N*-carbethoxypyrazole (**10**) (30 mg, 93.5%) (^1H NMR).

Under similar conditions of irradiation, an equimolar mixture of **9** and the presumed syn isomer **9′**[13] also produced **10** (^1H NMR) as the only nonvolatile product.

Reaction of Oxepin (11) with 2,4-Dimethyl-3,4-diphenylcyclopentadienone (12): Formation of 13. A solution of oxepin (**11**)[26] (470 mg, 5.0 mmol) and 2,5-dimethyl-3,4-diphenylcyclopentadienone (**12**) (1.3 g, 2.5 mmol) in deaerated (N_2) benzene (10 mL) was maintained at the reflux temperature under nitrogen for 48 h. Removal of the solvent at the water aspirator afforded a pale yellow solid which was dissolved in the minimum amount of chloroform and placed on a 300 × 12 mm jacketed column maintained at ca. −15 °C and wet-packed (petroleum ether) with activity III Woelm neutral alumina (20 g). Elution with petroleum ether (100 mL) and then petroleum ether/ethyl ether (9:1 v/v, 200 mL) gave **13** as a foamy solid which was recrystallized from hot ethanol to produce a pure specimen of white needles: mp 164–165 (dec); IR (KBr) prominent maxima at 2900, 1760, 1660, 1440, 1350, 1140, 970, 910, 820, 810, 780, 740, 730, 700 cm^{-1}; UV (hexane) max 257 (ϵ 9100), 222 nm (18 700); ^1H NMR (60 MHz, $CDCl_3$) τ 2.9 (10H, m, phenyls), 3.55 (2H, d, H^2(H^7), $J_{2,3}$ = 8.0 Hz), 5.20 (2H, ddd, H^3(H^6), $J_{3,2}$ = 8.0, $J_{3,4}$ = 2.5, $J_{3,5}$ = 1.5 Hz), 7.08 (2H, m, H^4(H^5)), 8.60 (6H, s, methyls); MS *m/e* 354 (P^+, 24.4), 260 (100).

Anal. Calcd: C, 84.72; H, 6.25; O, 9.08. Found: C, 84.63; H, 6.40; O, 9.03.

Thermolysis of Cycloadduct 13. A vacuum-sealed (ca. 0.005 mm) Pyrex tube (3 mm × 25 cm) containing a solution of **13** (354 mg, 1 mmol) in deaerated (N_2) benzene (10 mL) was immersed in a bath of boiling ethylene glycol (ca. 192 °C) for 10 min. The tube was then cooled to −78 °C (dry ice/acetone) and filed open, and the bright red solution was concentrated at the water aspirator to yield a dark semisolid residue which we dissolved in the minimum amount of chloroform and placed on a 500 × 15 mm jacketed column maintained at ca. −15 °C and wet packed (petroleum ether) with activity III Woelm neutral alumina (40 g). Elution with petroleum ether (100 mL) afforded a pure specimen of **11** (50 mg) (^1H NMR, IR). Continued elution with petroleum ether/ethyl ether (9:1 v/v, 200 mL) afforded pure **12** (200 mg) as a white solid: mp 182 °C (IR).

Similar results were obtained on conducting the thermolysis of **13** at 163 °C (boiling mesitylene).

Preparation of 2-Oxabicyclo[3.2.0]hepta-3,6-diene (15).[27] A solution of oxepin (2.2 g, 0.023 mol) in freshly distilled, deaerated (N_2) ethyl ether was equally distributed in eight 125 × 15 mm Pyrex test tubes. The test tubes were tightly capped under nitrogen and irradiated for 2 days at ambient temperature in a Rayonet photochemical reactor with a bank of 16 3500-Å lamps, leading to slow decoloration of the initially yellow ether solution. The contents of the test tubes were combined, and the colorless photosylate was concentrated at atmospheric pressure and ca. 31 °C to yield a colorless mobile liquid which was vacuum distilled at the water aspirator and ambient temperature to produce a pure sample of 2-oxabicyclo[3.2.0]hepta-3,6-diene (**15**) (2.0 g, 95%): ^1H NMR (60 MHz, $CDCl_3$) τ 3.33 (1H, pseudo-t, J = 3.0 Hz), 3.70 (1H, d, J = 3.0 Hz), 4.00 (1H, dd, J = 1.5, 3.0 Hz), 4.80 (1H, m), 6.25 (2H, m).

Reaction of 2-Oxabicyclo[3.2.0]hepta-3,6-diene (15) with 2,5-Dimethyl-3,4-diphenylcyclopentadienone (12): Formation of 16. A vacuum-sealed (ca. 0.005 mm) Pyrex tube (3 mm × 25 cm) containing a solution of 2-oxabicyclo[3.2.0]hepta-3,6-diene (850 mg, 8 mmol) and **12** (1.4 g, 4 mmol) in deaerated benzene (6 mL) was maintained at ca. 77 °C (boiling ethyl acetate) for 2 h. The tube was then cooled to −78 °C (dry ice/acetone) and filed open, and the colorless solution concentrated at the water aspirator to produce a white foamy residue (2.2 g, ~ 100%). Two recrystallizations of this material from ethanol afforded analytically pure **16** as white needles: mp

142–143 °C; IR ($CHCl_3$) prominent maxima at 2900, 1760, 1610, 1605, 1480, 1440, 1380, 1140, 1050, 950, 705 cm^{-1}; UV (C_6H_{14}) max 258 (ϵ 10 000) and 222 nm (20 000); ^1H NMR (100 MHz, $CDCl_3$)[22] τ 2.80 (5H, m, phenyl), 2.96 (5H, m, phenyl), 3.54 (1H, dd, H^3, $J_{3,4}$ = 2.5 H, $J_{3,5}$ = 1.0 Hz), 4.88 (1H, pseudo-t, H^4, $J_{3,4} = J_{4,5}$ = 2.5 Hz), 5.38 (1H, dd, H^1, $J_{1,5}$ = 7.0, $J_{1,7}$ = 2.0 Hz), 6.85 (1H, m, H^5), 7.18 (1H, broad d, H^7, $J_{7,6}$ = 8.5 Hz), 7.48 (1H, dd, H^6, $J_{6,7}$ = 8.5, $J_{5,6}$ = 2.0 Hz), 8.70 (3H, s, methyl), 8.74 (3H, s, methyl); MS *m/e* 354 (P^+, 4.3), 94 (100).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 84.71; H, 6.27; O, 9.01. Found: C, 84.52; H, 6.34; O, 8.79.

Thermal Fragmentation of 16. A vacuum-sealed (ca. 0.005 mm) NMR tube containing a solution of **16** (100 mg, 0.685 mmol) in benzene-d_6 (ca. 0.4 mL) was maintained in a bath of boiling ethylene glycol (ca. 192 °C), and the contents were periodically monitored by ^1H NMR, revealing the presence of furan and 1,4-dimethyl-2,3-diphenylbenzene (**17**). After a total in-bath time of 4 h, the tube was cooled to −78 °C (dry ice/acetone) and filed open, and its contents concentrated at the water aspirator to yield **17** (65 mg, 95%) as a white solid. One recrystallization of this material from ethanol afforded a pure specimen as white needles: mp 106–107 °C; MS *m/e* 258 (P^+, 100); identical in all respects (mp, IR) with authentic material.[28] Similar results were obtained when the thermolysis of **16** was conducted at 163 °C (boiling mesitylene).

The ^1H NMR-determined thermal half-life of **16** is 18 min at 192 °C and 4 h at 163 °C.

Reaction of Oxabicyclo[3.2.0]hepta-3,6-diene (15) with α-Pyrone (3): Formation of C. A vacuum-sealed (three freeze–thaw cycles) Pyrex tube (3 mm × 25 cm) containing a solution of oxabicyclo[3.2.0]hepta-3,6-diene (**15**) (1.5 g, 16 mmol) and α-pyrone (**3**)[29] (9.6 g, 0.1 mol) in benzene (5 mL) was maintained in a bath of boiling ethyl acetate (77 °C) for 3 days. The tube was then cooled to −78 °C (dry ice/acetone) and filed open, and its contents concentrated at the water aspirator to yield a yellow oil consisting of C and unreacted α-pyrone (^1H NMR). The α-pyrone (6.7 g) was removed by vacuum distillation (ca. 0.01 mm) at a bath temperature of ca. 50 °C, the residue was dissolved in ethyl ether (50 ml), and the resulting solution was pressure-filtered (N_2) through a layer of Florisil (30 g) to remove polymer. The filtrate was concentrated at the water aspirator, and the resulting yellow mobile liquid was heated at ca. 50 °C under vacuum (ca. 0.01 mm) to remove any residual α-pyrone, yielding C (2.0 g) as the residue.

Pyrolysis of C: Formation of 9-Oxa-*cis*^{1,8},*cis*^{2,7},*trans*^{7,8}-tricyclo[6.3.0.0^{2,7}]undeca-3,5,10-triene (18). A sample of C (2.0 g, ~10.5 mmol) was pyrolyzed dry under vacuum (0.05 mm) at a bath temperature of 170 °C in a short-path distillation unit. Gas evolution was observed, the yellow distillate was collected in a flask maintained at −78 °C (dry ice/acetone) and dissolved in the minimum amount of ethyl ether, and the resulting solution was placed on a 760 × 15 mm jacketed column wet packed (petroleum ether) with activity II Woelm neutral alumina (60 g) and maintained at ca. −15 °C. Elution with petroleum ether (300 mL) afforded **18** (490 mg, 21%) as an air-sensitive colorless oil. An analytical sample of **18** was obtained by vacuum distillation (0.01 mm) at a bath temperature of ca. 30 °C: IR (neat) prominent maxima at 2900, 1600, 1400, 1380, 1300, 1270, 1250, 1170, 1130, 1050, 1010, 1000, 980, 870, 760, 700 cm^{-1}; UV (C_6H_{14}) max 283 (ϵ 1750), 220 nm (6250); ^1H NMR (60 MHz, $CDCl_3$) τ 3.65 (1H, dd, H^3, $J_{3,4}$ = 3.0, $J_{3,5}$ = 1.5 Hz), 4.28 (4H, m, $H^8 + H^4 + H^5 + H^6$), 4.80 (1H, pseudo-t, H^4, $J_{3,4} = J_{4,5}$ = 3.0 Hz), 5.08 (1H, dd, H^1, $J_{1,5}$ = 7.5, $J_{1,11}$ = 4.0 Hz), 6.50 (1H, m, H^5), 6.90 (1H, dt, H^{11}, $J_{11,6}$ = 12.0, $J_{1,11} = J_{10,11}$ = 3.0 Hz), 7.08 (1H, dt, H^6, $J_{6,11}$ = 12.0, $J_{6,5} = J_{6,7}$ = 3.0 Hz); MS *m/e* 146 (P^+, 1), 78 (100).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.88; O, 10.94. Found: C, 82.10; H, 6.96; O, 11.05.

Continued elution with petroleum ether/ethyl ether (9:1 v/v, 400 mL) produced a colorless viscous oil (ca. 400 mg) believed to be a C_4H_4 homologue of **18**. GLPC analysis of this oil (conditions C[20]) revealed the presence of a single component (~35 min) which was collected: IR (neat) prominent maxima at 2800, 2600, 1600, 1390, 1340, 1315, 1290, 1150, 1125, 1050, 1010, 985, 945, 930, 865, 835, 800, 760, 720, 690 cm^{-1}; UV (C_6H_{14}) max 266 (sh) (ϵ 1680), 258 (3860), 249 (sh) (1840); ^1H NMR (100 MHz, $CDCl_3$) τ 3.55 (1H, dd, J = 1.5, 3.0 Hz), 4.10 (4H, m), 4.65 (2H, broad d, J = 10.0 Hz), 4.82 (1H, pseudo-t, J = 3.0 Hz), 5.18 (2H, dd, J = 4.0, 7.0 Hz), 6.8–7.2 (4H, m); MS *m/e* 198 (P^+, <1), 78 (100).

Anal. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.66; H, 7.16.

Thermolysis of 18: Formation of Furan (19) and Benzene. A vacuum-sealed medium-wall NMR tube containing a degassed solution of **18** (80 mg, 0.578 mmol) in acetonitrile-d_3 (ca. 0.4 mL) was heated in a bath of boiling toluene (110.4 °C), and the consumption of reactant **18** was quantitatively monitored by ^1H NMR spectroscopy at ambient temperature to yield $k = 4.49 \pm 0.39 \times 10^{-4}$ s^{-1} ($\Delta G^{\ddagger}$ = 28.5 kcal/mol). Heating was continued for a total of 6 h, at which time ^1H NMR analysis showed only furan and benzene.

Direct Irradiation of 18 at 0 °C: Formation of Furan (19) and Benzene. An NMR tube containing a deaerated (N_2) solution of **18** (50 mg, 0.342 mmol) in acetone-d_6 (ca. 0.4 mL) was placed in an ice bath, and its contents were irradiated with a 450-W Hanovia mercury arc along the external surface of a quartz immersion well for 10 h. ^1H NMR analysis of the resulting photolysate showed the presence of only furan and benzene.

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Registry No.—**2,** 2955-79-5; **3,** 504-31-4; **4,** 64056-59-3; **5,** 64045-80-3; **6,** 64082-14-0; **7,** 4277-64-9; **8,** 42068-20-2; **9,** 64056-60-6; **8′,** 64090-69-3; **10,** 10199-59-4; **11,** 291-70-3; **12,** 26307-17-5; **13,** 64056-61-7; **15,** 13920-54-2; **16,** 64082-13-9; **17,** 13102-23-3; **18,** 64090-70-6; **20,** 64056-63-9; **21,** 64056-65-1; **22,** 64090-68-2; **23,** 64056-52-6; **24,** 64056-53-7; **25,** 64056-54-8; **26,** 64056-55-9; **28,** 64082-15-1; A isomer I, 64056-64-0; A isomer II, 64056-58-2; B, 64056-56-0; C, 64056-57-1; 3-carbethoxypyrrole, 37964-17-3; D, 64045-81-4; 2,3,4,5-tetrahydro-1-benzazepine, 1701-57-1; ethyl chloroformate, 541-41-3; *N*-carbethoxy-1,2-diazepine, 17377-08-1.

References and Notes

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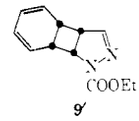
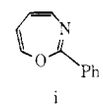
(13) Upon careful chromatographic processing of the photolysate one also



9′

isolates small quantities (ca. 3.5% yield) of a third component tentatively formulated as **9′** (see Experimental Section).
(14) E. Vogel and H. Günther, *Angew. Chem., Int. Ed. Engl.*, **6,** 385 (1967).
(15) It is notable in this connection that the azoxepin shown in i was recently[6]



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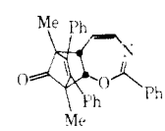
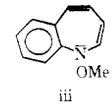


ii

shown to yield tricyclic cycloadduct ii on thermal exposure to dienone **12.**
(16) J. M. Holovka and P. D. Gardner, *J. Am. Chem. Soc.*, **89,** 6390 (1967).
(17) The syn counterpart of **18** was recently prepared photochemically from benzene and furan: J. C. Berridge, D. Bryce-Smith, A. Gilbert, and T. S. Cantrell, *J. Chem. Soc., Chem. Commun.*, 611 (1975), and references cited therein. We are grateful to Professor A. Gilbert for kindly supplying us with detailed information relating to the preparation and characterization of this substance.
(18) As far as we can ascertain, the compound tentatively formulated as iii (V.



iii

Rantenstrauch, *Chem. Commun.*, 1122 (1969)) constitutes the sole published reference to an "unrestricted" 1-benzazepine.
(19) A substance believed to be the *N*-cyano counterpart of **25** was prepared in these laboratories by H. Yamamoto (Ph.D. Dissertation, 1973).
(20) All melting points and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer 137B spectrophotometer, NMR spectra were recorded on a Varian A-60 or XL-100 spectophotometer, ultraviolet spectra were determined on a Cary 18 spectrophotometer, and mass spectra were obtained with a Hitachi Perkin-Elmer Model RMU-6E single-focusing spectrometer. Gas chromatographic analyses were performed on a Varian Aerograph A90-P3 instrument operating under the following conditions: (A) 7 ft × 0.25 in aluminum column packed with SE-30 on Chromosorb W at 188 °C with the vaporizer at 205 °C, the detector at 210 °C, and a helium flow of 100 cm^3/min; (B) same as in (A) except the column temperature was 177 °C; (C) 6 ft × 0.25 in aluminum column packed with SF-96 on Chromosorb W at 140 °C with the vaporizer at 150 °C, the detector at 170 °C, and a helium flow of 85 cm^3/min. Microanalyses were performed by Galbraith Laboratories Knoxville, Tenn. All solvents were ACS Reagent Grade and were used without further purification, except for ethyl ether and tetrahydrofuran which were freshly distilled from lithium aluminum hydride.
(21) This procedure constitutes a modification of that described in ref 10.
(22) Proper analysis of this spectrum required the use of double irradiation.
(23) B. D. Astill and V. Boekelheide, *J. Am. Chem. Soc.*, **77**, 4079 (1955).
(24) This procedure represents a modification of that described in ref 11.
(25) A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *J. Org. Chem.*, **35**, 433 (1970); T. Sasaki, K. Kanematsu, A. Kakehi. I. Ichikawa, and K. Hayakawa, *ibid.*, **35**, 426 (1970).
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(27) This procedure was developed on the basis of brief descriptions given in ref 16.
(28) C. F. Allen, R. W. Ryan, and J. A. Van Allen, *J. Org. Chem.*, **27**, 778 (1962), and references cited therein.
(29) It is essential that the α-pyrone employed in this reaction be freshly distilled from potassium carbonate. Failure to do so results in the exothermic rearrangement of **15** to phenol.

Benzo- and Indoloquinolizine Derivatives. 13.[1] Conformation of the Perhydrobenzo[*c*]quinolizines

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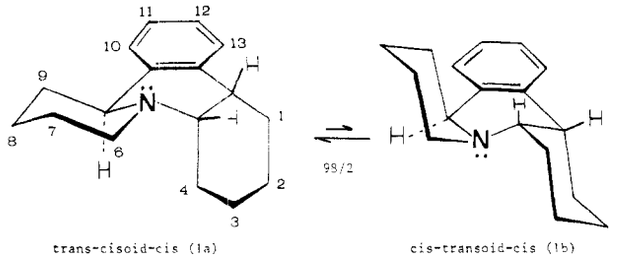
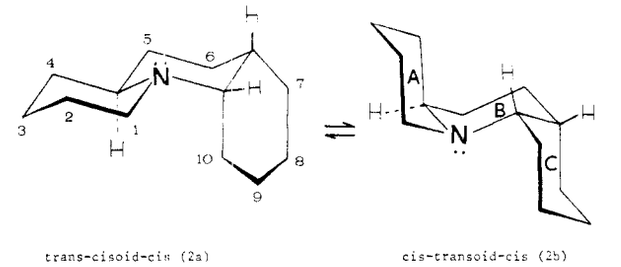
The conformation of three isomers of perhydrobenzo[*c*]quinolizine is determined by the study of their ^{13}C and 270-MHz ^1H NMR spectra. The previous cis-transoid-cis conformation assignment for one of the isomers is shown to be erroneous. The proposed trans-cisoid-cis conformation is further corroborated by molecular-mechanics calculations.

We recently were able to show by variable-temperature ^{13}C NMR that in the *rel*-(4a*β*,9a*α*,13b*β*) isomer (1) of 1,2,3,4,4a,6,7,8,9,13b-decahydro-9a*H*-pyrido[1,2-*f*]phenanthridine the trans-cisoid-cis conformation (**1a**) is strongly



favored over the cis-transoid-cis one (**1b**)[1] ($\Delta G°_{243}$ = 7.5 kJ/mol (1.8 kcal/mol)).

On the other hand, Ohki[2] reported the cis-transoid-cis isomer (**2b**)[3] as the preferred conformation for the analogous isomer of perhydrobenzo[*c*]quinolizine (**2**). This result seemed

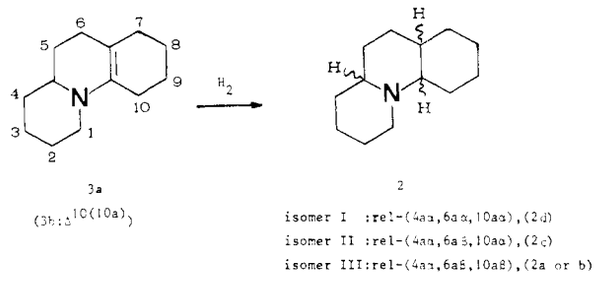


improbable to us since the trans-cisoid-cis conformation **2a** does not experience the destabilizing allylic strain[6] which occurs between the C-9 and C-10 protons and between the C-1 and C-13 protons in **1a**. Therefore, we expected the trans-cisoid-cis conformation to be even more favored in **2** than **1**.

In the carbocyclic analogues, the trans-cisoid-cis conformation of perhydrophenanthrene has been calculated to be more stable than the cis-transoid-cis isomer by 6.7–7.5 kJ/mol (1.6–1.8 kcal/mol).[7,8] We parametrized the molecular-mechanics calculations for the introduction of a nitrogen atom,[9] taking into account the lone-pair influence as described by Allinger[10] for oxygen compounds. These calculations indicate a net preference for **2a** over **2b** by 5.4–6.7 kJ/mol (1.3–1.6 kcal/mol), depending on the importance of the lone-pair interaction parameters.

In order to solve the ambiguity, we reinvestigated the conformational equilibrium in **2**, mainly by the use of ^{13}C NMR.

Synthesis of Compounds. Three isomers (I–III) of **2** were



obtained by the reduction of the enamine **3**[2] or its perchlorate salt (Table I). The fourth isomer, which was present in a very minute amount, could not be isolated.

The excellent agreement in the isomeric composition for the catalytic and the sodium borohydride reductions, along with the gas liquid chromatographic data, established the identity of the isomers as those reported by Ohki.[2]

Conformational Analysis. Infrared Spectroscopy. As already observed by Ohki,[2] isomers I and II show strong Bohlmann bands in the 2700–2800-cm^{-1} region of their in-

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