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REACTIONS OF 2-DIALKYLAMINO-3H-AZEPINES WITH OXIDANTS AND ELECTROPHILES‡

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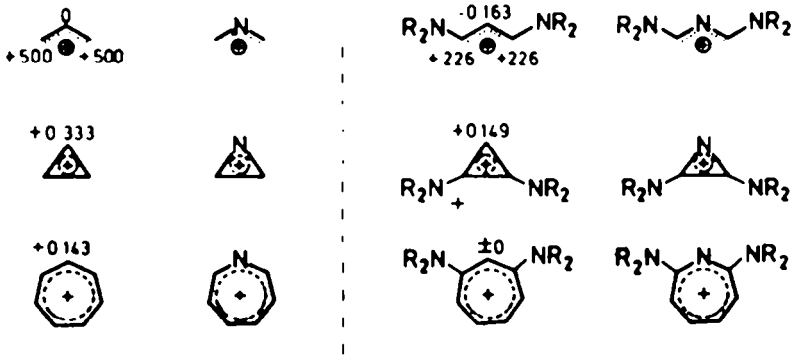
Summary- 2-n-Butoxy-3H-azepine (**2**) reacts with amines, anthranilic acid and active methylene compounds to afford 2-aminoazepines **3** and **13**, quinazolinoazepine **4** and 2-methylene-1,2-dihydro-3H-azepines **6**, **7**, **9** and **10** respectively. The reaction of **3** with trityl tetrafluoroborate provides 3-amino-7-trityl-2-aza-1H$^+$-norcaradienium salts **22** which on deprotonation gives 7-amino-3-trityl-3H-azepines **20**. Azepines **20** on heating are converted to 2-amino-6-trityl-3H-azepines **19**; they react with trialkyl oxonium salts, diazonium salts and 2-methylthio-1,3-dithiolium methylsulfate to give 2-alkyl-7-trityl-2-aza-norcaradienium salts **23**, azepine-3-one arylhydrazones **32** and dihydro-azadithiasesquifulvalene **34**, respectively. The reaction of **3** with dimethylmethylthiosulfonium tetrafluoroborate produces salts **24** of 2-amino-6-methylthio-3H-azepines **25**. TCNQ reacts with **25** to yield 2-amino-6-methylthio-1H$^+$,3H-azepinium tetracyanoquinodimethanide **29**. **24** is used as a starting material for the synthesis of 2,6-bis-methylthio-3H-azepine **31**.

Like benzene and pyridine, tropylium and azatropylium cations are pairs of 6 π-electron systems. In terms of heats of formation (H_f, kcal/mole [MNDO]; $\Delta H_f0 = H_f(PhCH{=}NPh) - H_f(PHCH{=}CHPh) = 7.6$; $\Delta\Delta H_f = H_f(azaAr) - H_f(Ar) - 7.6$), pyridine is as stable as benzene ($\Delta\Delta H_f = -0.1$). The azatropylium cation **1**, however, is significantly less stable than the tropylium cation ($\Delta\Delta H_f = 10.7$). All the same, **1** as a Hückel system is more stable than its open-chain analogue, and salts with this "aromatic" cation are expected to be fairly stable. Predictions as to the influence of a ring nitrogen atom on the stability of cations of the allylic type can also be made on the basis of their charge distribution. As the charge density at C-2 of the allyl cation is zero (HMO, cf. table 1) a nitrogen atom at this position does not change the energy of the π-electron system. The situation is different, however, with the tropylium cation. Here, all ring positions are positively charged and a nitrogen atom

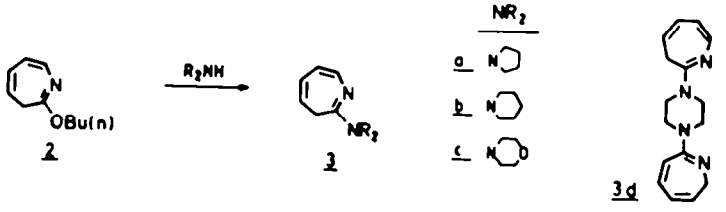
Table 1 Charge densities (HMO)



‡) Dedicated to Professor Edward C. Taylor on the occasion of his 65th birthday.

therefore destabilizes the π-electron system. By virtue of their amino groups, 1,3-diaminoallyl cations, the so-called vinamidinium salts, have a partial negative charge at C-2. Thus, a nitrogen atom at this position is supposed to stabilize the π-electron system. In 1,3-diaminotropylium cations the charge density at C-2 is zero and 2,7diaminoazatropylium cations are therefore expected to have roughly the same stability as their carbon analogues. Surprisingly, neither azatropylium nor aminoazatropylium salts have been prepared so far. The only indication for azatropylium ions has been found in the mass spectra of 1-methylisoquinoline[1], 2-alkoxy-3H-azepinyl-3-carboxamides[2] and some phenyl azides and anilines.[3,4]

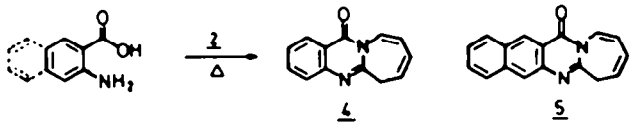
Tropylium salts can be readily prepared by dehydrogenation of tropylidenes.[5] Thus, azepines, in particular derivatives with electron-releasing substituents, are supposed to be convertible to azatropylium salts by way of oxidation. 2-Dialkylamino(anilino)-3H-azepines have been prepared through thermolysis or photolysis of aryl azides in the presence of secondary amines or aniline[6-13] and through reduction of nitrosobenzene[14] or nitrobenzenes[15] with phosphanes in the presence of secondary amines. Since these methods have several disadvantages we have employed the following reaction sequence. 2-n-Butoxy-3H-azepine **2**, readily available from nitrobenzene with tri-n-butylphosphane and n-butanol in high yield[16], reacts with secondary



2 **3** **3d**

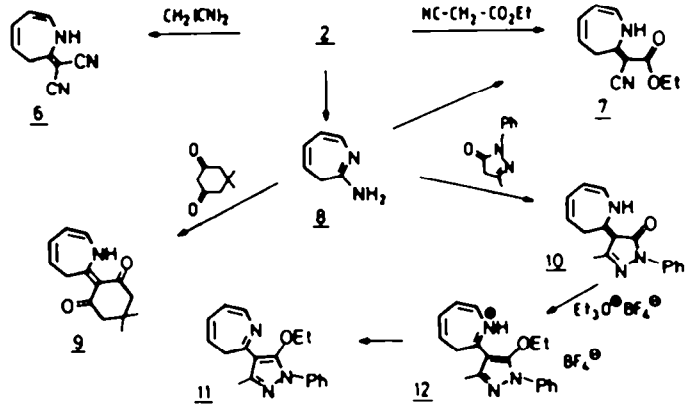
amines to produce the aminoazepines **3** in 80-90% yields (spectroscopic data of new compounds cf. Table 2). Only **3b** has been prepared before by another method[15].

2 can also be used as starting material for the preparation of some further azepine derivatives. Brief heating with anthranilic acid (Niementowski reaction[17,18]) or 3-amino-2-naphthoic acid to 120 °C (150 °C) gives rise



4 **5**

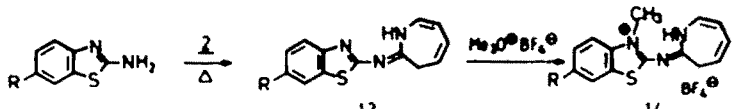
to the quinazoline derivatives **4** and **5**, respectively.The reaction of **2** with active methylene compounds (ma-



6 **7** **8** **9** **10** **11** **12**

lononitrile, ethyl cyanoacetate, 3-methyl-1-phenyl-5-pyrazolone) provides the methylene-azepines **6**, **7**, **10**. As in a number of enamines[19] the signals of H-7 in the ^{1}H-NMR spectra of **7** and **10** appear as doublets of doublets. The spectra indicate the presence of hydrogen bonds as in β-amino-acrylates.[20,21] The yield of **7** is rather low. It can be improved from 11% to 54% by using 2-amino-3H-azepine (**8**)[16] as starting material. Dimedone, which doesn't react with **2**, can also be condensed with **8** to yield **10**. The merocyanine dye **10** upon alkylation furnishes the pale yellow salt **12** which can be depronated to give the azepinyl-pyrazole **11**.

When **2** is heated with 2-aminobenzothiazoles, the yellow imines **13** are formed. The alkylation of **13** with



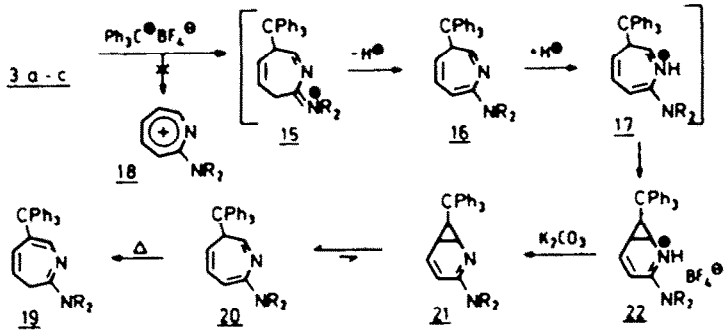
a. R = H
b R = OMe

trimethyloxonium tetrafluoroborate yields the yellow azacyanine dye **14**.

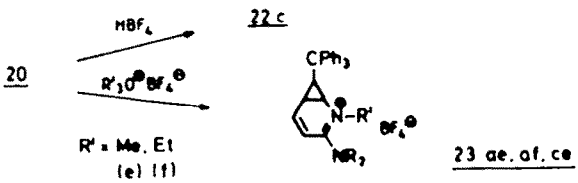
The aminoazepines **3a-c** when treated with trityltetrafluoroborate (cf. preparation of carbenium tetrafluoroborates[5,22-25]) deliver salts **22** of azanorcaradienes **21** instead of 2-aminoazatropylium salts **18**. The ^{1}H-NMR spectra of **22** are consistent with structures **15** and **22**; however, the signals at 36.81, 36.29 and 19.63 in the ^{13}C-NMR spectrum of **22c** agree only with **22**. Obviously, **3** is attacked by the electrophile at C-6 to give **15** which subsequently rearranges through deprotonation and reprotonation of **16** to **17** which in turn gives rise to **18**.

When the salts **22** are treated with potassium carbonate in acetone, the 7-amino-3 trityl-3H-azepines **20** are obtained in high yields. In contrast to **22**, the azanorcaradienes **21** formed from **22** rearrange spontaneously to **20**. The ^{1}H-NMR and ^{13}C-NMR spectra of **20** show each only one high-field signal indicating the absence of **21** at room temperature.

22 are the first derivatives of 2-azanorcaradienes. 3-Azanorcaradienes have been detected by Sauer[26] as



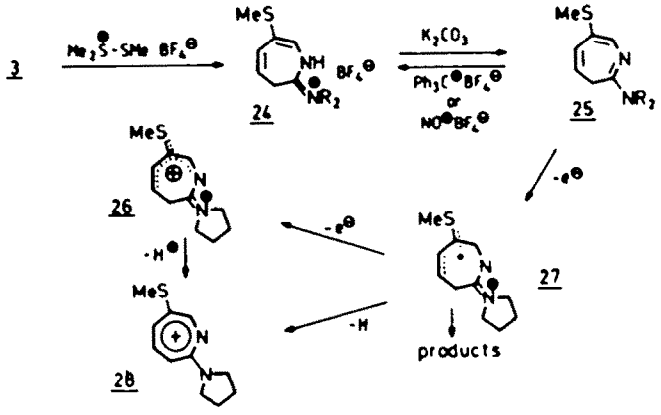
valence isomers of 4H-azepines. On treatment of **20** with tetrafluoroboric acid, **22** is reformed. This reaction could occur either via N-protonation of **20** and subsequent rearrangement of the azepinium salt so formed or via protonation of a small equilibrium concentration of **21**. The fact that the ^{13}C-NMR signals of C-2 and C-4



in **20a** experience an upfield-shift at lower temperatures (35 °C: δ = 108.14, 80.12; - 40 °C: δ = 86.47, 60.16 (in $CDCl_3/CD_3OD$ 1:1)) whereas the other signals remain essentially unchanged is in favour of the second possibility. A similar phenomenon has been observed with alkoxyiminium-tropylidenes.[27] The reaction of **20b,c** with trialkyloxonium tetrafluoroborates yields N-alkyl-2-azonia-norcaradiene salts **23**.

Attempts to trap **21** with dienophiles failed. Warming of **20** with or without dienophiles in polar solvents (acetonitrile) furnishes 2-amino-6-trityl-3H-azepines **19** in high yields. This rearrangement is typical for azepines.[28-30]

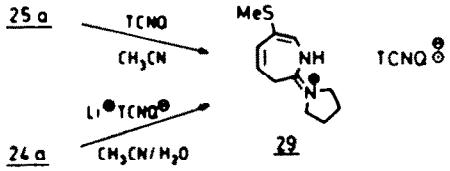
The high reactivity of the 6-position of **3** offers the possibility to prepare aminoazepines with electron-releasing substituents at this position which could be easier to oxidize than **3**. Dimethylmethylthiosulfonium tetrafluoroborate[31,32] can be used to synthesize methylthio derivatives of electron-rich aromatic[33] and heteroaromatic compounds.[34] The reaction of **3** with this reagent provides 6-methylthio-2-amino-3H-azepinium



salts **24** in good yields. It is remarkable that the azepinium salts **24**, in contrast to **17**, show no tendency to rearrange to azonia-norcaradienes (cf. **22**). The crystalline salts **24** are stable whereas the corresponding bases **25** are yellow oils which decompose on distillation and become dark when exposed to air.

The cyclovoltammogram of **25a** (10^{-3} M solution in acetonitrile + 0.1 M tetraethylammonium tetrafluoroborate, Pt electrode) features two irreversible waves at 0.58 and 0.90 V (vs. Ag/AgCl). The first wave can be assigned to the formation of the unstable radical cation **27**, the second one to the formation of the dication **26** that could be deprotonated to the azepinyl cation **28**. This mechanism is supported by the fact that solutions of **25** in dichloromethane turn deep green upon addition of trityl tetrafluoroborate or nitrosyl tetrafluoroborate. The colour fades slowly and work-up furnishes the salts **24**. The formation of **24** can be rationalized as a result either of the decomposition of **27** or a reaction of **28** with **25** or the solvent. The oxidation of azadithiafulvalenes with bromine or tetracyanoquinodimethane (TCNQ) gives rise to protonated starting materials too.[35]

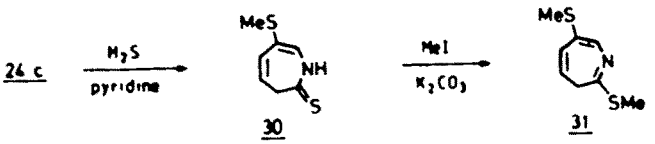
The reaction of **25a** with TCNQ takes the same course as that with trityl tetrafluoroborate. Instead of a salt



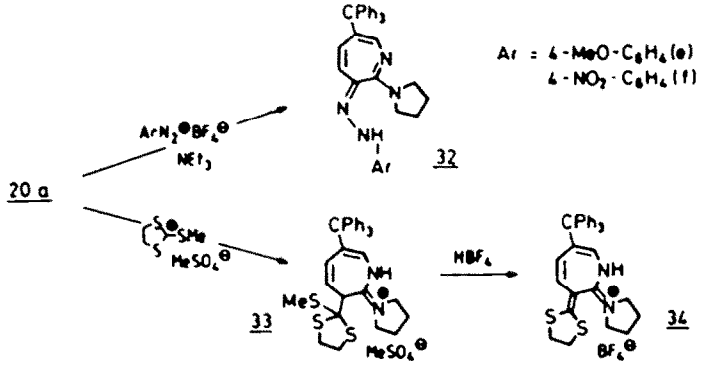
of **28** the "normal" deep blue salt **29** is produced. **29** is also obtained when **24a** is combined with lithium TCNQ.

2,6-Bis-methylthio-3H-azepine (**31**) is structurally related to **25**. It can be obtained by way of alkylation of the thione **30** (cf. alkylation of 3,5,7-trimethyl-azepine-2-thione[36]) which in turn is formed when the salts **24** are treated with hydrogen sulfide-pyridine.

Whereas the reactions of **20** with tetrafluoroboric acid or trialkyloxonium tetrafluoroborates give rise to 2-



azonia-norcaradienes **22** and **23**, respectively, by way of N-alkylation. **20a** behaves as an enamine in reactions with diazonium and dithiolium salts. Treatment of **20a** with 4-methoxy- and 4-nitro-benzene terafluoroborate, respectively, in dichloromethane solution in the presence of triethylamine provides after work-up the



yellow 3-azatropone hydrazone derivatives **32** that are in fact azatropolone derivatives.

2-Methylthio-1,3-dithiolanylium methylsulfate[37] also attacks C-6 of **20a** to give the colorless adduct **33** that on heating of its acetonitrile solution with a catalytic amount of tetrafluoroboric acid furnishes the pale yellow azaheptafulvene derivative **34**.

Table 2 Spectroscopic data of 3-7, 9-14, 19, 20, 22-25, 29-34

A: ^{1}H-NMR (60 MHz; $CDCl_3$) [δ (ppm)]; ***B***: ^{13}C-NMR (20 MHz; $CDCl_3$) [δ (ppm)]. ***C***: IR (KBr) [ν (cm^{-1})]. ***D***: UV/VIS (CH_2Cl_2) [λ_{max} (nm), (lg ε)]

3a: ***A***: 1.83 (mc; 4 H, $NCH_2C\underline{H}_2$), 2.62 (d, J = 8 Hz; 2 H, H-3), 3.40 (mc; 4 H, $NC\underline{H}_2CH_2$), 5.17 (dd, J =6Hz,J = 8 Hz; 1 H, H-4), 5.70 (dd, J = 8 Hz, J = 8 Hz; 1 H, H-6), 6.27 (dd, J = 6 Hz, J = 8 Hz; 1 H, H-5), 7.11 (d, J = 8 Hz; 1 H, H-7). ***C*** (neat): 2960, 2860, 1555, 1500. ***D***: 270 (sh, 3.73), 300 (3.89).

3c: ***A***: 2.62 (d, J = 8 Hz; 2 H, H-3), 3.33 (mc; 4 H, NCH_2),3.70 (mc; 4 H, OCH_2), 5.10 (q, J = 8 Hz; 1 H, H-4), 5.70 (dd, J = 6 Hz, J = 8 Hz; 1 H, H-6), 6.30 (dd, J = 6 Hz, J = 8 Hz; 1 H, H-5), 7.10 (d, J = 8 Hz; 1 H, H-7). ***C*** (film): 2955, 2860, 1563, 1501. ***D***: 275 (sh, 3.71), 302 (3.92).

3d: ***A***: 2.66 (d, J = 8 Hz; 4 H, H-3), 3.38 (s; 8 H, NCH_2), 5.13 (q, J = 8 Hz; 2 H, H-4), 5.88 (dd, J = 6 Hz, J = 8 Hz; 2 H, H-6), 6.40 (dd, J = 6 Hz, J = 8 Hz; 2 H, H-5), 7.00 (d, J = 8 Hz; 2 H, H-7). ***C*** (neat): 3020, 2860, 1576. ***D*** : 295 (3.94).

4: ***A***: 3.38 (d, J = 7 Hz; 2 H, H-6), 6.13 (mc; 3 H, H-3 - H-5), 7.45 (mc; 4 H, ArH, H-2), 8.25 (d, J = 8 Hz; 1 H, H-13). ***C***: 1690, 1595. ***D***: 263 (4.07), 285 (3.95), 332 (3.83).

5: ***D*** (DMF): 275 (4.59), 316 (3.90), 332 (3.90), 374 (3.62), 395 (sh, 3.48).

6: ***A*** (DMSO-d_6/$CDCl_3$) 3.00 (d, J = 8 Hz; 2 H, H-3), 5.30 (q, J = 8 Hz; 1 H, H-4), 5.90 (dd, J = 6 Hz, J = 8 Hz; 1 H, H-5), 6.25 (dd, J = 6 Hz, J = 8 Hz; 1 H, H-5), 6.50 (d, J = 8 Hz; 1 H, H-7). ***C***: 3220, 2220, 2200, 1610.

7: ***A***: 1.45 (t, J = 7 Hz; 3 H, $OCH_2C\underline{H}_3$), 3.10 (d, J = 8 Hz; 2 H, H-3), 4.25 (q, J = 7 Hz; 2 H, $OC\underline{H}_2CH_3$), 5.65 (q, J = 8 Hz; 1 H, H-4), 5.95 (dd, J = 6 Hz, J = 8 Hz; 1 H, H-6), 6.50 (dd, J = 6 Hz, J = 8 Hz; 1 H, H-5), 6.76 (dd, J = 4 Hz, J = 8 Hz; 1 H, H-7), 11 13 (s br; 1 H, NH). ***C***: 3195, 2215, 2202, 1669, 1606. ***D*** : 325 (4.29).

9: ***A***: 1.05 (s; 6 H, CH_3), 2.38 (s; 4 H, CH_2), 3.45 (d, J = 7 Hz; 2 H, H-3), 5.83 (mc; 1 H, H-4), 6.30 (mc; 2 H, H-5,6), 6.63 (mc; 1 H, H-7), 12.15 (s br; 1 H, NH). ***C***: 3436, 1637, 1574. ***D*** : 250 (4.08), 265 (sh, 3.93), 342 (4.23).

10: ***A***: 2.46 (s; 3 H, CH_3) 3.25 (d, J = 7 Hz, 2 H, H-3), 5.60 (dt, J = 7 Hz, J = 8 Hz; 1 H, H-4), 6.01 (dd, J = 8 Hz, J = 6 Hz; 1 H, H-6), 6.33 (dd, J = 8 Hz, J = 6 Hz; 1 H, H-5), 6.65 (dd, J = 4 Hz, J = 7 Hz; 1 H, H-7), 7.30, 7.95 (2 mc; 5 H, Ar-H), 12.58 (s br; 1 H, NH). ***C***: 3420, 1618, 1570. ***D***: 250 (4.27), 345 (4.21).

11: ***A***: 1.28 (t, J = 7 Hz; 3 H, $OCH_2C\underline{H}_3$), 2.38 (s; 3 H, CH_3), 2.95 (br, 2 H, H-3), 3.95 (q, J = 7 Hz, 2 H, OCH_2), 5.28 (q, J = 8 Hz; 1 H, H-4), 6.23 (q, J = 7 Hz; 1 H, H-6), 6.45 (mc, 1 H, H-5), 7.63 (mc; 6 H, ArH, H-7).

12: ***A***: 1.13 (t, J = 7 Hz; 3 H, $OCH_2C\underline{H}_3$), 2.85 (s; 3 H, CH_3), 3.30 (q, J = 7 Hz; 2 H, H-3), 4.00 (q, J = 7 Hz, 2 H, $OC\underline{H}_2CH_3$), 5.85 (mc; 1 H, H-4), 6.63 (mc; 2 H, H-5,6), 7.05 (mc; 1 H, H-7), 7.45 (mc; 5 H, Ar-H) ***C***: 3420, 1640. ***D***: 358 (4.21).

13a: ***A*** ($CDCl_3$/DMSO-d_6): 3.05 (d, J = 7 Hz; 2 H, H-3), 5.65 (dt, J = 7 Hz, J = 9 Hz, 1-H, H-4), 5.90 (dd, J =5, J = 9 Hz, 2 H, H-6), 6.20 (dd, J =5 Hz, J =9 Hz, 1 H, H-5), 6.53 (d, J = 9 Hz; 1 H, H-7), 7.07-7.85 (m; 4 H, Ar-H), 12.38 (s br, 1 H, NH). ***C***: 1615, 1577. ***D***: 259 (4.02), 340(4 32).

13b: ***A*** ($CDCl_3$/DMSO-d_6): 3.05 (d, J = 7 Hz; 2 H, H-3), 5.60 (dt, J = 7 Hz, J = 9 Hz, 1-H, H-4), 5.90 (dd, J =5, J = 9 Hz, 2 H, H-6), 6.20 (dd, J =5 Hz, J =9 Hz, 1 H, H-5), 6.50 (d, J = 9 Hz; 1 H, H-7), 6.80-7.80 (m; 3 H, Ar-H), 12.38 (s br, 1 H, NH). ***C***: 1615, 1572 ***D***: 260 (3.90), 345(4.40).

14a: ***A*** ($CDCl_3$/DMSO-d_6): 3.35 (d, J = 7 Hz; 2 H, H-3), 3.90 (s; 3 H, CH_3), 5.54 (mc; 1 H, H-4), 6.30-6.60(m; 2 H, H-5,6), 6.73 (d, J = 8 Hz, H-7), 7.35-8.15 (m; 4 H, Ar-H). ***C***: 1595, 1545, 1080. ***D***: 256 (4.12), 360 (4.32).

14b: ***A*** ($CDCl_3$/DMSO-d_6): 3.18 (d, J = 7 Hz; 2 H, H-3), 3.73 (s; 3 H, CH_3),3.83 (s; 3 H, OCH_3), 5.70 (dt, J =7 Hz, J = 8 Hz, 1 H, H-4), 6.38 (mc, 2 H, H-5,6), 6.63 (d, J = 8 Hz, 1 h, H-7), 7 05-7.68 (m; 3 H, Ar-H). ***C***: 1590, 1535, 1080. ***D***: 260 (3.98), 370 (4.37).

19a: ***A***: 1.80 (mc; 4 H, $NCH_2C\underline{H}_2$), 2.76 (d, J = 7 Hz; 2 H, H-3), 3.34 (mc; 4 H,NCH_2), 5.06 (dt, J = 7 Hz, J = 8 Hz; 1 H, H-4), 5.87 (d, J = 8 Hz; 1 H, H-5), 7.13 (mc; 16 H, Ph_3C, H-7). ***C***: 3050, 1560. ***D***: 269 (3.99), 302 (3.94).

19b: ***A***: 1.55 (mc; 6 H, $NCH_2C\underline{H}_2C\underline{H}_2$), 2.81 (d, J = 8 Hz; 2 H, H-3), 3.39 (mc; 4 H, NCH_2), 5.05 (q, J = 8 Hz; 1 H, H-4), 5.95 (d, J = 8 Hz; 1 H, H-5), 7.20 (mc; 16 H, Ph_3C, H-7).

19c: ***A***: 2.72 (d, J = 8 Hz; 2 H, H-3), 3.35 (mc; 4 H, NCH_2), 3.57 (mc; 4 H, OCH_2), 4.97 (q, J = 8 Hz; 1 H, H-5), 5.88 (d, J = 8 Hz; 1 H, H-5), 7.10 (mc; 16 H, Ph_3C, H-7).

20a: ***A***:1.90 (mc; 4 H, $NCH_2C\underline{H}_2$), 2.20 (t, J = 6 Hz; 1 H, H-6), 3.30 (mc; 4 H, NCH_2),, 4.20 (dd, J = 6 Hz, J =8 Hz, 1H, H-5), 5.20 (d, J = 8 Hz; 1 H, H-3), 5.85 (d, J = 6 Hz; 1 H, H-7), 6.40 (t, J = 8 Hz; 1 H, H-4), 7.20 (mc; 15 H, Ph_3C). ***C***: 3050, 2960, 1590, 1510. ***D***: 297 (4 10).

20b: ***A***: 1.63 (mc; 6 H, $NCH_2C\underline{H}_2C\underline{H}_2$), 2.30 (t, J = 6 Hz; 1 H, H-6), 3.25 (mc; 4 H, NCH_2), 4.48 (dd, J = 6 Hz, J =8 Hz, 1 H, H-5), 5.50 (d, J = 8 Hz; 1 H, H-3), 5.98 (d, J = 6 Hz; 1 H, H-7), 6.35 (t, J = 8 Hz; 1 H, H-4), 7.20 (mc; 15 H, Ph_3C).

20c: ***A***: 2.28 (t, J = 6 Hz, 1 H, H-6), 3.25 (mc; 4 H, NCH_2), 3.78 (mc; 4 H, OCH_2), 4.55 (dd, J = 6 Hz, J =8 Hz, 1 H, H-5), 5.53 (d, J = 8 Hz; 1 H, H-3), 6.08 (d, J = 6 Hz; 1 H, H-7), 6 38 (t, J = 8 Hz; 1 H, H-4), 7.18 (mc; 15 H, Ph_3C).

22a: ***A***: 2.00 (mc; 6 H, $NCH_2C\underline{H}_2$, H-6,7), 2.84 (dd, J =4 Hz, J = 8 Hz, 1 H, H-1), 3.50 (mc; 4 H, NCH_2), 6.30 (d, J = 10 Hz, 1 H, H-4), 7.25 (mc; 16 H, Ph_3C, H-5). ***C***: 1660, 1590, 1080. ***D***: 263 (4 05).

22b: ***A***: 1.75 (mc; 8 H, $NCH_2C\underline{H}_2C\underline{H}_2$, H-6,7), 3.00 (t, J = 6 Hz, 1 H, H-1), 3.50 (mc; 4 H, NCH_2), 6.28 (d, J = 10 Hz; 1 H, H-4), 7.30 (mc; 16 H, Ph_3C, H-5).

22c: ***A***: 1.70 (mc, 1 H, H-6), 2.19 (t, J = 5 Hz, 1 H, H-7), 2.88 (dd, J = 5 Hz, J = 7 Hz, 1 H, H-1), 3.65 (mc; 8 H, NCH_2CH_2O), 6.38 (d, J = 10 Hz; 1 H, H-4), 7.20 (mc; 16 H, Ph_3C, H-5), 7.90 (s br; 1 H, NH). ***B*** (CD_3CN): 19.69 (d; C-7), 36.29 (d; C-1?), 36.81 (d; C-6?), 47.05 (t; NCH_2), 56.86 (s, $\underline{C}Ph_3$), 65.76 (t; OCH_2), 111.01 (d; C-4), 127.55 (d; Ph-m), 128 67 (d; Ph-p), 130.00 (d; Ph-o), 145 73 (s; (Ph-i), 149.88 (d; C-5), 159.90 (s; C-3).

23ae: ***A*** (CF_3CO_2H): 1.85 (mc; 2 H, H-6,7), 2 13 (mc; 4 H, $NCH_2C\underline{H}_2$), 2.91 (t, J = 6 Hz; 1 H, H-1), 3.43 (s; 3 H, NCH_3), 3.71 (mc; 4 H, NCH_2), 6.38 (d, J = 9.5 Hz; 1 H, H-4), 7.22 (mc; 16 H, CPh_3, H-5) ***C***: 3080, 3050, 3025, 2980, 2870, 1640, 1560, 1490, 1440, 1420, 1080.

23af: ***A*** (CF_3CO_2H): 1.38 (t, J = 7 Hz; 3 H, $CH_2C\underline{H}_3$), 2.20 (mc; 6 H, $NCH_2C\underline{H}_2$, H-6,7), 2.94 (t, J = 6 Hz, 1 H, H-1), 3.77 (mc; 6 H, $NC\underline{H}_2CH_2$, $C\underline{H}_2CH_3$), 6.46 (d, J = 10 Hz; 1 H, H-4), 7.24 (mc; 1 H, H-5), 7.24 (mc, 15 H, CPh_3).

23ce: ***A*** (CD_3CN): 1.70 (mc; 1 H, H-6), 2.19 (t, J = 5 Hz, 1 H, H-7), 2.80 (dd, J = 5 Hz, J = 8 Hz, 1 H, H-1), 3.30 (s; 3 H, NCH_3), 3.55 (mc; 4 H, NCH_2), 3.78 (mc; 4 H, OCH_2), 6.35 (d, J = 10 Hz; 1 H, H-4), 7.20 (mc; 15 H, CPh_3), 7.38 (mc; 1 H, H-5).

24a: ***A*** ($CDCl_3$/DMSO-d_6): 2.00 (mc; 4 H, $NCH_2C\underline{H}_2$), 2.30 (s; 3 H, SCH_3), 3.20 (d, J = 7 Hz; 2 H, H-3), 3.65 (mc; 4 H, NCH_2), 5.65 (dd, J = 7 Hz, J =9 Hz, 1 H, H-4), 6.40 (d, J = 9 Hz; 1 H, H-5), 6 60 (s; 1 H, H-7) ***C***: 3440, 1641, 1583, 1084. ***D***: 300 (4 01).

24b: ***A*** ($CDCl_3$/DMSO-d_6): 1.73 (mc; 6 H, $NCH_2C\underline{H}_2C\underline{H}_2$), 2.32 (s; 3 H, SCH_3), 3.23 (d, J = 8 Hz; 2 H, H-3), 3.68 (mc; 4 H, NCH_2), 5.75 (q, J = 8 Hz; 1 H, H-4), 6.46 (d, J = 8 Hz; 1 H, H-5), 6.70 (s; 1 H, H-7).

24c: ***A*** ($CDCl_3$/DMSO-d_6): 2.33 (s; 3 H, SCH_3), 3.21 (d, J = 7 Hz; 2 H, H-3), 3.64 (mc; 4 H, NCH_2), 3 85 (mc; 4 H, OCH_2), 5.73 (dt,J = 7 Hz,J = 9 Hz; 1 H, H-4), 6.46 (d, J = 9 Hz; 1 H, H-5), 6.69 (s; 1 H, H-7).

25a: ***A***: 1.70 (mc; 4 H, $NCH_2C\underline{H}_2$), 2.30 (s; 3 H, SCH_3), 2.72 (d, J = 7 Hz; 2 H, H-3), 3.28 (mc; 4 H, NCH_2), 5.15 (dt, J = 7 Hz;J = 9 Hz; 1 H, H-4), 6.40 (d, J = 9 Hz; 1 H, H-5), 7.45 (s; 1 H, H-7). ***C*** (film): 2970, 2869, 1592, 1558

25b: ***A***: 1.59 (mc; 6 H, $NCH_2C\underline{H}_2C\underline{H}_2$), 2.30 (s; 3 H, SCH_3), 2.73 (d, J = 8 Hz; 2 H, H-3), 3.43 (mc; 4 H, NCH_2), 5.17 (q, J = 8 Hz; 1 H, H-4), 6.33 (d, J = 8 Hz; 1 H, H-5), 7.37 (s; 1 H, H-7).

25c: ***A***: 2.28 (s; 3 H, SCH_3), 2.71 (d, J = 8 Hz; 2 H, H-3), 3.50 (mc; 4 H, NCH_2), 3.71 (mc; 4 H, OCH_2), 5 21 (q, J = 8 Hz; 1 H, H-4), 6.43 (d, J = 8 Hz; 1 H, H-5), 7.43 (s; 1 H, H-7).

29: ***C***: 2178, 1642, 1581. ***D*** (CH3CN): 280 (4.05), 395 (4.31), 406 (4.36), 420 (4.39), 435 (4.24), 665 (3.78), 680 (3.88), 695 (3.86), 725 (4.15), 743 (4.36), 760 (4.28), 843 (4.63).

30: ***A***: 2.25 (s; 3 H, SCH_3), 3.43 (d, J = 7 Hz; 2 H, H-3), 5.73 (dt, J = 7 Hz, J = 9 Hz; 1 H, H-4), 6.20 (d, J = 9 Hz; 1 H, H-5), 6.45 (d, J = 4 Hz; 1 H, H-7), 9.00 (s br, 1 H, NH). ***D***: 329 (4.24), 395 sh (3.95).

31: ***A***: 2.28 (s; 3 H, C6-SCH_3), 2.38 (s; 3 H, C2-SCH_3), 2.85 (d, J = 7 Hz; 2 H, H-3), 5.30 (dt, J = 7 Hz, J = 8 Hz, 1 H, H-4), 6.30 (dd,J = 1 Hz, J = 8 Hz, 1 H, H-5), 7.45 (d, J = 1 Hz; 1 H, H-7). ***C*** (film): 2919, 1574, 1501.

32e: *A*: 1.87 (mc; 4 H, $NCH_2C\underline{H}_2$), 3.54 (mc; 4 H, NCH_2), 3.73 (s; 3 H, OCH_3), 5.67 (d, J = 11 Hz; 1 H, H-5), 6.13 (d, J = 11 Hz; 1 H, H-4?), 6.86 (mc; 4 H, $C_6\underline{H}_4OCH_3$), 7.16 (mc; 16 H, Ph_3C, H-7). *B*: 24.63, 25.98 (mc; $NCH_2\underline{C}H_2$), 47.92, 48.95 (mc; NCH_2), 55.67 (q; OCH_3), 64.15 (s; $\underline{C}Ph_3$), 111.22 (dd; C-4), 114.52 (d; $\underline{C}_6H_4OCH_3$-o), 114.77 (d; $C_6\underline{H}_4OCH_3$-m), 125.70 (d; CPh_3-p), 127.45 (d; CPh_3-m), 127.79 (s; C-6), 131.06 (d; CPh_3-o), 136.21 (s; $\underline{C}_6H_4OCH_3$-i), 138.51 (d; C-5), 138.78 (s; $\underline{C}_6H_4OCH_3$-p), 143.21 (d; C-7), 145.96 (s; CPh_3-i), 148.81 (s; C-3), 154.08 (s; C-2). *C*: 3080, 3050, 3020, 2960, 2860. *D* ($CHCl_3$): 310 (4.22), 370; (CF_3CO_2H): 332 (4.01), 416 (4.01).

32f: *A* ($CDCl_3$/DMSO-d_6): 1.93 (mc; 4 H, $NCH_2C\underline{H}_2$), 3.50 (mc; 4 H, NCH_2), 6.05 (s; 2 H, H-4,5), 7.20 (mc; 17 H, CPh_3, $C_6\underline{H}_4NO_2$-m), 7.98 (d, J = 12 Hz; 2 H, $C_6\underline{H}_4NO_2$-o). *D* ($CHCl_3$): 300 (4.06), 404 (4.26); (CF_3CO_2H): 275 (sh), 383 (4.51).

33: *A* (DMSO-d_6): 1.96 (mc; 4 H, $NCH_2C\underline{H}_2$), 2.35 (s; 3 H, SCH_3), 3.43 (s; 7 H, $SCH_2C\underline{H}_2$, CH_3SO_4), 3.56, 4.00 (mc; 4 H, NCH_2), 4.87 (d; J = 10 Hz; 1 H, H-3), 5.59 (t, J = 10 Hz; 1 H, H-4), 6.12 (d, J = 10 Hz; 1 H, H-5), 6.44 (mc; 1 H, H-7), 7.25 (mc; 15 H, CPh_3).

34: *A* (CF_3CO_2H): 2.13 (s br; 4 H, $NCH_2C\underline{H}_2$), 3.63 (s br ; 8 H, NCH_2, SCH_2), 5.95 (s; 2 H, H-3,4), 6.44 (d, J = 4 Hz; 1 H, H-7), 7.26 (mc; 15 H, CPh_3), 7.91 (d, J = 4 Hz; 1 H, NH). *B* (DMSO-d_6): 24.44 (t; $NCH_2\underline{C}H_2$), 49.22 (t; NCH_2?), 50.98 (t; SCH_2?), 63.27 (s; $\underline{C}Ph_3$), 108.77 (s; C-3), 127.88 (d; CPh_3-m), 130.30 (d; CPh_3-o), 132.03 (d; C-7), 135.66 (s; C-6?), 143.72 (s; CPh_3-i), 151.05 (s; C=$\underline{C}$-S), 153.66 (s; C-2?). *C*: 3080, 3050, 3020, 2970, 2920, 2870, 1635, 1610, 1590, 1550, 1490, 1440, 1080. *D* (CH_3CN): 262 (4.29), 310 (4.07).

Experimental

^1H NMR spectra were measured on Varian EM 360 and Bruker WP 80 spectrometers, ^{13}C NMR spectra on a Bruker WP 80 spectrometer (TMS as internal standard). IR spectra were determined on Perkin-Elmer 125 and 157 spectrophotometers and UV/VIS spectra on a Zeiss spectrometer DMR 10. Electrochemical oxidation were performed with a Bioanalytical Systems Cyclic Voltammeter VV 1 B. Melting points were determined on a Büchi SMP-20 apparatus and are uncorrected.

General procedure for the preparation of aminoazepines 3. 3a: A mixture of 16.52 g (100 mmol) of 2-*n*-butoxy-3H-azepine (2) and 33.4 ml (400 mmol) of pyrrolidine was refluxed for 6 h, the excess pyrrolidine then removed by distillation and the residue distilled (Vigreux column). **3c** was analyzed as the oxalate.

General procedure for the preparation of azepinoquinazolines 4, 5. 4: A mixture of 0.83 g (5 mmol) of **2** and 0.68 g (5 mmol) of anthranilic acid were heated for 30 min to 120°C (1 h to 150°C for **5**), the product after cooling triturated with ether, the residue filtered off and recrystallized from ethyl acetate.

2-Dicyanomethylene-1,2-dihydro-3H-azepine (6): 3.24 g (20 mmol) of **2** and 1.22 g (20 mmol) of malononitrile were heated for 1 h to 150°C and the n-butanol formed during the time distilled off. The brown product was triturated with ether, the residue filtered off and recrystallized from ethyl acetate.

General procedure for the preparation of methyleneazepines 7, 9, 10. 7: 1.62 g (10 mmol) of **2** or 1.08 g (10 mmol) of 2-amino-3H-azepine (**8**), 1.06 g (10 mmol) of ethyl cyanoacetate and 0.2 ml (1.4 mmol) of triethylamine were refluxed in 30 ml of toluene for 12 h. The precipitate was filtered off (**10**) or the mixture was stripped of solvent under reduced pressure and the residue purified through column chromatography on silica gel (eluent CH_2Cl_2).

2-(5-Ethoxy-3-methyl-1-phenylpyrazol-4-yl)-1H$^+$,3H-azepinium tetrafluoroborate (12): To the solution of 2.65 g (10 mmol) of **10** in 50 ml of anhydrous CH_2Cl_2 were added 1.9 g (10 mmol) of triethyloxonium tetrafluoroborate. After 3 h at room temperature the mixture was stripped of solvent under reduced pressure and the residue recrystallized from ethanol.

2-(5-Ethoxy-3-methyl-1-phenylpyrazol-4-yl)-3H-azepine (11): The solution of 1.91 g (5 mmol) of **12** in 30 ml of CH_2Cl_2 was added to the solution of 1.27 g of sodium dihydrogenphosphate in 15 ml of water. The organic layer was separated and the water layer extracted twice with each 20 ml of CH_2Cl_2. The combined organic phases were dried over Na_2SO_4, filtered, the solvent removed in vacuo and the residue recrystallized from cyclohexane.

2-(2-Benzothiazolylimino)-1,2-dihydro-3H-azepine (13a): A mixture of 1.62 g (10 mmol) of **2** and 1.5 g (10 mmol) of 2-aminobenzothiazole was heated for 1 h to 160-180°C. The black tarry product was extracted with hot n-heptane; upon cooling, yellow crystals separated.

2-(3-Methyl-2-benzothiazolylimino)-1,2-dihydro-3H-azepinium tetrafluoroborate (14a): To the solution of 1.2 g (5 mmol) of **13a** in 30 ml of CH_2Cl_2 was added 0.74 g (5 mmol) of trimethyloxonium tetrafluoroborate. When after 12 h at room temperature ether was added to the mixture, yellow crystals separated.

General procedure for the preparation of 2-aza-2H$^+$-norcaradienium tetrafluoroborates 22. 22a: To the slurry of 16.5 g (50 mmol) of trityl tetrafluoroborate in 50 ml of anhydrous CH_2Cl_2 was added the solution of 8.11 g (50 mmol) of **3a** in 100 ml of anhydrous CH_2Cl_2. After 24 h at room temperature the mixture was stripped of solvent under reduced pressure. The brown oily residue solidified after adding i-propanol and a little ether.

General procedure for the preparation of 7-amino-3-trityl-3H-azepines 20. 20a: 4.92 g (10 mmol) of **22a** and 1.53 g (11 mmol) of K_2CO_3 were stirred for 3 h in 50 ml of acetone at room temperature. After filtration the solvent was removed in vacuo and the residue recrystallized from acetonitrile.

General procedure for the preparation of 2-amino-6-trityl-3H-azepines 19. 19a: 4.05 g (10 mmol) of **20a** were refluxed for 3 h in 30 ml of anhydrous acetonitrile. After cooling the product crystallized.

General procedure for the preparation of 2-alkyl-2-aza-norcaradienium tetrafluoroborates 23. 23ce: To the solution of 2.1 g (5 mmol) of **20c** in 30 ml of anhydrous CH_2Cl_2 was added 0.74 g (5 mmol)

trimethyloxonium tetrafluoroborate. After standing for 12 h at room temperature, followed by addition of ether, crystals separated that could be be recrystallized from acetonitrile/ethyl acetate.

General procedure for the preparation of 2-amino-6-methylthio-1H⁺,3H-azepinium tetrafluoroborates 24. 24a: a)To 1.96 g (10 mmol) of dimethylmethylthiosulfonium tetrafluoroborate suspended in 30 ml of anhydrous CH_2Cl_2 was added dropwise at 0°C the solution of 1.62 g (10 mmol) of **3a** in 20 ml of anhydrous CH_2Cl_2. After stirring the mixture for 3 h at room temperature the solvent was removed in vacuo and the brown solid recrystallized twice from CH_2Cl_2/ether. b) To 1.65 g (5 mmol) of trityl tetrafluoroborate suspended in 20 ml of anhydrous CH_2Cl_2 was added dropwise 1.04 g (5 mmol) of **25a** dissolved in 10 ml of anhydrous CH_2Cl_2. During the addition of 25a the mixture became a deep green solution. After adding ether to the solution, 0.9 g (61%) colorless platelets separated.

General procedure for the preparation of 2-amino-6-methylthio-3H-azepines 25. 25a: *To the* solution of 1.48 g (5 mmol) of **24a** in CH_2Cl_2 was added the solution of 1.38 g (10 mmol) of K_2CO_3 in 20 ml of water and the mixture stirred for 1 h. The organic layer was separated, dried over $MgSO_4$, filtered and the solvent removed in vacuo. The remaining yellow oil decomposed on distillation.

2-Pyrrolidino-6-methylthio-1H+,3H-azepinium 7,7,8,8-tetracyanoquinodimethanide (29): a) 1.02 g (5 mmol) of TCNQ and 1.04 g (5 mmol) of **25a** were refluxed for 10 min in 30 ml of anhydrous acetonitrile; during the time a deep green solution was formed. When after cooling ether was added, blue-black needles separated. b) The solution of 0.29 g (1 mmol) of **24a** in 10 ml of acetonitrile was added to the solution of 0.21 g (1 mmol) of Li^+ $TCNQ^-$ in 10 ml of water. The deep blue precipitate was filtered off and recrystallized from acetonitrile/ether.

6-Methylthio-1,2-dihydro-3H-azepin-2-thione (30): Into the solution of 3.12 g (10 mmol) of **24c** in 25 ml of anhydrous pyridine was passed H_2S for 3 h and then the solvent removed at 50°C in vacuo. The residue was dissolved in CH_2Cl_2 and the solution extracted with 0.5 N HCl. The organic phase was dried over $MgSO_4$, filtrated, the solvent removed in vacuo and the yellow-brown residue recrystallized from toluene/n-hexane.

2,6-Bis-methylthio-3H-azepine (31): 1.3 g 7.5 mmol) of **30**, 1.47 g (10 mmol) of methyl iodide and 1.65 g (12 mmol) of K_2CO_3 were stirred for 3 h in 30 ml of acetone at room temperature. After filtration the solvent was removed in vacuo and the residue subjected to Kugelrohr distillation.

2-Pyrrolidino-6-trityl-azepin-3-one p-methoxyphenylhydrazone (32e): To the stirring solution of 0.2 g (0.5 mmol) of **20a** and 0.07 ml (0.5 mmol) of triethylamine in 5 ml of CH_2Cl_2 was added a solution of 0.11 g (0.5 mmol) of 4-methoxybenzenediazonium tetrafluoroborate in 10 ml acetonitrile at room temperature. After 4 h the solvent was removed in vacuo, the residue dissolved in a little $CHCl_3$ and the solution passed through a column of silica gel, saturated with ethyl acetate. The first fraction was separated, evaporated to dryness and the residue recrystallized from ethanol/ether.

2-Pyrrolidino-6-trityl-azepin-3-one p-nitrophenylhydrazone (32f): To the stirring solution of 0.2 g (0.5 mmol) of **20a** and 0.07 ml (0.5 mmol) of triethylamine in 5 ml CH_2Cl_2 was added the solution of 0.12 g (0.5 mmol) of 4-nitrobenzenediazonium tetrafluoroborate in 10 ml of acetonitrile at room temperature. The red-brown solution was kept for 48 h at room temperature, after which it was filtered and the orange-yellow crystals recrystallized from chloroform/acetonitrile.

2-Pyrrolidino-6-trityl-3-(1-methylthio-1,3-dithiolan-1-yl)-1H⁺,3H-azepinium methylsulfate (33): 0.14 g (1 mmol) of 1,3-dithiolan-2-thione were heated with 0.15 g (1 mmol) of dimethyl sulfate for 5 min to 90 °C and the cooled mixture added to the stirring solution of 0.4 g (1 mmol) of **20a** in 10 ml of anhydrous acetonitrile. Crystals which has been formed after 4 h were filtered off and recrystallized from acetonitrile/-ether.

2-Pyrrolidino-3-(1,3-dithiolanyl-2-iden)-6-trityl-1H⁺,3H-azepinium tetrafluoroborate (34): To the solution of 0.2 g (0.3 mmol) of **33** in 2 ml of acetonitrile were added 3 drops of a 54% solution of tetrafluoroboric acid in ether. The mixture was then refluxed for 10 min, cooled and the crystals filtered off which were formed after addition of 3 ml of ether.

Table 3 Yields, melting points and elemental analyses of 3-7, 9-14, 19, 20, 22-25, 29-34

		yield g (%)	mp (°C)	molecular formula elemental analysis, C H N calcd / found
3a	2-Pyrrolidino-3H-azepine	14.5 (89)	bp 90-95 (0.1 Torr)	$C_{12}H_{14}N_2$ (162.2) 74.03 8.70 17.27 / 74.26 8.82 17.08
3b	2-Piperidino-3H-azepine	13.3 (75)	bp 139-144 (12 Torr), lit.15 bp 114-116 (0.7 Torr)	
3c	2-Morpholino-3H-azepine	14.5 (81)	bp 127-130 (0.01 Torr)	$C_9H_{14}N_2O \cdot C_2H_2O_4$ (167.3) 53.73 6.01 10.44 / 53.82 6.30 10.25
3d	N,N'-Bis-(3H-azepin-2-yl)-piperazine	0.85 (65)	163-164	$C_{16}H_{20}N_4$ (268.4) 71.61 7.51 20.88 / 71.59 7.42 20.90
4	6H-Azepino(2,1-b)quinazolin-12-one [beige platelets]	0.6 (52)	138.5-139.5	$C_{13}H_{10}N_2O$ (210.2) 74.27 4.79 13.33 / 73.85 4.82 13.30
5	6H-Azepino(2,1-b)benzo(g)-quinazolin-14-one [beige needles (DMF)]	0.9 (78)	178-179	$C_{17}H_{12}N_2O$ (260.3) 78.44 4.65 10.76 / 78.48 4.79 10.64
6	- [beige platelets]	1.9 (71)	195-196 (dec.)	$C_9H_6N_3$ (157.2) 68.78 4 49 26.73 / 68.77 4.59 26.47

7	Z-2-(Cyano-ethoxycarbonyl-methylen)-1,2-dihydro-3H-azepine [beige needles]	0.2 (10) 1.1 (53)	74-75	$C_{11}H_{12}N_2O_2$ (204.2) 64.69 5.92 13.71 / 64.90 5.86 13.58
9	2-(4,4-Dimethyl-2,6-dioxo-cyclohexylidene)-1,2-dihydro-3H-azepine [needles]	0.81 (35)	113-116	$C_{14}H_{19}NO_2$ (231.3) 72.70 7.41 6.06 / 72.87 7.56 6.12
10	2-(3-Methyl-5-oxo-1-phenyl-2-pyrazolin-4-ylidene)-3H-azepine [pale yellow rhombs]	1.6 (62)	140-141	$C_{16}H_{15}N_3O$ (265.3) 72.44 7.50 15.84 / 72.48 7.61 15.92
11	- [needles]	1.1 (75)	73.5-75	$C_{18}H_{19}N_2O$ (293.4) 73.70 6.53 14.32 / 73.57 6.33 14.92
12	- [yellow needles]	2.5 (65)	158-159	$C_{18}H_{20}BF_4N_3O$ (381.2) 56.72 5.29 11.02 / 55.61 5.41 11.07
13a	- [yellow needles]	0.9 (38)	128-129	$C_{13}H_{11}N_3S$ (241.3) 64.47 4.59 17.41 / 64.65 4.75 17.44
13b	2-(6-Methoxy-2-benzothiazolylimino)-1,2-dihydro-3H-azepine [yellow needles]	1.1 (41)	100-101	$C_{14}H_{13}N_3OS$ (271.3) 61.97 4.83 15.49 / 61.74 4.88 15.27
14a	- [dark yellow rhombs]	1.3 (76)	184-185	$C_{14}H_{14}BF_4N_3S$ (343.2) 49.00 4.11 12.25 / 48.73 4.18 12.30
14b	2-(3-Methyl-6-methoxy-2-benzothiazolimino)-1,2-dihydro-3H-azepinium tetrafluoroborate [dark yellow rhombs]	1.3 (70)	182.5-183.5	$C_{15}H_{16}BF_4N_3OS$ (372.2) 48.28 4.32 11.27 / 47.85 4.37 11.04
19a	2-Pyrrolidino-6-trityl-3H-azepine [beige needles]	2.9 (73)	235-237	$C_{29}H_{28}N_2$ (404.6) 86.09 6.98 6.93 / 85.57 6.91 7.00
19b	2-Piperidino-6-trityl-3H-azepine [beige crystals]	3.2 (77)	224-225	$C_{30}H_{30}N_2$ (418.6) 86.08 7.22 6.69 / 86.27 7.18 6.72
19c	2-Morpholino-6-trityl-3H-azepine [beige needles]	3.1 (75)	227-229	$C_{29}H_{28}N_2O$ (420.6) 82.82 6.71 6.66 / 82.34 6.85 6.76
20a	7-Pyrrolidino-3-trityl-3H-azepine [beige needles]	3.5 (87)	152-153	$C_{29}H_{28}N_2$ (404.6) 86.09 6.98 6.93 / 85.68 7.12 7.28
20b	7-Piperidino-3-trityl-3H-azepine [beige crystals]	3.4 (81)	151-152	$C_{30}H_{30}N_2$ (418.6) 86.08 7.22 6.69 / 86.02 7.39 6.83
20c	7-Morpholino-3-trityl-3H-azepine [beige crystals]	3.5 (83)	153-154	$C_{29}H_{28}N_2O$ (420.6) 82.82 6.71 6.66 / 83.05 6.79 6.61
22a	3-Pyrrolidino-7-trityl-2-aza-2H+-norcaradienium tetrafluoroborate [beige powder]	20.6 (83)	277-279	$C_{29}H_{29}BF_4N_2$ (492.4) 70 59 5.94 5.69 / 70.59 5.75 6.09
22b	3-Piperidino-7-trityl-2-aza-2H+-norcaradienium tetrafluoroborate [beige crystals]	21.5 (86)	250-252	$C_{30}H_{31}BF_4N_2$ (506.4) 71.16 6.17 5.53 / 70.93 6.18 5.32
22c	3-Morpholino-7-trityl-2-aza-2H+-norcaradienium tetrafluoroborate [beige crystals]	19.5 (78)	225-228 (dec.)	$C_{29}H_{29}BF_4N_2O$ (508.5) 68.50 5.75 5.53 / 67.89 5.60 5.49
23ae	2-Methyl-3-pyrrolidino-7-trityl-2-aza-norcaradienium tetrafluoroborate [colorless rhombs]	0.26 (51)	204-206	$C_{30}H_{31}BF_4N_2$ (506.4) 71.15 6.17 5.53 / 70.97 5.96 5.45
23af	2-Ethyl-3-pyrrolidino-7-trityl-2-aza-norcaradienium tetrafluoroborate [colorless rhombs]	0.4 (77)	218-220	$C_{31}H_{33}BF_4N_2$ (520.4) 71.54 6.39 5.38 / 71.81 6.30 5.72
23ce	2-Methyl-3-morpholino-7-trityl-2-aza-norcaradienium tetrafluoroborate [beige rhombs]	1.9 (71)	171-173	$C_{30}H_{31}BF_4N_2O$ (522.4) 68.98 5.98 5.36 / 69.07 6.22 5.44
24a	2-Pyrrolidino-6-methylthio-1H+,3H-azepinium tetrafluoroborate [colorless platelets]	1.6 (54)	176-177	$C_{11}H_{17}BF_4N_2S$ (296.1) 44.82 5.79 9.46 / 44.83 5.73 9.23
24b	2-Piperidino-6-methylthio-1H+,3H-azepinium tetrafluoroborate [colorless platelets]	1.4 (45)	157-157.5	$C_{12}H_{19}BF_4N_2S$ (310.8) 46.47 6.17 9.03 / 46.25 6.12 9.26
24c	2-Morpholino-6-methylthio-1H+,3H-azepinium tetrafluoroborate [colorless platelets]	1.9 (61)	160-161	$C_{11}H_{17}BF_4N_2OS$ (312.1) 42.33 5.49 8.97 / 42.26 5.53 8.96
25a	2-Pyrrolidino-6-methylthio-3H-azepine [pale yellow oil]	0.9 (87)		
25b	2-Piperidino-6-methylthio-3H-azepine [pale yellow oil]	1.05 (94)		
25c	2-Morpholino-6-methylthio-3H-azepine [pale yellow oil]	0.95 (81)		
29	-	0.9 (43)	202 (dec.)	$C_{23}H_{21}N_6S$ (413.5) 66.81 5.12 20.32 /66.93 5.30 20.20
30	-	1.5 (87)	135-136	$C_7H_9NS_2$ (171.3)

	[ocre needles]			49.09 5.30 8.18 / 49.39 5.12 7.90
31	-	0.9 (65)	bp 150 (0.01 Torr)	$C_8H_{11}NS_2$ (185.3)
	[pale yellow oil]			51.58 5.98 7.56 / 52.36 6.03 7.70
32a	-	0.1 (37)	187-188	$C_{36}H_{34}N_4O$ (538.6)
	[pale yellow rhombs]			80.28 6.36 10.40 / 79.73 6.34 10.53
32b	-	0.1 (36)	235-236	$C_{35}H_{31}N_5O_2$ (553.7)
	[orange-yellow needles]			75.93 5.64 12.65 / 75.51 5.64 12.72
33	-	0.44 (66)	221-222	$C_{34}H_{38}N_2O_4S_4$ (667.0)
	[colorless needles]			61.23 5.74 4.20 / 61.36 5.73 4.14
34	-	0.15 (84)	273-274	$C_{32}H_{31}BF_4N_2S_2$ (594.6)
	[pale yellow needles]			64.64 5.26 4.71 / 64.93 5.25 4.65.

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References and Notes

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