The flask was immersed in a constant-temperature water bath and maintained to within 0.1° of the required temperature overnight, after which period the theoretical amount of nitrogen had evolved. The mixture was then filtered free of any traces of precipitate that might be present and a glpc sample (*ca.* 1 ml) taken from the filtrate and analyzed for type of hydrocarbon present, under conditions B. The remainder of the filtrate was then concentrated first under water-aspirator pressure at *ca.* 30–40° and then at 3–5 mm and room temperature to yield a light orange viscous oil (*ca.* 2 g), which exhibited strong characteristic –NHCN infrared absorption at 3200 (N-H) and 2200 cm^{-1} (C≡N). The cyanamide mixture was then converted to an amine mixture by treatment with a great excess of lithium aluminum hydride in boiling tetrahydrofuran as described in the preceding paper.[12] The mixture of amines was analyzed by gas–liquid partition chromatography under conditions A, and the amines of interest were identified by direct comparison of their glpc retention times and mass spectrometric cracking patterns with those of authentic samples. The relevant data employed in the identification are shown in Table III. The quantitative results are compiled in Tables IV and V. The yields tabulated were calculated from the weights of the crude amine mixtures in conjunction with the total glpc area observed in each case. For example, the yield of reaction 7 based on weight of amine mixture (assuming a 1:1 mixture of amino and methylamino compounds) is 39% which, after correction for total amount of volatile material, becomes 39 × 87/100 = 34%. The various reaction numbers correspond to those shown in Tables I and II.

Acknowledgment. The author is indebted to Miss Patricia Canfield for the glpc determinations.

The Preparation and Properties of 13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene and Its Derivatives

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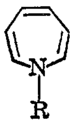
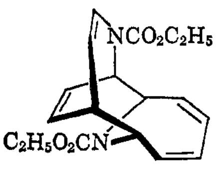
Abstract: The thermodynamically more stable dimers of 1-cyano-, 1-ethoxycarbonyl, 1-*t*-butoxycarbonyl, and 1-methylazepine are all representatives of the new 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene ring system. These compounds are formed from kinetically produced isomers which rearrange on further thermal treatment to the doubly bridged piperazine system. The chemistry of this system and the fully reduced 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane system is discussed in detail.

Recently, brief descriptions have appeared[1] of the dimers of 1-cyanoazepine (**1a**),[1a,b] 1-ethoxycarbonylazepine (**1b**),[1c] and 1-methylazepine (**1c**).[1d] Our more recent observation of the dimerization of 1-*t*-butoxycarbonylazepine (**1d**) suggests that this is a general property of the azepine nucleus. This paper is concerned with the thermally more stable dimers which belong to the new 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene ring system (**3**).



1a, R = CN
b, R = $CO_2C_2H_5$
c, R = CH_3
d, R = $CO_2C(CH_3)_3$
e, R = CON_3
f, R = CO_2CH_3

At relatively low temperatures, the parent azepines dimerize readily to kinetically controlled products which lack an element of symmetry. In particular, **1a** dimerizes at 25–60° to a white crystalline product, mp 220–221° dec,[1a,b] **1b** dimerizes at 130° to a white solid, mp 78°,[1c] and **1c** forms a colorless solid, mp 66°.[1d] The structure of the dimer of **1a** is different from that postulated for the dimers of **1b** (**2**)[1c] and **1c**[2] and it will be discussed elsewhere.[3] At higher temperatures, thermally more stable isomers are obtained which are 13,14-disubstituted 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraenes (**3**). Specifically, the dimer



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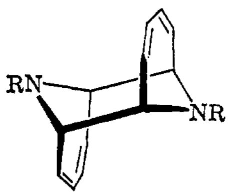

3a, R = CN
b, R = $CO_2C_2H_5$
c, R = CH_3
d, R = $CO_2C(CH_3)_3$
e, R = $CONH_2$
f, R = H
g, R = NO
h, R = C_2H_5
i, R = $CH_2CH{=}CH_2$
j, R = $CH_2CH_2CH{=}CH_2$
k, R = *trans*-$CH_2CH{=}CHC_6H_5$
l, R = CH_3CO
m, R = *cis*-$COCH{=}CHCO_2H$
n, R = C_6H_5CO
o, R = *p*-BrC_6H_4CO
p, R = C_6H_5NHCO
q, R = C_6H_5NHCS
r, R = $CO_2C_{10}H_{15}$
s, R = $COCH_2Cl$
t, R = $COCH_2N(C_2H_5)_2$
u, R = $CH_2CO_2C_2H_5$

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(1) (a) F. D. Marsh and H. E. Simmons, *J. Am. Chem. Soc.*, **87**, 3529 (1965); (b) A. L. Johnson and H. E. Simmons, *ibid.*, **88**, 2591 (1966); (c) L. A. Paquette and J. H. Barrett, *ibid.*, **88**, 2590 (1966); (d) K. Hafner and J. Mondt, *Angew. Chem.*, **78**, 822 (1966).

(2) K. Hafner, private communication.

(3) F. D. Marsh, A. L. Johnson, and H. E. Simmons, in preparation.

of **1a** is converted smoothly to **3a** at 210°,[1b] either **1b** or **2** is converted to **3b** at 200°,[1c] **1c** to **3c** above 0°,[1d] and **1d** to **3d** at 156°. The presence of dimeric products in the solid fraction of the reaction product from which 1-azidocarbonylazepine (**1e**) was obtained[4] also seems likely. The generality of the formation of ring system **3** is clearly demonstrated by its preparation from four different azepines.

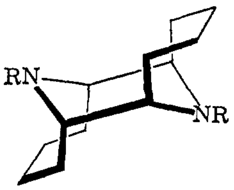
The stability of system **3** is illustrated by the high melting points of its derivatives and by its resistance to strong mineral acid. Hydrolysis of 13,14-dicyano-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (**3a**) with 50% sulfuric acid at 100–120° proceeds in two stages through the biscarbamoyl derivative **3e** to the parent diamine **3f**. The latter is produced immediately when the bis-*t*-butoxycarbonyl derivative **3d** is treated with hydrogen bromide in glacial acetic acid.[5] The common difunctional derivatives **3g–u** of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (**3f**) were prepared by conventional methods, and their analytical and spectral properties clearly indicate their relationship to **3f**.

The concerted formation of the (6 + 6) addition products **3a–d** from the monocycles **1a–d** is a thermally forbidden process according to the Woodward–Hoffmann rules.[6] The proposed (2 + 6) addition of tetracyanoethylene to 1-ethoxycarbonylazepine, **1b**,[7] has since been shown to be the normal thermally allowed (2 + 4) Diels–Alder addition.[8] The same results were obtained for a series of substituted 1-methoxycarbonylazepines, **1f**, with tetracyanoethylene.[9] It therefore seems reasonable that the thermal formation of structures **3** from **1** must involve an allowed intermediate (2 + 4) *endo* Diels–Alder product or a (4 + 6) *exo* product (*e.g.*, **2**)[1c] which rearranges to the symmetrical isomer at higher temperatures. In our case (**1a** → **3a**) the symmetrical compound arises solely by rearrangement of the dimer of **1a**.

The proof of structure **3a** is based upon these observations. (1) Zinc dust distillation of **3a** at 350° produces aniline in low yield as the only volatile product.

(2) The parent diamine **3f** readily absorbs 4 molar equiv of hydrogen on hydrogenation in dilute hydrochloric acid over platinum oxide. The relationship of the octahydro derivative, 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane (**4a**), to **3f** and to the simple difunctional derivatives (**4b–g**) is apparent from their analytical and spectral properties.

(3) In contrast to their precursor, the dimer of **1a**, compounds **3** show only weak carbon–carbon double bond absorption in the 1600-cm^{-1} region of the infrared spectrum. This fact, coupled with polarization studies[10] on the intense Raman band at 1615 cm^{-1} observed in compounds **3c** and **f** ($CHCl_3$ solution), can be accounted for by the symmetrical diene vibration of the proposed centrosymmetric C_{2h} structure.



4a, R = H
b, R = NO
c, R = CH_3
d, R = C_2H_5
e, R = C_6H_5CO
f, R = C_6H_5NHCO
g, R = C_6H_5NHCS

(4) The constancy of position and intensity of the ultraviolet maxima of compounds **3** in the 230–240-mμ region (ε 9500–21,000) (Table I) is consistent with the presence of two independent cisoid diene chromophores[11] rather than azepine, enamine, or enamide functions.[12] This absorption remains constant even in the dihydrochloride of **3f** and the monomethiodide of **3c**, indicating that the nitrogen atoms are isolated from the diene chromophores.[12b,e,i] In most cases, two maxima separated by 5–8 mμ and of approximately the same intensity can be resolved (Table I). In two examples (**3g**, **3k**) the extra chromophores are attributed to independent absorption by the nitrogen substituent. As expected, the saturated compounds **4** do not show diene absorption in the ultraviolet.

(5) The simple nmr spectra of these compounds enable the protons to be assigned readily. In compounds **3** the eight-proton vinyl signal usually appears as a broad singlet in the τ 3.5–4.0 region, while the four tertiary bridgehead protons adjacent to nitrogen are observed in the τ 5.2–5.8 region. In compounds **4** the vinyl proton signals of **3** are replaced by a broad 16-proton methylene multiplet near τ 8.3, and the bridgehead protons are now shifted upfield by 1.0–1.5 ppm. These generalizations are illustrated for the parent compounds **3f** and **4a** in Figures 1 and 2. The rigidity of system **3** provides an ideal case in which to study the effects of nitrogen substituents on nearby proton signals.[13] The four equatorial bridgehead

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[4] L. E. Chapman and R. F. Robbins, *Chem. Ind.* (London), 1266 (1966).

[5] This hydrolysis procedure is described by G. W. Anderson and A. C. McGregor, *J. Am. Chem. Soc.*, **79**, 6180 (1957).

[6] (a) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); (c) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 4388 (1965); (d) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

[7] K. Hafner, *Angew. Chem. Intern. Ed. Engl.*, **3**, 165 (1964).

[8] (a) J. H. van den Hende and A. S. Kende, *Chem. Commun.*, 384 (1965); (b) A. S. Kende, P. T. Izzo, and J. E. Lancaster, *J. Am. Chem. Soc.*, **87**, 5044 (1965).

[9] (a) J. E. Baldwin and R. A. Smith, *ibid.*, **87**, 4819 (1965); (b) I. C. Paul, J. E. Baldwin, and R. A. Smith, *ibid.*, **88**, 3653 (1966).

[10] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945, p 360.

[11] *Cf.*: (a) 1,3-cycloheptadiene, λ_{max} 248 mμ (ε 7500), E. Pesch and S. L. Friess, *J. Am. Chem. Soc.*, **72**, 5756 (1950); (b) 9-cyano-9-azabicyclo[4.2.1]nona-2,4,7-triene, $\lambda_{max}^{CH_3CN}$ 255 mμ (ε 4500), A. G. Anastassiou, *ibid.*, **87**, 5512 (1965).

[12] These data are rather scattered in the literature; some typical values of λ_{max} (ε) are: (a) enamines $C{=}CNR_2$, 223–238 mμ (5100–9600), N. J. Leonard and D. M. Locke, *ibid.*, **77**, 437 (1955); (b) dienamines $C{=}C{-}C{=}CNR_2$, 250–305 mμ (7050–34,200), L. A. Paquette, *ibid.*, **86**, 4092 (1964); L. A. Paquette, *Tetrahedron Letters*, 2027 (1963); G. Opitz and W. Merz, *Ann.*, **652**, 139 (1962); (c) bisenamines $C{=}C{-}NH{-}C{=}C$, 226–233.5 mμ (16,350–17,200), 315–350 mμ (7650–15,500), M. Anderson and A. W. Johnson, *J. Chem. Soc.*, *Org.*, 1075 (1966); (d) enamides $C{=}CNHCOR$, 240 mμ (6600), G. Rosencranz, O. Mancera, F. Sondheimer, and C. Djerassi, *J. Org. Chem.*, **21**, 520 (1956); (e) dienamides $C{=}C{-}C{=}CNRCOR'$, 252–255 mμ (4900–6300), L. A. Paquette, *J. Am. Chem. Soc.*, **84**, 4987 (1962); L. A. Paquette, *ibid.*, **85**, 3288 (1963); L. A. Paquette, *ibid.*, **86**, 500 (1964); E. Vogel and R. Erb, *Angew. Chem.*, **74**, 76 (1962); L. A. Paquette and J. K. Reed, *J. Med. Chem.*, **6**, 771 (1963); (f) α,β-unsaturated urethans $C{=}CNRCO_2R'$, 229–255 mμ (4200–9000);[1c,8,9] (g) N-cyanoenamines $C{=}CNCN$, 249–251 mμ (2800–4900), A. G. Anastassiou, *J. Org. Chem.*, **31**, 1131 (1966); (h) α,β-unsaturated amides $C{=}CCONR_2$, 218 mμ (11,800), R. H. Mazur, *ibid.*, **26**, 1289 (1961); (i) azepines, 293–332 mμ (338–1440), 202–219.5 mμ (9750–36,300),[1a] K. Hafner and C. König, *Angew. Chem.*, **75**, 89 (1963); K. Hafner, D. Zinser, and K.-L. Moritz, *Tetrahedron Letters*, 1733 (1964); W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963); W. Lwowski and T. J. Maricich, *ibid.*, **87**, 3630 (1965); R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964).

[13] *E.g.*, *cf.* the cases of (a) the more flexible 2,3,5,6-tetramethylpiperazines, R. K. Harris and N. Sheppard, *J. Chem. Soc.*, *Phys. Org.*,

Table I. Ultraviolet Maxima of 13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraenes (**3**)[a]

Compd	R	Solvent	λ_{max} mμ (ϵ_{max})
3a	CN	CH_3CN	237 (16,300), 230 (15,150)
b	$CO_2C_2H_5$	CH_3CN	237 (14,200), 232 (13,750)
c	CH_3	CH_3OH	237 (14,100), 230 (13,900)
d	$CO_2C(CH_3)_3$	C_2H_5OH	238 (14,350), 233 (13,700)
e	$CONH_2$	50% H_2SO_4	234 (9,450)
f	H	CH_3CN	240 (15,800), 234 (16,400)
f·2HCl	$H_2{}^+Cl^-$	H_2O	235 (16,400) 230 (16,600)
g	NO	CH_3CN	375 (132), 365 (142) 235 (19,000)
10	N_aCH_3, $N_b(CH_3)_2{}^+I^-$	CH_3OH	240 (17,500), 232 (21,100) 224 (22,400)
3h	C_2H_5	CH_3OH	239 (14,300), 232 (14,100)
i	$CH_2CH{=}CH_2$	CH_3OH	238 (13,800), 232 (13,700)
j	$CH_2CH_2CH{=}CH_2$	CH_3OH	240 (15,700), 232 (14,700)
k	*trans*-$CH_2CH{=}CHC_6H_5$	CH_3CN	292 (3,500), 282 (sh 5,350) 250 (22,100)
l	CH_3CO	CH_3OH	238 (14,500), 230 (14,100)
m	*cis*-$COCH{=}CHCO_2H$	C_2H_5OH	234 (19,400)
s	$COCH_2Cl$	CH_3CN	231.5 (16,200)
t	$COCH_2N(C_2H_5)_2$	CH_3OH	234.5 (14,350)
u	$CH_2CO_2C_2H_5$	C_2H_5OH	239 (14,300), 232 (14,400)

[a] Determined in 1-cm solution cells on a Cary Model 14 spectrophotometer.

Table II. Proton Nmr Data on 13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraenes (**3**)[a]

			Proton assignments		
Compd	Substituent	Solvent	Vinyl	Tertiary bridgehead	Other
3f	H	$CDCl_3$	361	214	NH 101
f·2HCl	$H_2{}^+Cl^-$	D_2O	398–361[b]	240	HOD 246
g	NO	$(CD_3)_2SO$	349	342	
e	$CONH_2$	4FK·D_2O[c]	362	280	HOD 280
a	CN	4FK·D_2O[c]	375	255,249	HOD 295
c	CH_3	$CDCl_3$	371–334 (m)	201,196	CH_3 133
c·2HCl	CH_3·HCl	D_2O	400–350[b]	285,280	HOD 285, NCH_3 175
h	C_2H_5	$CDCl_3$	353	206,202	CH_2 142 (q, J = 7 cps) CH_3 54 (t, J = 7 cps)
i	$CH_2CH{=}CH_2$	$CDCl_3$	370–292[d]	205,200	NCH_2 177 (d, J = 5 cps)
j	$CH_2CH_2CH{=}CH_2$	$CDCl_3$	370–285[d]	204,200	NCH_2CH_2 153–120 (m)
k	*trans*-$CH_2CH{=}CHC_6H_5$	$CDCl_3$	385–334[d]	208,203	C_6H_5 434, NCH_2 187 (d, J = 6 cps)
u	$CH_2CO_2C_2H_5$	$CDCl_3$	358	215,210	OCH_2 246 (q, J = 7 cps) CH_3 71 (t, J = 7 cps)
b	$CO_2C_2H_5$	$CDCl_3$	353	296,287	OCH_2 246 (q, J = 7 cps) CH_3 71 (t, J = 7 cps)
d	$CO_2C(CH_3)_3$	$CDCl_3$	353	294,284	$C(CH_3)_3$ 83
r	$CO_2C_{10}H_{15}$[e]	$CDCl_3$	352	291,283	$C_{10}H_{15}$ 123–96 (m)
m	*cis*-$COCH{=}CHCO_2H$	$(CD_3)_2SO$	350	311,271	CH=CH 387, 356 (2 doublets, J = 12 cps)
l	CH_3CO	CF_3CO_2H[c]	339	313,270	CH_3 118
n	C_6H_5CO	CF_3CO_2H[c]	342	314,250	C_6H_5 418
o	*p*-BrC_6H_4CO	4FK·D_2O[c]	357	330,269	*p*-BrC_6H_4CO 459, 430 (2 doublets, J = 8 cps)
s	$COCH_2Cl$	CF_3CO_2H[c]	334	303,264	$COCH_2Cl$ 225
t	$COCH_2N(C_2H_5)_2$	$CDCl_3$	354	322	$NCOCH_2$ 191 (d, J = 3 cps) NCH_2 149 (q, J = 7 cps) CH_3 59 (t, J = 7 cps)
10	N_aCH_3, $N_b(CH_3)_2{}^+I^-$	$(CD_3)_2SO$	378–355[b]	277, 272[f] 225[f]	Axial NCH_3 201 Equatorial NCH_3 191 Tertiary NCH_3 127

[a] Recorded at 60 Mc/sec on a Varian Associates A-60 spectrometer. Signals are recorded in cycles per second downfield from internal tetramethylsilane as singlets unless otherwise noted: d, doublet; t, triplet; q, quartet; m, multiplet. [b] Charged nitrogen produces a complex multiplet for the diene proton signals. [c] External tetramethylsilane calibration 4FK = $CF_2ClCOCF_2Cl$. [d] Diene protons appear as a broad singlet superimposed upon the —$CH{=}CH_2$ system multiplet. [e] $C_{10}H_{15}$ = 1-adamantyl. [f] Two distinct sets of bridgehead protons are seen because of the chemical nonequivalence of the two nitrogen atoms.

protons are quite sensitive to substituents on nitrogen and show the expected dependence of chemical shift upon substituent electronegativity. With simple linear substituents (*e.g.*, H, NO) a single, broad, unresolved signal is observed. With a cyano or alkyl substituent the bridgehead proton signal is a doublet (J = 4–6 cps). The origin of this splitting is the adjacent vinyl proton since the more intense member of the doublet lies on the downfield side and in some cases the vinyl region

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200 (1966); (b) the rigid boat-ring piperazines in the 2,5-diazabicyclo-[2.2.1]heptane system, P. S. Portoghese and A. A. Mikhail, *J. Org. Chem.*, **31**, 1059 (1966).

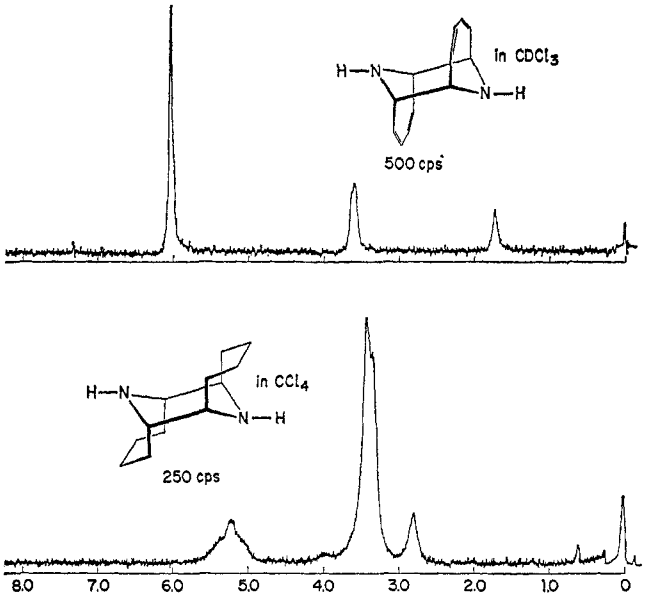
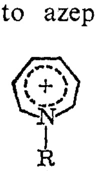


Figure 1 (top). Proton spectrum (60 Mc/sec) of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (**3f**) (500-cps sweep width).

Figure 2 (bottom). Proton spectrum (60 Mc/sec) of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane (**4a**) (250-cps sweep width).

becomes resolved into a complex multiplet. Alkoxycarbonyl and acyl substituents cause the bridgehead protons to exhibit two broad signals equal in area and separated by 8–60 cps. This is clearly a case of amide isomerism in which two of the bridgehead protons have a different chemical shift from the other two.[14] Collapse of these two signals to a single broad signal was observed at temperatures of 60–100° in the case of the alkoxycarbonyl derivatives **3b** and **3d**, but not in the acyl derivative **3m**. Protonation or quaternization of one or both nitrogen atoms of system **3** resolves the usual broad vinyl signal into a complex multiplet. Obviously, the proximity of a further substituent increases the nonequivalence of the central and terminal protons of the diene system. These observations are summarized in Table II.

(6) The mass spectra of the unsaturated compounds **3** confirm the expected molecular weights and consistently exhibit half-parent ions as the base peak unless the nitrogen substituent is more readily fragmented. The lower mass values fall into a pattern characteristic of the azepine. Clearly, structure **3** undergoes ready fragmentation into azepinium ions[15] $C_6H_6NR^+$ (**5**).



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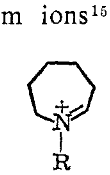

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The mass spectra of compounds **4** also confirm their molecular weights and usually exhibit base peaks corresponding to protonated half-parent ions $C_6H_{11}NR^+$ (**6**). Their features are illustrated in Figures 3 and 4 for the parent compounds **3f** and **4a**.

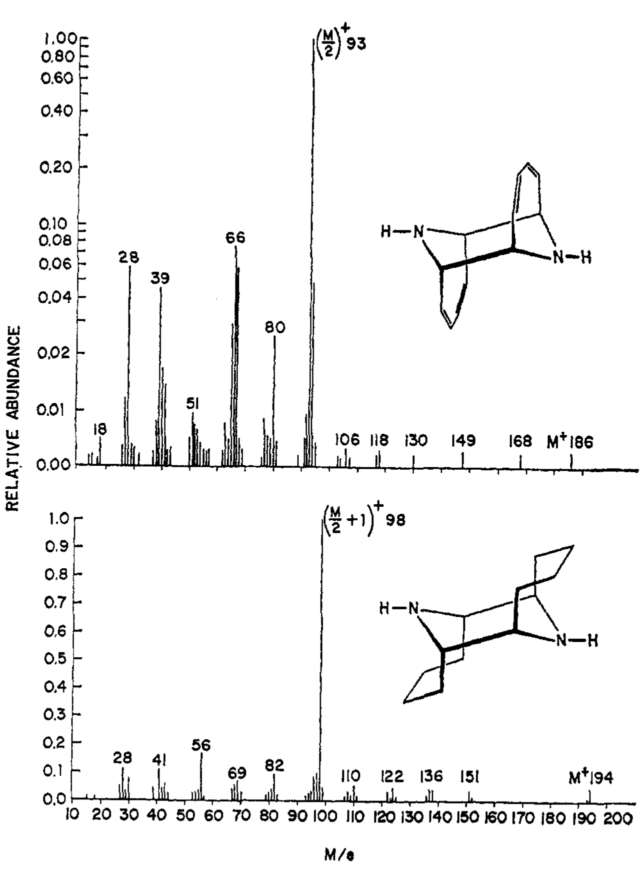
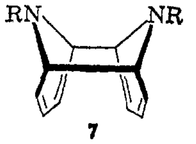


Figure 3 (top). Mass spectrum of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (**3f**).

Figure 4 (bottom). Mass spectrum of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane (**4a**).

(7) Examination of Dreiding models of **3f** and **4a** indicates that they are very rigid structures. The *trans* arrangement of the two four-carbon bridges is almost certainly favored over the *cis* arrangements **7** and **8** from the viewpoint of nonbonded interactions and the unusual thermal stability of the compounds in the two series. The low dipole moment (0.57 D. in carbon tetrachloride) of **3c** lends support to this structural assignment. "Angstrom ruler" calculations of the nonbonded H–H repulsion energies[16] place structure **8** (R = H) 63 kcal/mole above structure **4a** in energy. Similar arguments have been advanced for the structure and stereochemistry of the parent carbocyclic system, tricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene-13,-14-dione.[17]



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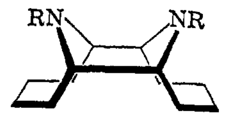

8

(8) The conversion of 1-cyanoazepine (**1a**) to 1-ethoxycarbonylazepine (**1b**) was observed according to Scheme I. Paquette's compound **3b**^{1c} was prepared independently by the reaction of ethyl chloroformate with the parent diamine **3f**. Direct photolysis of **3b**

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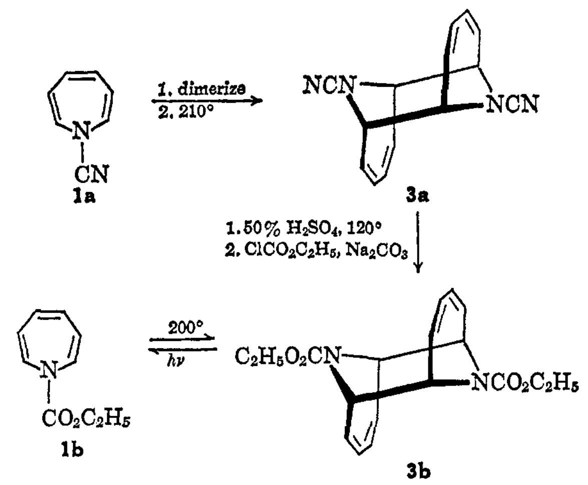
[14] In the case of the ethoxycarbonyl derivative **3b**, Paquette^{1c} has incorrectly described the bridgehead signals as a doublet (J = 8.5 cps). At 100 Mc/sec, the separation of the bridgehead signals increases to 16.5 cps in **3b**, and to 17.0 cps in **3d**, but is unaffected in **3c**.

[15] *Cf.* F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963, p 506.

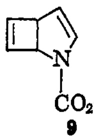
[16] H. E. Simmons and J. K. Williams, *J. Am. Chem. Soc.*, **86**, 3222 (1964).

[17] T. Mukai, T. Tezuka, and Y. Akasaki, *ibid.*, **88**, 5025 (1966).

Scheme I



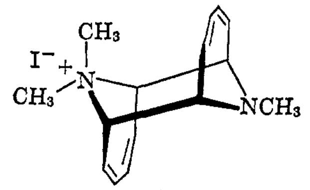
in acetonitrile solution using a 2537-A source gave the monomer **1b**, isolated in 12% yield by distillation. The generality of the photodecomposition of structure **3** was examined for a number of derivatives. Under the same conditions, the bis-*t*-butoxycarbonyl derivative **3d** reverted to the monomer **1d** in 13% yield. In other cases (**3a**, **c**, **f**, **n**, and **r**) recognizable products were not obtained. The vibrations induced in the diene chromophore on irradiation must be sufficient to break the two relatively weak central bonds linking the monomer units (*cf.* the mass spectrometry observations). The azepine can only be isolated if it is reasonably stable to further degradation. The amount of time required to cause the further cyclization of **1b** to **9** observed by Paquette[18] provides further evidence of the stability of this particular azepine. Under our irradiation conditions detectable amounts of bicyclic products like **9** were not observed as products from structure **3**.



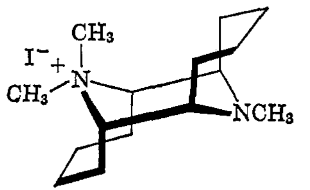
9

A further consequence of the geometry of ring systems **3** and **4** is seen in the formation of metallic complexes. Since both parent diamines **3f** and **4a** have their six-membered piperazine ring frozen into the chair conformation, bonding of both nitrogen atoms to the same metal atom is impossible. The cobalt(II) halides readily form 1:1 complexes $C_{12}H_{14}N_2CoX_2$ (X = Cl, Br, I) with **3f** in ethanol solution. With larger anions 2:1 complexes such as $[C_{12}H_{14}N_2]_2Co(SCN)_2$ and $[C_{12}H_{14}N_2]_2Co(ClO_4)_2 \cdot 4H_2O$ are produced. Analytical, spectral, and magnetic evidence suggests that the halides and thiocyanate contain tetrahedral cobalt(II).[19] Attempts to produce cobalt(II) complexes of the more hindered compound **4a** were unsuccessful. Reaction of cobalt(II) chloride hexahydrate with **4a** produced only the monohydrochloride of **4a**.

Quaternization of the dimethyl derivatives **3c** and **4c** in both systems proceeds under moderately vigorous conditions to form the monomethiodides **10** and **11**.[1b,d] The formation of only monoquaternary derivatives is not unusual and has been observed with other bridged piperazines.[20] The Hofmann elimination on **10** proceeds in up to 92% yield and produces an unstable solid diamine, $C_{15}H_{20}N_2$, whose properties appear to be consistent with a product of further cyclization, such as **12**, rather than the cyclododecapentaene derivative **13** postulated by Hafner.[1d] The stable crystalline bismethiodide of this product eliminates trimethylamine on further Hofmann reaction, indicating that a dimethylamino group is produced in the first elimination. The other products of this second Hofmann reaction are produced in low yield and have not yet been characterized.



10



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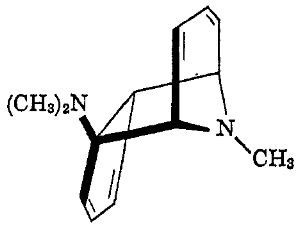
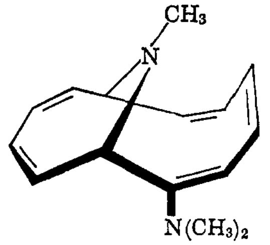


12



13

Experimental Section[21]

13,14-Dicyano-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3a). Crude 1-cyanoazepine dimer was purified by dissolving 200-g lots in boiling dichloromethane, filtering, and passing the filtrate down a 4-in. layer of Florisil packed into a chromatography column 3 ft in length and 4 in. in diameter. Each batch required a total of 10 l. of dichloromethane to elute the purified material, which was isolated by evaporation. A 5-l., four-necked Morton flask equipped with mechanical stirrer, thermometer, two hot water reflux condensers, and a heating mantle was charged with practical grade naphthalene (1000 g) and flushed with nitrogen. After the naphthalene had melted, the stirrer was started, and at a liquid temperature of 140°, powdered 1-cyanoazepine dimer (200 g) was added rapidly down one condenser. The dimer dissolved in the hot naphthalene, and when the temperature of the mixture reached 190°, a mildly exothermic reaction began in which the product precipitated and the temperature rose spontaneously to 210° where it was maintained for 30 min. After the mixture had cooled to 100°, it was diluted with 2500 ml of benzene and filtered. The brown finely crystalline residue of 13,14-dicyano-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene was washed with a further 1250 ml of benzene and air dried. The yield of almost pure product was 137.0–145.6 g (69–73%). Analytically pure material was obtained by continuous chromatography using an extractor 3 ft in height and 4 in. in diameter with dichloromethane as the eluent. The column was packed successively with 3 in. of 4-mm glass beads, 0.5 in. of fine silica sand, 3 in. of Florisil, and 14.5 g of colored product. Elution for 96 hr produced 5.38 g of pure

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[18] L. A. Paquette and J. H. Barrett, *J. Am. Chem. Soc.*, **88**, 1718 (1966).

[19] (a) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 913; (b) D. H. Busch in "Cobalt, Its Chemistry, Metallurgy and Uses," R. S. Young, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 120, and references cited therein; (c) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961); (d) M. Goodgame, *J. Chem. Soc., Phys.*, 63 (1966); (e) A. B. P. Lever and S. M. Nelson, *ibid.*, 859 (1966).

[20] M. V. Rubtsov and E. S. Nikitskaya, *Usp. Khim.*, **34**, 1040 (1965).

[21] Melting points are uncorrected and were determined in a Mel-Temp capillary apparatus. Infrared spectra in potassium bromide, Nujol, or solution media were determined on Perkin-Elmer 21 and 221 instruments. Raman spectra were determined on a Cary Model 83 spectrophotometer. Dipole moments were measured in solution on a WTW Dipolimeter Type DMO1. Molecular weights and mass spectra were determined by direct injection into a CEC 21-103 instrument.

white, finely crystalline dicyano compound **3a**, mp >400° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3040 (CH=CH), 2210 (C≡N), 1660, and 1625 cm^{-1} (C=C); *m/e* 236 (parent), 208, 195, 194, 193, 181, 169, 168, 167, 153, 144, 131, 119, 118 (base peak), 105, 91, 69, 57, and 55.

Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72. Found: C, 71.03, 71.36; H, 5.14, 5.13; N, 23.77, 23.74.

An intimate mixture of 13,14-dicyano-13,14-diazatricyclo-[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (1.0 g) and zinc dust (10 g) was heated in a pyrolysis tube at 350 ° for 30 min. The distillate (0.1 ml) was identified as aniline by infrared spectrum, azo dye formation, and gas chromatography.

13,14-Biscarbamoyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,-9,11-tetraene (3e). A mixture of 13,14-dicyano-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (5.6 g) and 50% sulfuric acid (50 ml) was stirred under nitrogen at 100–120° for 6 hr. The mixture was cooled, neutralized with sodium bicarbonate, and filtered to leave a residue of the crude biscarbamoyl compound (5.25 g, 81%). Two recrystallizations from 20-ml portions of 1:2 dichlorotetrafluoroacetone–water with Darco G-60 treatment produced 2.4 g of fine white crystalline 13,14-biscarbamoyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene, mp >300° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3420, 3300, 3160, 1650, and 1585 cm^{-1} ($NCONH_2$); *m/e* 272 (parent), 229, 228, 212, 211, 186, 185, 183, 170, 169, 168, 167, 154, 149, 144, 143, 136 (base peak), 123, 118, 106, 97, 93, 87, 85, 83, 81, 69, 57, 56, 55, 43, 42, 41, 31, 29, 28, 27, and 18.

Anal. Calcd for $C_{14}H_{16}N_4O_2$: C, 61.75; H, 5.92; N, 20.58. Found: C, 62.08, 62.02; H, 6.17, 5.98; N, 20.01.

A 2:1 mixture of *p*-toluenesulfonic acid monohydrate and water was equally effective in promoting this hydrolysis.

13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3f). A 5-l., four-necked Morton flask equipped with heating mantle, mechanical stirrer, two long reflux condensers, nitrogen inlet, and thermometer was charged with a cold mixture of sulfuric acid (500 ml), water (1000 ml), and 13,14-dicyano-13,14-diazatricyclo-[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (140 g). The apparatus was flushed with nitrogen, and the temperature of the mixture was gradually raised to 110–120° where it was maintained for 24 hr. The dark brown mixture was cooled to 50°, poured onto 600 g of ice, mixed with Celite, and filtered. The residue was discarded, and the filtrate was stirred and cooled in a 4-l. erlenmeyer flask while it was cautiously basified with sodium hydroxide (~750 g). The precipitate was filtered at room temperature, air dried, and extracted with chloroform in a Soxhlet apparatus. Evaporation of the dried chloroform extracts yielded 49–63 g (45–58%) of yellow powdery diamine **3f**, mp 141–145° dec, which was sufficiently pure for most purposes. Analytically pure material was obtained by repeated crystallization from water with Darco G-60 treatment (50% recovery) or by sublimation at 110° (0.1 mm) (87% recovery). Pure 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene forms fine white crystals, mp 147–148° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3420, 3290 (NH), 3030 (CH=CH), and 1655 cm^{-1} (C=C).

Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.33; H, 7.72; N, 15.10, 14.84.

Derivatives of this diamine were prepared as follows.

13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene Dihydrochloride (3f·2HCl). A suspension of the diamine **3f** (2.25 g) in acetone (20 ml) was treated with concentrated hydrochloric acid (3.2 ml). The precipitate was recrystallized from 1% hydrochloric acid (20 ml) and acetone (350 ml). The white crystals of the dihydrochloride (1.38 g) had mp >300° dec; $\nu_{\max}^{\mathrm{KBr}}$ 2940–2680 (NH_2^+), 1630 (C=C), and 1550 cm^{-1} (NH_2^+).

Anal. Calcd for $C_{12}H_{16}N_2Cl_2$: C, 55.60; H, 6.22; N, 10.81. Found: C, 55.88; H, 6.38; N, 11.16.

13,14-Dinitroso-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3g). A mixture of the diamine **3f** (1.86 g, 0.01 mole), water (10 ml), and concentrated hydrochloric acid (3.3 ml, 0.03 mole) was stirred at 0° and treated with a solution of sodium nitrite (1.52 g, 0.022 mole) in water (5 ml) for 1.5 hr. Two recrystallizations of 0.30 g of the crude product from 60–80 ml of ethanol produced 0.12 g of pure dinitroso compound as golden needles, mp >250° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3030 (CH=CH), 1625 (C=C), 1450, 1370, and 1055 cm^{-1} (N—N=O); *m/e* 184 (parent − 2NO), 105, 93, 92 (base peak, half parent − NO), 80, 79, 78, 66, 65, 63, 52, 51, 39, 38, 30 (NO), and 27.

Anal. Calcd for $C_{12}H_{12}N_4O_2$: C, 59.01; H, 4.95; N, 22.94. Found: C, 59.07, 59.02; H, 5.03, 5.14; N, 22.72.

13,14-Dimethyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3c). Methyl iodide (80 ml) at 0° in a polymer tube was treated gradually with diamine **3f** (8.0 g). The tube was sealed and heated overnight at 100°. The contents of the tube were evaporated to dryness, stirred with 30 ml of water, and basified with 25% sodium hydroxide. The dried precipitate was sublimed at 125° (0.1 mm) to provide colorless crystals of the dimethyl compound (6.70 g, 73%), mp 165–166° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3080, 3030 (CH=CH), and 1450 cm^{-1} (NCH_3); *m/e* 214 (parent), 108, 107 (base peak), 106, 95, 94, 93, 92, 91, 82, 81, 80, 79, 78, 77, 67, 66, 65, 64, 63, 55, 54, 53, 52, 51, 50, 44, 43, 42, 41, 40, 39, 38, 28, 26, 18, and 15.

Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.60; H, 8.56; N, 13.09.

13,14-Diethyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3h). A mixture of diamine **3f** (1.86 g, 0.01 mole), ethanol (30 ml), ethyl bromide (10 ml), and anhydrous sodium carbonate (1.20 g, 0.011 mole) was heated overnight under reflux. After evaporation and addition of water (20 ml) to the residue, the insoluble material was distilled at 100–120° (0.1 mm) to produce 1.71 g (71%) of white crystalline diethyl derivative, mp 93–94.5°; $\nu_{\max}^{\mathrm{KBr}}$ 3060 (CH=CH) and 3000–2850 cm^{-1} (CH, NC_2H_5).

Anal. Calcd for $C_{16}H_{22}N_2$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.59; H, 9.30; N, 11.50.

13,14-Diallyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3i). The procedure for preparing the diethyl derivative **3h** was repeated using allyl bromide in place of ethyl bromide and a reflux time of 2 hr. The crude product was sublimed at 95° (0.1 mm), yield 2.22 g (84%) of colorless crystalline diallyl derivative, mp 103–104°; $\nu_{\max}^{\mathrm{KBr}}$ 3080, 3070, 3020, 3010 (CH=CH, $CH=CH_2$), 1640, and 1620 cm^{-1} (C=C). This compound and the dibutenyl derivative **3j** rapidly darken on standing and should be sealed under nitrogen and stored at 0° in a dark place.

Anal. Calcd for $C_{18}H_{22}N_2$: C, 81.16; H, 8.33; N, 10.52. Found: C, 81.53; H, 8.35; N, 10.93.

13,14-Bis-4-butenyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,-11-tetraene (3j). The above procedure was repeated using 4-bromo-1-butene (5 ml) in place of ethyl bromide. The crude product was distilled at 110° (0.1 mm), yield 2.26 g (77%) of colorless plates of the bis-4-butenyl derivative, mp 53–55°; $\nu_{\max}^{\mathrm{KBr}}$ 3070, 3060, 3010 (CH=CH, $CH=CH_2$), 1630, and 1610 cm^{-1} (C=C).

Anal. Calcd for $C_{20}H_{26}N_2$: N, 9.52. Found: N, 9.63.

13,14-Dicinnamyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3k). A mixture of diamine **3f** (1.86 g, 0.01 mole), benzene (30 ml), triethylamine (2.50 g, 0.025 mole), and *trans*-3-chloropropenylbenzene (3.20 g, 0.021 mole) was heated under reflux overnight. The crude product was isolated as above. The pure dicinnamyl derivative was obtained as pale yellow needles (1.48 g), mp 156–157°, by recrystallization from a mixture of chloroform (20 ml) and *n*-hexane (200 ml). It had $\nu_{\max}^{\mathrm{KBr}}$ 3085, 3010 (CH=CH, C_6H_5), and 1600 cm^{-1} (C=C).

Anal. Calcd for $C_{30}H_{30}N_2$: C, 86.08; H, 7.22. Found: C, 86.04, 85.95; H, 7.59, 7.59.

13,14-Diacetyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3l). A suspension of diamine **3f** (2.0 g) in methanol (100 ml) was treated with acetic anhydride (10 ml).[22] After standing overnight at 25°, the fine white crystalline precipitate of the diacetyl derivative was filtered (2.43–2.51 g, 84–87%) and purified by Soxhlet extraction with methanol, mp 317–319° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3060 (CH=CH) and 1650 cm^{-1} ($NCOCH_3$).

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.19, 71.11; H, 7.08, 7.20; N, 10.24, 10.29.

13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene-13,14-bis(*cis*-4-oxo-2-butenoic acid) (3m). A mixture of diamine **3f** (1.0 g), benzene (25 ml), and maleic anhydride (1.05 g) was heated under reflux for 6 hr. The precipitated maleamic acid derivative (1.84 g, 90%) was recrystallized twice from ethanol as a white powder, mp >350° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3030 (CH=CH), 1710 (CO_2H), and 1625 cm^{-1} (NCOR).

Anal. Calcd for $C_{20}H_{18}N_2O_6$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.52; H, 4.77; N, 7.26.

13,14-Dibenzoyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3n). To a suspension of diamine **3f** (3.72 g, 0.02 mole) in 5% aqueous sodium hydroxide (40 ml) was added slowly a solution of benzoyl chloride (6.50 g, 0.046 mole) in chloroform (50 ml). One gram of the precipitate of crude dibenzoyl derivative (7.70 g, 97%) was recrystallized from a mixture of trifluoroacetic acid (7 ml) and water (200 ml) as a white powder, mp 312–313° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3030 (C_6H_5, CH=CH) and 1645 cm^{-1} ($NCOC_6H_5$).

Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62; N, 7.10. Found: C, 78.76; H, 5.57; N, 7.36.

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(22) *Cf.* A. L. Johnson, R. H. Gourlay, D. S. Tarbell, and R. L. Autrey, *J. Org. Chem.*, **28**, 300 (1963).

13,14-Bis-*p*-bromobenzoyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3o). The above method was used with *p*-bromobenzoyl chloride to obtain the crude bis-*p*-bromobenzoyl derivative in 60% yield. This derivative was recrystallized from a mixture of dichlorotetrafluoroacetone hydrate (2 ml) and water (1 ml) as colorless crystals, mp 322–323° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3040 (C_6H_4, CH=CH), 1675, and 1630 cm^{-1} ($NCOC_6H_4Br$); *m/e* 554, 552, 550 (parents), 278, 277, 276, 275 (half-parents), 264, 262, 186, 185, 183 (base peak), 168, 157, 155, 104, 92, 76, 65, 50, and 39.

Anal. Calcd for $C_{26}H_{20}N_2O_2Br_2$: C, 56.65; H, 3.65. Found: C, 56.76; H, 3.42.

13,14-Bisphenylcarbamoyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3p). To a stirred solution of diamine **3f** (1.86 g, 0.01 mole) in carbon tetrachloride (20 ml) was added dropwise a solution of phenyl isocyanate (2.50 ml, 0.023 mole) in carbon tetrachloride (20 ml). The mixture was heated under reflux for 30 min, cooled, and filtered. The residue of bisphenylcarbamoyl derivative was recrystallized in 1-g lots from a mixture of dimethylformamide (55 ml) and water (1000 ml) as a white powder, mp >350 ° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3320 (NH), 3130, 3060, 3030 (C_6H_5, CH=CH), 1640, 1600, 1530, and 1500 cm^{-1} ($NCONHC_6H_5$).

Anal. Calcd for $C_{26}H_{24}N_4O_2$: N, 13.20; mol wt, 424. Found: N, 12.97; mol wt, 424.

13,14-Bisphenylthiocarbamoyl-13,14-diazatricyclo[6.4.1.1^{2,7}]-tetradeca-3,5,9,11-tetraene (3q). A solution of diamine **3f** (0.26 g) in ethanol (1 ml) was treated with 50% ethanolic phenyl isothiocyanate (2.8 ml). After brief warming, the white crystalline bisphenylthiourea was filtered (0.39 g, 63%) and purified by Soxhlet extraction with ethanol, mp 211–212° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3040 (C_6H_5, CH=CH), 1600, 1345, and 1230 cm^{-1} ($NCSNHC_6H_5$).

Anal. Calcd for $C_{26}H_{24}N_4S_2$: C, 68.39; H, 5.30; N, 12.27; S, 14.05. Found: C, 68.23; H, 5.36; N, 12.05; S, 14.14.

13,14-Bisadamantyloxycarbonyl-13,14-diazatricyclo[6.4.1.1^{2,7}]-tetradeca-3,5,9,11-tetraene (3r). Adamantyl chloroformate was prepared in benzene solution.[23] A slurry of diamine **3f** (1.86 g, 0.01 mole), sodium carbonate (1.06 g, 0.01 mole), and ether (20 ml) was treated slowly with 34 ml of the benzene solution of adamantyl chloroformate (4.3 g, 0.02 mole). After being stirred overnight, the mixture was evaporated to dryness, stirred with 25 ml of water, and filtered. The crude residue of bisadamantyloxycarbonyl derivative was recrystallized from a mixture of chloroform (25 ml) and ethanol (50 ml), yield 2.94 g (56%) of colorless crystals, mp 313–314° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3020 (CH=CH) and 1690 cm^{-1} (NCO_2R).

Anal. Calcd for $C_{34}H_{42}N_2O_4$: C, 75.24; H, 7.80; N, 5.16. Found: C, 75.22, 75.22; H, 7.34, 7.18; N, 5.49.

13,14-Bisethoxycarbonyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3b) and Its Photolysis to 1-Ethoxycarbonylazepine (1b). A suspension of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,-9,11-tetraene (**3f**) (7.44 g) and anhydrous sodium carbonate (4.14 g) in ether (70 ml) was stirred at room temperature and treated dropwise with a solution of ethyl chloroformate (8.50 g) in ether (100 ml). After standing overnight, the solvent was evaporated, and the residue was stirred with water and filtered. Two recrystallizations of the crude damp yellow product from ethanol (20 ml) produced 7.72 g (59%) of fine white crystalline bisethoxycarbonyl derivative,[24] mp 196.5–197.5° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3070, 3030 (CH=CH), 1700 ($NCO_2C_2H_5$), and 1650 cm^{-1} (C=C); *m/e* 330 (parent), 166, 165 (base peak), 152, 137, 130, 128, 118, 117, 115, 108, 106, 104, 103, 93, 92, 80, 66, 65, and 29.

Anal. Calcd for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.39, 65.66; H, 6.52, 6.54; N, 8.65, 8.76.

A mixture of the bisethoxycarbonyl derivative **3b** (4.1 g) and acetonitrile (400 ml) was agitated with a nitrogen bubbler in a water-cooled (12°) quartz apparatus and photolyzed with a low-pressure unfiltered 2537-A source. The progress of the reaction was followed by gas chromatography at 140° on a 6-ft, 20% silicone 200 on 60–80 AWFB column and by ultraviolet spectroscopy in acetonitrile solution. The reaction was complete after 24-hr irradiation. After evaporation of the solvent, the dark red residue was distilled at 80° (0.1 mm) to give 1-ethoxycarbonylazepine (**1b**) as an orange oil (0.5 g, 12%) identified by gas chromatography retention time (7.9 min) and infrared and nmr spectra. This material was identical with that prepared by reaction of benzene with ethoxycarbonylnitrene.[12i,25] Similar irradiation of compounds **3a**, **c**, **f**, and **n** produced tars from which the corresponding azepines (**1**) were not obtained.

13,14-Bis-*t*-butoxycarbonyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3d) and Its Photolysis to 1-*t*-Butoxycarbonylazepine (1d). 1-*t*-Butoxycarbonylazepine (**1d**) was prepared according to Hafner[12i] and Cotter and Beach[12i] from a solution of *t*-butyl azidoformate (50 g, Aldrich) in benzene (4 l.) at 125° for 2 hr. In addition to the azepine (12.80 g) (63% yield based on azidoformate not converted to oxazolidone), bp 40–60° (0.1 mm), there was isolated 22.4 g of hexane-insoluble 5,5-dimethyl-2-oxazolidone,[26] mp 80–81°, produced by intramolecular insertion of the nitrene.[27] A 7.2-g charge of the azepine was degassed, sealed *in vacuo*, and heated at 156° for 2 hr. The contents of the tube were rinsed out with hexane and filtered. The insoluble residue (2.75 g, 38%) of bis-*t*-butoxycarbonyl derivative **3d** was recrystallized twice from 50 ml of 1:1 ethanol–water with Darco G-60 treatment to give colorless needles of the pure compound, mp 205–206° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3030, 3010 (CH=CH), and 1680 cm^{-1} ($NCO_2C(CH_3)_3$); *m/e* 386 (parent), 274, 230, 193 (half-parent), 186, 185, 168, 138, 137, 130, 124, 120, 118, 107, 106, 94, 93, (base peak), 92, 81, 80, 79, 69, 67, 66, 65, 58, 57, 56, 55, 53, 51, 44, 43, 42, 41, 40, 39, 38, 29, 27, and 15.

Anal. Calcd for $C_{22}H_{30}N_2O_4$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.35; H, 7.58; N, 7.36, 7.38.

Chemical proof of the structure of **3d** was obtained by conversion to **3f** with hydrogen bromide in glacial acetic acid.[5] When 0.5 g of the bis-*t*-butoxycarbonyl compound was added to 5 ml of 30% $HBr–CH_3CO_2H$ (Eastman) there was an immediate evolution of gas (C_4H_8 and CO_2). The mixture was poured onto ice, basified with sodium hydroxide, and extracted with chloroform. The chloroform extracts yielded the parent diamine **3f**, identified by mixture melting point and infrared and nmr spectra.

The bis-*t*-butoxycarbonyl derivative (2.0 g) was dissolved in 250 ml of acetonitrile and photolyzed in the same way as the bisethoxycarbonyl derivative. Recovered starting material weighed 0.80 g, and after distillation 0.16 g (13%) of 1-*t*-butoxycarbonylazepine (**1d**) was obtained, identified by comparison of infrared and nmr spectra with those of authentic material.

13,14-Bischloroacetyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3s). A solution of diamine **3f** (1.86 g) and triethylamine (2.50 g) in benzene (30 ml) was treated with a solution of chloroacetyl chloride (2.50 g) in benzene (10 ml). The product was isolated by evaporation and recrystallized from a mixture of trifluoroacetic acid (35 ml) and water (200 ml), yield 2.54 g (75%) of the bischloroacetyl derivative, mp >215° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3030 (CH=CH) and 1660 cm^{-1} ($NCOCH_2Cl$).

Anal. Calcd for $C_{16}H_{16}N_2O_2Cl_2$: N, 8.26. Found: N, 8.17, 8.41.

13,14-Bisdiethylaminoacetyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3t). A mixture of the bischloroacetyl derivative **3s** (0.90 g), ethanol (40 ml), and diethylamine (10 ml) was heated under reflux overnight. The product was isolated by evaporation and recrystallization from 50% methanol (10 ml), yield 0.69 g (63%) of colorless crystals, mp 165–166°, $\nu_{\max}$ 3030 (CH=CH) and 1640 cm^{-1} ($NCOCH_2N(C_2H_5)_2$).

Anal. Calcd for $C_{24}H_{36}N_4O_2$: C, 69.87; H, 8.80; N, 13.58. Found: C, 69.99, 69.95; H, 9.06, 9.11; N, 13.61, 13.64.

13,14-Bisethoxycarbonylmethyl-13,14-diazatricyclo[6.4.1.1^{2,7}]-tetradeca-3,5,9,11-tetraene (3u). A solution of ethyl bromoacetate (3.34 g) in benzene (15 ml) was added dropwise to diamine **3f** (3.72 g) in ethanol (15 ml).[28] After being stirred overnight, the precipitate of **3f**·2HBr (3.27 g, 94%) was filtered, and the filtrate was evaporated to leave 3.27 g (91%) of crude bisethoxycarbonylmethyl derivative. Recrystallization of the derivative from 50% ethanol (55 ml) produced 1.67 g of colorless needles, mp 99–100°; $\nu_{\max}^{\mathrm{KBr}}$ 3030 (CH=CH) and 1750 cm^{-1} ($CO_2C_2H_5$).

Anal. Calcd for $C_{20}H_{26}N_2O_4$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.00; H, 7.52; N, 8.10.

13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradecane (4a). A mixture of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (**3f**) (20.0 g), water (150 ml), concentrated hydrochloric acid (25 ml), and platinum oxide (2.0 g) was hydrogenated overnight in a Parr shaker.

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(23) W. L. Haas, E. V. Krumkalns, and K. Gerzon, *J. Am. Chem. Soc.*, **88**, 1988 (1966).

(24) This product gave no mixture melting point depression and was identical in its spectral properties with Paquette's thermally prepared compound.[1c]

(25) Dr. M. E. Hermes, Plastics Department, E. I. du Pont de Nemours and Co., personal communication.

(26) W. J. Close, *J. Am. Chem. Soc.*, **73**, 95 (1951).

(27) (a) R. Kreher and G. H. Bockhorn, *Angew. Chem.*, **76**, 681 (1964); (b) R. Puttner and K. Hafner, *Tetrahedron Letters*, 3119 (1964); (c) R. Kreher and D. Kühling, *Angew. Chem.*, **77**, 42 (1965).

(28) *Cf.* G. Fodor, J. Tóth, and I. Vincze, *J. Chem. Soc.*, 3504 (1955).

The mixture was filtered; the residue was rinsed with water, and the combined filtrate and washings were concentrated to 40 ml and basified with 30% sodium hydroxide. After cooling to 0°, the precipitate of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane was filtered, air dried, and sublimed at 70° (0.1 mm). The pure saturated base was a colorless crystalline solid (15.3 g, 73%), mp 61–62°; ν_{max}^{KBr} 3290 and 1450 cm^{-1} (NH); nmr (CCl$_4$) τ 7.29 (multiplet, four tertiary protons), 8.29 (multiplet, 16 CH$_2$ protons), and 8.50 (singlet, two exchangeable NH protons).

Anal. Calcd for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.06, 74.08; H, 11.13, 11.33; N, 14.36, 14.43.

In an analytical scale experiment using an atmospheric pressure hydrogenator, 4 molar equiv of hydrogen was absorbed at 25° (760 mm) over 5.5 hr.

The dihydrochloride and dihydrobromide of **4a** were prepared by the same procedure as the dihydrochloride of **3f**. 13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradecane dihydrochloride forms white crystals, mp >320° dec; ν_{max}^{Nujol} 2740, 2700, 2630, and 1575 cm^{-1} (NH$_2^+$); nmr (D$_2$O) τ 5.30 (singlet, four NH$_2^+$ protons), 6.00 (multiplet, four tertiary protons), and 8.10 (multiplet, 16 CH$_2$ protons).

Anal. Calcd for $C_{12}H_{24}N_2Cl_2$: C, 53.94; H, 9.06. Found: C, 53.88; H, 8.99.

13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradecane dihydrobromide is a white powder, mp >320° dec; ν_{max}^{KBr} 2820–2600 and 1570 cm^{-1} (NH$_2^+$); nmr (D$_2$O) τ 5.34 (singlet, four NH$_2^+$ protons), 6.02 (multiplet, four tertiary protons), and 8.18 (multiplet, 16 CH$_2$ protons); *m*/*e* 356, 355, 354 (parents), 194, 138, 137, 124, 123, 122, 111, 110, 109, 108, 107, 106, 99, 98 (base peak), 97, 96, 95, 94, 93, 91, 84, 83, 82, 81, 80, 79, 69, 68, 67, 57, 56, 55, 54, 53, 44, 43, 42, 41, 39, 30, 29, 28, 27, and 18.

Anal. Calcd for $C_{12}H_{24}N_2Br_2$: C, 40.47; H, 6.79; N, 7.78. Found: C, 40.71; H, 6.79; N, 7.98.

13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradecane monohydrochloride, described below as a reaction product from diamine **4a** and cobalt(II) chloride, was prepared independently by (a) neutralization of **4a** with 1 equiv of hydrochloric acid and (b) mixing equimolar amounts of **4a** and its dihydrochloride in chloroform.

13,14-Dinitroso-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane (4b). The crude nitroso compound, prepared in the same way as **3g**, was obtained in 92% yield after two recrystallizations from aqueous ethanol as pale yellow crystals, mp 180–182.5° dec; $\lambda_{max}^{CH_3OH}$ 363 mμ (ϵ 153), 355 mμ (ϵ 146), and 248 mμ (ϵ 12,300); ν_{max}^{KBr} 1460, 1450, 1430, 1370, and 1355 cm^{-1} (N—N=O); nmr (CDCl$_3$) τ 4.89 (multiplet, four tertiary protons) and 8.60 (multiplet, 16 CH$_2$ protons).

Anal. Calcd for $C_{12}H_{20}N_4O_2$: C, 57.11; H, 7.99; N, 22.21. Found: C, 57.32, 57.17; H, 7.79, 7.68; N, 22.24, 22.12.

13,14-Dimethyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane (4c). A mixture of diamine **4a** (6.0 g), methanol (100 ml), anhydrous sodium carbonate (3.50 g), and methyl iodide (20 ml) was heated under reflux for 20 hr. The mixture was evaporated to dryness; the residue was stirred with water (35 ml), cooled to 0°, and filtered. The crude dimethyl compound was purified by sublimation at 100–110° (0.1 mm). The colorless waxy product (6.66 g, 97%) had mp 125–130°;[29] ν_{max}^{KBr} 2780 and 1440 cm^{-1} (NCH$_3$); nmr (CCl$_4$) τ 7.35 (singlet, four tertiary protons), 7.45 (singlet, six NCH$_3$ protons), and 7.90–8.50 (broad multiplet, 16 CH$_2$ protons); *m*/*e* 222 (parent), 208, 207 (parent − CH$_3$), 192, 180, 179, 166, 165, 151, 138, 124, 123, 122, 113, 112 (base peak, half-parent + H), 111, 110, 109, 108, 98, 97, 96, 95, 94, 84, 83, 82, 81, 70, 68, 67, 58, 57, 55, 42, 41, 39, 30, 29, 28, 27, and 15.

Anal. Calcd for $C_{14}H_{26}N_2$: C, 75.61; H, 11.79; N, 12.60. Found: C, 75.78; H, 11.69; N, 12.75.

13,14-Diethyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane (4d). The above procedure was employed substituting ethanol for methanol and ethyl iodide for methyl iodide. The yield of pure diethyl derivative, bp 95° (0.1 mm), was 2.15 g (86%) of colorless crystals, mp 35–37°; ν_{max}^{KBr} 2960–2850, 1465, and 1440 cm^{-1} (NC$_2$H$_5$); nmr (CCl$_4$) τ 7.12 (quartet, *J* = 7 cps, + broad multiplet, four NCH$_2$ + four tertiary protons), 8.0–8.60 (broad multiplet, 16 CH$_2$ protons), and 8.96 (triplet, *J* = 7 cps, six CH$_3$ protons).

Anal. Calcd for $C_{16}H_{30}N_2$: C, 76.74; H, 12.08; N, 11.19. Found: C, 76.90; H, 11.79; N, 11.43.

13,14-Dibenzoyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane (4e). A mixture of diamine **4a** (1.94 g, 0.01 mole) and 10% sodium hydroxide (40 ml) was shaken with benzoyl chloride (5 ml). The crude product was recrystallized twice from a mixture of ethanol and chloroform, mp 319.5–320.5° dec; ν_{max}^{KBr} 3070 (C$_6$H$_5$), 1635, and 1595 cm^{-1} (C$_6$H$_5$CO); nmr (CDCl$_3$) τ 2.65 (doublet, *J* = 6 cps, ten aromatic protons), 5.04 (multiplet, two tertiary protons), 6.36 (multiplet, two tertiary protons), and 8.33 (multiplet, 16 CH$_2$ protons). Temperature probe nmr experiments between −60 and +126° did not cause any coalescence of the tertiary proton signals. The mass spectrum showed *m*/*e* 402 (parent), 298, 297, 296, 295 (base peak), 294, 293, 292, 291, 289, 277, 276, 275, 202, 201, 200, 199, 198, 197, 105, 85, 81, 71, 69, 57, and 55.

Anal. Calcd for $C_{26}H_{30}N_2O_2$: N, 6.96. Found: N, 6.72.

13,14-Bisphenylcarbamoyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane (4f). The crude bisphenylcarbamoyl derivative, obtained in 94% yield by a procedure analogous to that used to prepare **3p**, was purified by Soxhlet extraction with ethanol as a white powder, mp 374–375° dec; ν_{max}^{KBr} 3320 (NH), 3060 (C$_6$H$_5$), 1640, 1595, 1530, and 1505 cm^{-1} (NCONHC$_6$H$_5$).

Anal. Calcd for $C_{26}H_{32}N_4O_2$: C, 72.19; H, 7.46; N, 12.95; mol wt, 432. Found: C, 72.12, 72.06; H, 7.48, 7.55; N, 13.08, 13.20; mol wt, 432.

13,14-Bisphenylthiocarbamoyl-13,14-diazatricyclo[6.4.1.1^{2,7}]-tetradecane (4g). The white crystalline bisphenylthiocarbamoyl derivative obtained analogously to **3q** in 84% yield was purified by Soxhlet extraction with ethanol. The pure material had mp 289–289.5° dec; ν_{max}^{KBr} 3070 (C$_6$H$_5$), 1605, 1505, 1450, 1375, and 1340 cm^{-1} (NCSNHC$_6$H$_5$).

Anal. Calcd for $C_{26}H_{32}N_4S_2$: C, 67.20; H, 6.94; N, 12.06; S, 13.80; mol wt, 464. Found: C, 67.35, 67.30; H, 7.04, 7.02; N, 11.83, 11.84; S, 14.02, 14.22; mol wt, 464.

Cobalt(II) Complexes of 13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (3f). The general procedure was to heat under reflux for 30 min a mixture of the cobalt(II) salt (5–10 mmoles), ethanol (50 ml), and diamine **3f** (1.86 g, 10 mmoles). After cooling to 25°, the precipitated complex was filtered, rinsed with chloroform, and dried at 25–100° (0.1 mm). The insolubility of these complexes in common organic solvents precluded the measurement of solution ultraviolet or nuclear magnetic resonance spectra. In the donor solvents water, dimethylformamide, and dimethyl sulfoxide, these complexes dissolved with decomposition.

(a) Cobalt(II) chloride hexahydrate formed a blue powder in 90% yield, mp >300° dec; ν_{max}^{KBr} 3450, 3200 (NH), 3030, and 1625 cm^{-1} (CH=CH); μ = 4.54 BM.[30]

Anal. Calcd for $C_{12}H_{14}N_2CoCl_2$: C, 45.59; H, 4.46; N, 8.86; Co, 18.65; Cl, 22.43. Found: C, 45.28, 45.28; H, 4.57, 4.68; N, 8.73, 8.70; Co, 18.51; Cl, 21.50, 21.50.

(b) Cobalt(II) bromide formed a blue powder in 90% yield, mp >280° dec; ν_{max}^{KBr} 3190 (NH), 3030, and 1620 cm^{-1} (CH=CH), μ = 4.53 BM.

Anal. Calcd for $C_{12}H_{14}N_2CoBr_2$: C, 35.68; H, 3.49; N, 6.93; Co, 14.59. Found: C, 35.32, 35.46; H, 3.85, 3.96; N, 6.99, 7.07; Co, 14.40, 14.41.

(c) Cobalt(II) iodide formed a green powder in 75% yield, mp >380° dec; ν_{max}^{KBr} 3190 (NH), 3040, and 1600 cm^{-1} (CH=CH); μ = 4.69 BM.

Anal. Calcd for $C_{12}H_{14}N_2CoI_2$: C, 28.89; H, 2.83; N, 5.61; Co, 11.81. Found: C, 28.24, 28.34; H, 3.14, 3.14; N, 5.31, 5.40; Co, 11.98, 12.09.

(d) Cobalt(II) nitrate hexahydrate formed a gray powder which was a mixture of products.

(e) Cobalt(II) acetate tetrahydrate did not form a complex under these conditions.

(f) Cobalt(II) thiocyanate formed a violet powder in 46% yield, mp >200° dec; ν_{max}^{KBr} 3340, 3220 (NH), 3030, 1605 (CH=CH), 2170 cm^{-1} (SCN); μ = 4.83 BM.

Anal. Calcd for $C_{26}H_{28}N_6S_2Co$: Co, 10.76; N, 15.35; S, 11.71. Found: Co, 11.11; N, 15.07; S, 12.08.

(g) Cobalt(II) perchlorate hexahydrate formed a pale green powder in 30% yield, mp 270° dec; ν_{max}^{KBr} 3600, 3300, 3130 (OH, NH), 1610 (C=C), and 1080 cm^{-1} (ClO$_4$).

Anal. Calcd for $C_{24}H_{36}N_4Cl_2O_{12}Co$: C, 41.04; H, 5.17; Co, 8.39; Cl, 10.10. Found: C, 40.87; H, 5.34; Co, 8.68; Cl, 9.74.

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[29] Our freshly sublimed and analytically pure material contracted near 95° and melted at 125–130°. Paquette[10,24] observed mp 128–145° for sublimed product and mp 148–150° for sublimed product recrystallized from Skellysolve B at 0 to −5°. On the basis of direct comparison of analytical and spectral data of these differently prepared samples we have concluded that they are identical.

[30] The magnetic susceptibility of the four compounds at 297°K was independent of field from 18 to kgauss. Diamagnetic contributions were calculated from Pascal's constants.

Reaction of 13,14-Diazatricyclo[6.4.1.1^{2,7}]tetradecane (4a) with Cobalt(II) Chloride. A mixture of cobalt(II) chloride hexahydrate (1.0 g), ethanol (50 ml), and diamine **4a** (1.60 g) was heated under reflux for 24 hr, cooled, and filtered free of cobalt(II) chloride (0.40 g). Evaporation of the filtrate left a solid (1.71 g) from which 0.40 g of unreacted diamine was sublimed at 70° (0.1 mm). The residue (1.30 g) was recrystallized twice from a mixture of ethanol (10 ml) and acetone (20 ml) to produce colorless needles of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane monohydrochloride (0.55 g), mp 270–280° dec; no $\lambda_{\max}^{\mathrm{H_2O}}$ 208–400 mμ; $\nu_{\max}^{\mathrm{KBr}}$ 1590 cm^{-1} (NH_2^+); nmr ($CDCl_3$) τ 6.79 (4 protons) and 8.07 (16 protons).

Anal. Calcd for $C_{12}H_{23}N_2Cl$: C, 62.44; H, 10.05; N, 12.14; Cl, 15.37. Found: C, 62.63; H, 9.71; N, 11.86; Cl, 15.75.

13,14-Dimethyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene Monomethiodide (10) Method a. A mixture of 13,14-diazatricyclo[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (**3f**) (18.6 g, 0.10 mole), methanol (200 ml), anhydrous sodium carbonate (15.9 g, 0.15 mole), and methyl iodide (31 ml, 0.50 mole) was heated under reflux for 24 hr. After evaporation to dryness, the residue was stirred with ice-water (50 ml) and filtered. The residue was recrystallized from acetonitrile (500 ml), yield 27.77 g (78%) of monomethiodide.

Method b. A mixture of 13,14-dimethyl-13,14-diazatricyclo-[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene (**3c**) (3.0 g), acetonitrile (15 ml), and methyl iodide (15 ml) was heated overnight in a sealed tube at 100°. Evaporation of the mixture produced 4.44 g (89%) of the monoquaternary iodide. The analytical sample was recrystallized twice from acetonitrile as white crystals, mp 300–302° dec; $\nu_{\max}^{\mathrm{KBr}}$ 3110, 3085, 3020 (CH=CH), 2970, 2935, 2890, 2870, 2830, and 2790 cm^{-1} (CH, NCH_3).

Anal. Calcd for $C_{13}H_{21}N_2I$: C, 50.58; H, 5.94; N, 7.87. Found: C, 50.62, 50.41; H, 5.80, 5.63; N, 8.01, 7.84.

13,14-Dimethyl-13,14-diazatricyclo[6.4.1.1^{2,7}]tetradecane Monomethiodide (11). Application of method a above with **4a** produced only the dimethyl compound **4c**. Method b above with **4c** produced an 84% yield of the desired monomethiodide after recrystallization from ethanol. Two further recrystallizations from ethanol produced long colorless needles of **11**, mp 246–248° dec; $\nu_{\max}^{\mathrm{KBr}}$ 2960–2790 and 1470 cm^{-1} (CH, NCH_3); nmr ($CDCl_3$) τ 6.37 (multiplet, two tertiary protons), 6.57 (singlet, three axial NCH_3 protons), 6.65 (singlet, three equatorial NCH_3 protons), 6.80 (multiplet, two tertiary protons), 7.15 (singlet, three tertiary NCH_3 protons), and 7.50–8.33 (broad multiplet, 16 CH_2 protons),

Anal. Calcd for $C_{15}H_{29}N_2I$: N, 7.52; I, 34.83. Found: N, 7.60, 7.61; I, 35.64.

Hofmann Elimination on 13,14-Dimethyl-13,14-diazatricyclo-[6.4.1.1^{2,7}]tetradeca-3,5,9,11-tetraene Monomethiodide (10). 1. A mixture of the monomethiodide **10** (7.29 g), water (50 ml), methanol (275 ml), and freshly prepared silver oxide (from 10 g of silver nitrate) was stirred at room temperature overnight. The silver salts were filtered, washed with methanol, and air dried (yield 9.55 g, theory). Evaporation of the filtrate left a brown viscous residue which was heated at 120° (0.1 mm) for 30 min, then distilled in a short-path still at 120° (0.1 mm). Redistillation produced the Hofmann product **12** as a pale yellow oil (4.29 g, 92%) from which the color was removed completely after one further distillation. The unstable distillate crystallized on cooling to −78°. The crystalline dimethylamino-N-methylazatricyclotridecatetraene (**12**) had mp 43–44°; $\lambda_{\max}^{\mathrm{CH_3OH}}$ 250 mμ (ϵ 9700); $\nu_{\max}^{\mathrm{CCl_4}}$ 3040, 3020 (CH=CH), and 1470 cm^{-1} (NCH_3); nmr ($CDCl_3$) τ 4.14–4.32 (complex multiplet, eight vinyl protons), 6.53 (multiplet, one tertiary proton), 7.12 (doublet, J = 4 cps, two tertiary protons), 7.62 (singlet, six $N(CH_3)_2$ protons), and 7.75 (singlet, three NCH_3 protons).

Anal. Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27; mol wt, 228. Found: C, 78.39; 78.31; H, 8.75, 8.92; N, 12.01; mol wt, 228.

2. A solution of the Hofmann product **12** (8.38 g) in acetonitrile (150 ml) was treated dropwise with methyl iodide (30 ml) and stirred overnight at 25°. The crude crystalline bismethiodide (5.01 g, 26%) was filtered. Two recrystallizations of 1.45 g of this product from water (25 ml) and acetone (300 ml) with Darco G-60 treatment produced 0.92 g of the white crystalline bismethiodide of **12**, mp 160–165° dec; $\lambda_{\max}^{\mathrm{H_2O}}$ 260 mμ (sh, ϵ 8000), 227 mμ (ϵ 28,800); $\nu_{\max}^{\mathrm{KBr}}$ 3080, 3050, 3025, 3010 (CH=CH), 1485, 1460, 1440, and 1410 cm^{-1} (NCH_3); nmr (CF_3CO_2H) τ 3.45–4.28 (complex multiplet, eight vinyl protons), 4.64 (triplet, J = 7 cps, two tertiary protons), 5.73 (multiplet, one tertiary proton), 6.55 (singlet, 12 NCH_3 protons), and 6.82 (singlet, three NCH_3 protons).

Anal. Calcd for $C_{17}H_{26}N_2I_2$: C, 39.86; H, 5.12; N, 5.47. Found: C, 40.15; H, 4.99; N, 5.54.

Evaporation of the mother liquors from this reaction left a dark intractable gum.

3. A further Hofmann degradation on 2.45 g of the bismethiodide of **12** with the silver oxide from 3 g of silver nitrate in water (20 ml) and methanol (30 ml) produced 3.23 g of silver salts (theory 3.19 g) and a gummy residue which formed a brown oily distillate at 180° (0.1 mm). Redistillation produced 0.06 g of a yellow unstable oil which appeared to consist of several products. Addition of 10% hydrochloric acid to the pump trap followed by evaporation produced 0.42 g (1 molar ratio) of trimethylamine hydrochloride, identified by conversion to trimethylammonium picrate, mp 215–217° dec (lit.[31] mp 216°).

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