BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3187—3191 (1972)

Compounds Related to Acridine. VIII.[1] Reaction of 9-Vinylacridine with *p*-Substituted Nitrosobenzenes

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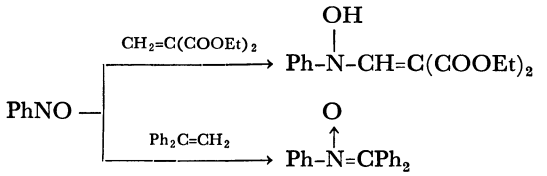
(Received May 17, 1972)

In the presence of hydrochloric acid, 9-vinylacridine reacts with nitrosobenzenes having electron-donating groups such as *p*-nitroso-*N*,*N*-dialkylaminoaniline and *p*-methylnitrosobenzene to yield a four-membered oxazetidine, as the first example of a non-fluorinated oxazetidine ring system. A new 2 : 2 adduct, to which the perhydro-1,2,7-oxadiazepine structure is assigned tentatively, is formed in the reaction of 9-vinylacridine with nitrosobenzene or *p*-chloronitrosobenzene under similar conditions.

So far no report has been given on non-fluorinated oxazetidines.[4,5] Hepfinger *et al.*[6] have shown that the oxazetidines reported by Ingold and Weaver[7] from the reaction of nitrosobenzene with diethyl methylenemalonate and 1,1-diphenylethylene are diethyl *β*-*N*-hydroxy-*N*-phenylmethylenemalonate and triphenylnitrone as proposed by Lapworth *et al.*[8]

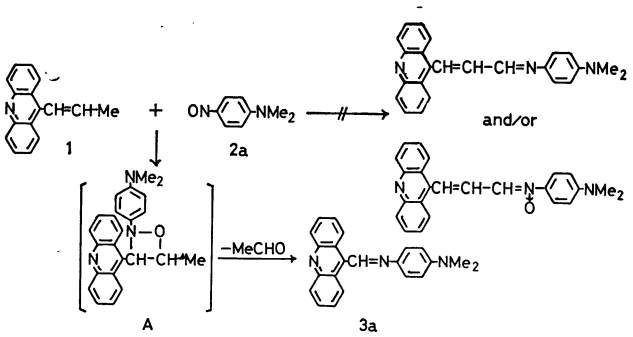


We reported[9,10] that hydrochloric acid (HCl) is an extremely effective catalyst for the condensation of *p*-substituted nitrosobenzenes with 9-methyl- and 9-ethylacridine. Furthermore, even 9-ethynylacridine undergoes condensation with two moles of *p*-nitroso-*N*,*N*-dialkylaniline in the presence of HCl to yield 1-(9-acridinyl)-1,2-bis(*p*-dialkylaminophenylimino)-ethane *N*,*N*-dioxide.[11]

We report herewith that in the presence of HCl, 9-vinylacridine reacts with nitrosobenzenes having electron-donating groups to give oxazetidine compounds as the first example of a non-fluorinated oxazetidine ring system. With nitrosbenzene or *p*-chloronitrosobenzene, a new 2 : 2 adduct was obtained.

Results and Discussion

From previous results,[9-11] *cis*- or *trans*-1-(9-acridinyl)-2-methylethylene (**1**) might be expected to react with *p*-nitroso-*N*,*N*-dialkylaniline to give the *α*,*β*-unsaturated anil and/or nitrone. Contrary to expectation, the reaction of **1** with *p*-nitroso-*N*,*N*-dimethylaniline (**2a**) in the presence of HCl in refluxing ethanol afforded acridine-9-carboxaldehyde-*N*-(*p*-*N*,*N*-dimethylaminophenyl)anil (**3a**), whose structure was confirmed by comparison with the authentic sample.[9] Olefin **1** did not react with **2a** in the presence of HCl at room temperature nor in the presence (or absence) of a basic catalyst such as potassium carbonate in ethanol.[12]



Scheme 1.

1) Part VII of this series: O. Tsuge and A. Torii, This Bulletin, **43**, 2920 (1970).

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3) Present address: Department of Industrial Chemistry, Kurume Technical College, Komorino, Kurume, 830.

4) D. A. Barr and K. N. Haszeldine, *J. Chem. Soc.*, **1955**, 1881.

5) V. A. Cinsburg, S. S. Dubov, A. N. Medvedev, L. L. Martynova, B. I. Tetel'baum, M. N. Vasil'eva, and A. Ya. Yakubovich, *Dokl. Akad. Nauk SSSR*, **152** (5), 1104 (1963).

6) N. F. Hepfinger, C. E. Griffin, and B. L. Shapiro, *Tetrahedron Lett.*, **1963**, 1365.

7) C. K. Ingold and S. D. Weaver, *J. Chem. Soc.*, **125**, 1146 (1924).

8) G. N. Burkhardt and A. Lapworth, *ibid.*, **127**, 1748 (1925); G. N. Burkhard, A. Lapworth, and J. Walkden, *ibid.*, **127**, 2458 (1925).

9) O. Tsuge, M. Nishinohara, and M. Tashiro, This Bulletin, **36**, 1477 (1963).

10) O. Tsuge, M. Nishinohara, and K. Sadano, K. Sadano, *ibid.*, **37**, 436 (1964); O. Tsuge, M. Nishinohara, and K. Sadano, *ibid.*, **38**, 2037 (1965).

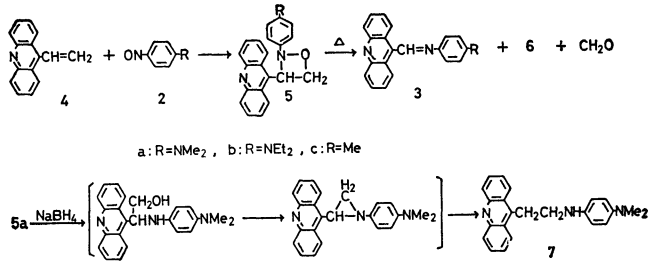
11) O. Tsuge and A. Torii, *ibid.*, **43**, 2920 (1970).

It is conceivable that **3a** might have been formed *via* the oxazetidine intermediate **A** with the elimination of acetaldehyde, although an attempt at isolation of **A** was unsuccessful (Scheme 1).

On the other hand, 9-vinylacridine (**4**) reacted easily with **2a** in the presence of HCl at room temperature to afford a 1 : 1 adduct **5a**, mp 156—157°C (decomp.), as violet prisms, while under reflux in ethanol **3a** was obtained.

The structure of the 1 : 1 adduct was established to be 3-(9-acridinyl)-2-(*p*-*N*,*N*-dimethylaminophenyl)-oxazetidine (**5a**) on the basis of spectra data and chemical conversions. The IR spectrum of **5a** showed a characteristic band ascribable to ν_{C-O-N} at 1050 cm^{-1}. The mass spectrum exhibited a parent peak (M^+) at *m/e* 355 together with major fragment peaks at *m/e* 341 (M^+-CH_2), 339 (M^+-O), 337 (M^+-H_2O), 325 (M^+-CH_2O), 324 (325^+-H), 221 (341^+-  $-NMe_2$), 217 (337^+-  $-NMe_2$), and 204 (324^+-  $-NMe_2$). However, the NMR spectrum could not be obtained owing to the insolubility of organic solvents.

When a solution of **5a** in ethanol was refluxed, anil **3a**, a new compound **6** and formaldehyde were formed. This indicates that **3a** was formed from **5a** by the elimination of formaldehyde.[13] Reduction of **5a** with sodium borohydride gave 1-(9-acridinyl)-2-(*p*-*N*,*N*-dimethylanilino)ethane (**7**), whose structure was confirmed by spectral data as well as by microanalysis. Although the exact pathway for the formation of **7** is not clear, it seems to have been caused by the initial reductive cleavage of oxazetidine, followed by the formation of an aziridine by the loss of water and subsequent ring opening as shown in Scheme 2.

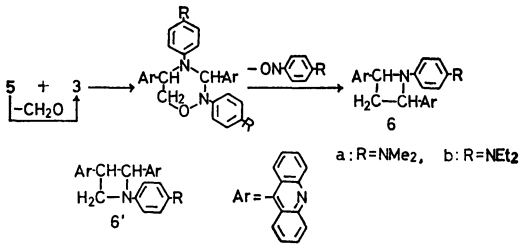


Scheme 2.

Similarly, the reaction of **4** with *p*-nitroso-*N*,*N*-diethylaniline (**2b**) or *p*-methylnitrosobenzene (**2c**) in the presence of HCl at 0°C afforded the corresponding oxazetidine compound **5b** or **5c**. Refluxing of an ethanol solution of **5b** or **5c** gave the corresponding anils **3b** and **3c**, and **6b**. In the case of **5c**, however, the compound of type **6** could not be isolated.

The results of microanalyses and mass spectra of **6a** and **6b** agreed with the molecular formulas of the corresponding 1 : 1 adduct of **4** and **3**. The IR spectra of **6a** and **6b** were very similar to each other, and showed no bands ascribable to ν_{NH}. The NMR spectrum of **6a** exhibited signals at δ 2.85 (2H, multiplet, CH_2), 2.95 (6H, singlet, $N(CH_3)_2$), and 6.7—8.7 ppm (22H, complicated, aromatic (20H) and two methine protons). It was thus deduced that the most reasonable structure for **6** is 2,4-di(9-acridinyl)-1-(*p*-*N*,*N*-dialkylaminophenyl)azetidine rather than the 2,3-di(9-acridinyl)azetidine compound **6'**.

The reaction of **4** with **3a** did not occur and starting materials were recovered. It is thus conceivable that the formation of **6** might have taken place from a secondary reaction of **5** with **3** by the elimination of nitroso compound **2**. Although no increase in the yield of **6a** was observed in the thermolysis of **5a** in the presence of **3a**, the formation of **6** can be viewed as proceeding by the initial formation of the perhydro-1,2,4-oxadiazine intermediate from the reaction of **5** with **3**, followed by the elimination of nitroso compound **2** as illustrated in Scheme 3.



Scheme 3.

4 reacted with nitrosobenzene (**2d**) in the presence of HCl to afford a 2 : 2 adduct **8d** as pale yellow prisms, accompanied by a large amount of tarry material. In a similar reaction of **4** with *p*-chloronitrosobenzene (**2e**), a 2 : 2 adduct **8e** was isolated together with a small amount of oxazetidine **5e**. However, *p*-nitronitrosobenzene did not react with **4** but was converted into *p*,*p'*-dinitroazobenzene.

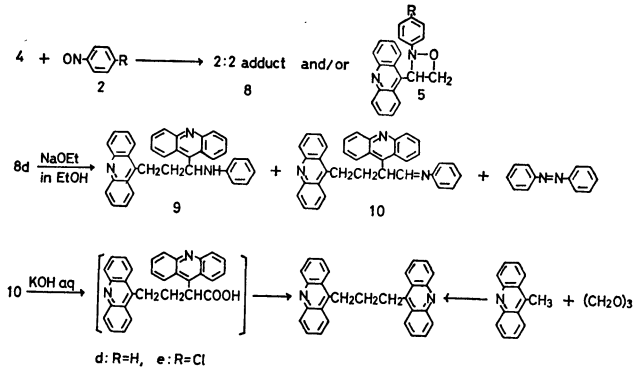
Although the formation of 1 : 2 adduct of styrene and trifluoronitrosomethane[5] and 1 : 2 adduct of styrene and nitrosobenzene[14] was observed in the reaction of styrene with the respective nitroso compound, formation of 2 : 2 adducts from olefin and nitroso compound has not been reported.

Although **8d** was stable against reduction with sodium borohydride and lithium aluminum hydride, its treatment with sodium ethoxide in ethanol afforded 1-anilino-1,3-di(9-acridinyl)propane (**9**) and 2,4-di-(9-acridinyl) butyraldehyde-*N*-phenylanil (**10**), accompanied by a trace amount of azobenzene. Structures of **9** and **10** were confirmed by their spectral data as well as by the results of microanalyses. **10** was hydrolyzed with aqueous potassium hydroxide to give 1,3-di(9-acridinyl)propane (**11**) *via* the carboxylic acid, which could not be isolated in a pure form; **11** was identified by comparison with an authentic sample prepared from the Mannich reaction of 9-methylacridine with paraformaldehyde (Scheme 4).

12) The reaction of *trans*-9-styryl- and *trans*-9-(*p*-nitrostyryl)-acridine with **2a** did not take place under various conditions.

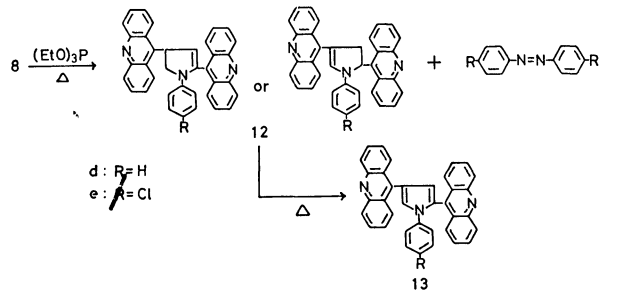
13) Formaldehyde in exhaust gas was identified by means of the fuchsin-sulfuric acid color test. It was reported that perfluoroxazetidine obtained from trifluoronitrosomethane and tetrafluoroethylene decomposed thermally to form perfluoromethylenemethylamine and carbonylfluoride.[4]

14) N. F. Hepfinger and C. E. Griffin, *Tetrahedron Lett.*, **1963**, 1361.



Scheme 4.

Contrary to oxazetidine **5**, 2 : 2 adducts **8d** and **8e** were stable in refluxing ethanol. Heating of **8d** in triethylphosphite for 10 hr afforded a new compound **12d**, mp 276—277°C, and azobenzene. On the basis of its spectral data and reaction with triethylphosphite, compound **12d** was assumed to be either 2,3-di(9-acridinyl)-1-phenyl-Δ^2- or -Δ^4-pyrroline. On heating with triethylphosphite, **12d** was converted into 2,3-di(9-acridinyl)-1-phenylpyrrole (**13d**), mp 280—281°C, whose structure was established by its spectral data. Similarly, treatment of **8e** with triethylphosphite gave the corresponding pyrroline **12e** and *p,p'*-dichloroazobenzene (Scheme 5).



Scheme 5.

The NMR spectrum of **8d** exhibited multiplets at δ 2.5 (2H, CH_2), 4.0 (2H, CH_2), 6.2 (2H, $\rightarrow$CH), and 6.7—9.5 ppm (26H, aromatic protons).

From the above NMR spectra and chemical conversions it is evident that the 2 : 2 adducts **8** have the moiety **B** in the molecule, while three types of arrangements **C**, **D**, and **E** are possible for the remainder of the adduct (Fig. 1). 1,2,3-Oxadiazolidin 3-oxide **F** and 1,2,5-oxadiazolidin 2-oxide **G** were proposed, respectively, for the 1 : 2 adducts of styrene with trifluoronitrosomethane[5] and with nitrosobenzene.[14] Structures **F** and **G** correspond to **E** and **C**, respectively.

The results of reduction and deoxygenation of **8** eliminate the possibility of a structure incorporating **E**. Thus, perhydro-1,2,7-oxadiazepin 1-oxide **8-1**, 7-oxide **8-2** (from **B** and **C**), and perhydropyridazine 1,2-dioxide **8-3** (from **B** and **D**) are possible structures for adducts **8**. From the spectral data it could not be decided which type of structure **8-1**—**8-3** would be most reasonable for **8**. However, perhydro-1,2,7-oxadiazepine structure **8-1** or **8-2** was assumed to be

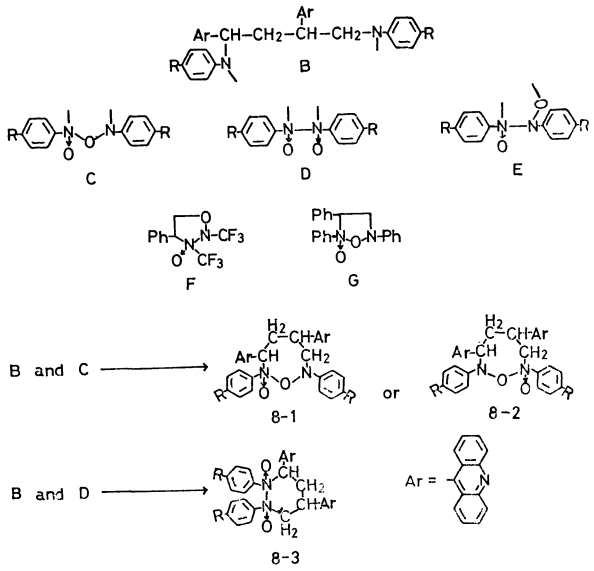


Fig. 1.

more reasonable than perhydropyridazine structure **8-3**, because pyrrole **13** was obtained on deoxygenation of **8** but no pyridazine. Furthermore, hydrolysis of **8d** with hydrochloric acid afforded the 1-(*p*-chlorophenyl)pyrroline compound **12e**; formation of **12e** seems to take place by the hydrolytic cleavage of –N–O– bond in the ring, followed by the Orton rearrangement. This seems to support the proposed structure **8-1** or **8-2** for **8**.

Experimental

All melting points are uncorrected. The IR spectra were measured as KBr pellets and the UV spectra were determined in ethanol solutions. The mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet and an ionization energy of 70 eV. The NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer, with TMS as an internal reference. The microanalyses were carried out by Miss M. Akita.

Materials. 1-(9-Acridinyl)-2-methylethylene (**1**)[15] (*cis*: mp 56—58°C; *trans*: mp 98—99°C); *trans*-9-styrylacridine,[16] mp 184—185°C; *trans*-9-(*p*-nitrostyryl)acridine,[16] mp 291—292°C, and 9-vinylacridine (**4**),[15] mp 87—88°C, were prepared by our previous methods.

Nitrosobenzenes were prepared by methods described in literature: *p*-nitroso-*N,N*-dimethylaniline (**2a**), mp 93—94 °C (lit,[17] mp 92—95°C); *p*-nitroso-*N,N*-diethylaniline (**2b**), mp 84—85°C (lit,[17] mp 84°C); *p*-methylnitrosobenzene (**2c**), mp 49°C (lit,[18] mp 48.5°C); nitrosobenzene (**2d**), mp 65—66°C (lit,[19] mp 64—67°C); *p*-chloronitrosobenzene (**2e**), mp 90—91°C (lit,[18] mp 89.5°C); *p*-nitronitrosobenzene, mp 118°C (lit,[20] mp 118°C).

15) O. Tsuge, A. Torii, and T. Tomita, *Nippon Kagaku Zasshi*, **90**, 1263 (1969).
16) O. Tsuge, T. Tomita, and A. Torii, *ibid.*, **89**, 1104 (1968).
17) H. E. Fiez-David and L. Blangey, "Grundlegends Operationen der Farbenchemie," Springer-Verlag (1943), p. 292.
18) E. Bamberger, *Ber.*, **28**, 247 (1895).
19) G.H. Coleman, C. M. McClosky, and F. A. Stuart, "Organic Syntheses," Coll. Vol. III, p. 668 (1961).
20) E. Bamberger and E. Huebner, *Ber.*, **36**, 3803 (1903).
21) HCl used in this paper: d^{27} 1.1748.

*Reaction of **1** with **2a**.* A typical reaction is as follows. To a solution of 1.0 g of **1** (*trans*) and 0.8 g of **2a** in 20 m*l* of ethanol was added 0.05 m*l* of HCl[21] at room temperature, and the reaction mixture was heated under reflux for 8 hr. After it was allowed to stand overnight, filtration gave reddish crystals which on recrystallization from ethanol afforded 0.16 g (15%) of acridine-9-carboxaldehyde-*N*-(*p*-*N*,*N*-dimethylaminophenyl)anil (**3a**), mp 249—250°C (lit.,[9] mp 248°C). The structure of **3a** was established by identification with an authentic sample.[9]

*Reaction of **4** with **2a**.* To a solution of 1.0 g of **4** and 0.8 g of **2a** in 20 m*l* of ethanol was added 0.1 m*l* of HCl. The reaction mixture was then stirred at room temperature for 1 hr. Filtration gave 0.6 g (35%) of 3-(9-acridinyl)-2-(*p*-*N*,*N*-dimethylaminophenyl)oxazetidine (**5a**), mp 156—157°C (decomp.), as violet prisms, which was subjected to microanalysis without further purification.

Found: C, 77.31; H, 5.93; N, 11.75%. Calcd for $C_{23}H_{21}N_3O$: C, 77.72; H, 5.96; N, 11.82%.

UV λ_{max} nm ($\log\varepsilon$): 253 (4.5), 537 (4.4).

The reaction of **4** with **2a** in refluxing ethanol gave anil **3a**. The effects of reaction conditions on yields of products are given in Table 1.

Table 1. Reaction of **4** with **2a**[a]

Run	Reaction conditions			Product, Yield (%)	
	2a/**4** (mol/mol)	Time (hr)	HCl (m*l*)	**3a**	**5a**
1	1	1	0.1	—	35
2	2	1	0.1	—	64
3	3	1	0.1	—	65
4	1	8	0.05	11	—
5	1	8	0.1	9	—
6	1	8	0.2	8	—
7	2	8	0.1	15	—
8	3	8	0.1	22	—

a) A mixture of 1.0 g of **4**, the specified amounts of **2a** and HCl in 20 m*l* of ethanol was stirred at room temperature (Runs 1-3) or under reflux (Runs 4-8).

*Reaction of **4** with **2b**.* One gram of **4** was reacted with 1.8 g of **2b** in the presence of 0.1 m*l* of HCl in 20 m*l* of ethanol at 0°C for 15 min to give 1.35 g (69%) of 3-(9-acridinyl)-2-(*p*-*N*,*N*-diethylaminophenyl)oxazetidine (**5b**) monohydrate, mp 112—113°C (decomp.), as violet prisms.

Found: C, 74.81; H, 6.73; N, 10.47%. Calcd for $C_{25}H_{25}N_3O\cdot H_2O$: C, 74.95; H, 7.07; N, 10.54%.

IR cm^{-1}: ν_{C-O-N} 1045. UV λ_{max} nm ($\log\varepsilon$): 253 (4.8), 539 (4.2). Mass spectrum *m/e*: 383 (M^+), 369 (M^+-CH_2), 367 (M^+-O), 365 (M^+-H_2O), 353 (M^+-CH_2O), 205 (M^+—**2b**).

Similarly, the reaction of 0.5 g of **4** with 0.6 g of **2c** in the presence of 0.05 m*l* of HCl in 10 m*l* of ethanol at 0°C for 2.5 hr gave 0.25 g (31%) of 3-(9-acridinyl)-2-(*p*-tolyl)oxazetidine (**5c**), mp 192—193°C (decomp.), as violet prisms.

Found: C, 80.60; H, 5.46; N, 8.54%. Calcd for $C_{22}H_{18}N_2O$: C, 80.98; H, 5.52; N, 8.59%.

IR cm^{-1}: ν_{C-N-O} 1045. UV λ_{max} nm ($\log\varepsilon$): 253 (4.8), 524 (4.4). Mass spectrum *m/e*: 326 (M^+), 312 (M^+-CH_2), 310 (M^+-O), 308 (M^+-H_2O), 296 (M^+-CH_2O), 205 (M^+—**2c**).

*Thermolysis of Oxazetidine **5**.* A solution of 2.0 g of **5b** in 20 m*l* of ethanol was refluxed for 8 hr, during which time evolution of formaldehyde was confirmed by means of fuchsin-sulfurous acid color test. The reaction mixture was concentrated *in vacuo* to leave a residue, which was then chromatographed on alumina using benzene as an eluent to obtain 0.42 g (23%) of anil **3b**, mp 168°C (lit,[9] mp 168—169 °C) and 0.4 g (15%) of 2,4-di(9-acridinyl)-1-(*p*-*N*,*N*-diethylaminophenyl)azetidine (**6b**), mp 295—296°C, as pale yellow prisms.

Found: C, 83.71; H, 5.94; N, 9.90%. Calcd for $C_{39}H_{34}N_4$: C, 83.84; H, 6.13; N, 10.03%.

UV λ_{max} nm ($\log\varepsilon$): 247 (4.8), 365 (3.9).

NMR (in $CDCl_3$) δ ppm: 1.15 (6H, triplet, $-CH_2-CH_3$), 3.0—3.6 (6H, multiplet, CH_2), 6.7—8.55 (22H, complicated, aromatic (20H) and two methine protons).

Mass spectrum *m/e*: 558 (M^+).

Similarly, heating of **5a** or **5c** in ethanol afforded anil **3a** (22%) and azetidine **6a** (32%), or anil **3c** (22%), mp 180—181°C (lit,[22] mp 182—183°C), respectively.

Azetidine **6a**: mp 294—295°C, yellow needles.

Found: C, 84.02; H, 5.51; N, 10.63%. Calcd for $C_{37}H_{30}N_4$: C, 83.74; H, 5.70; N, 10.56%.

UV λ_{max} nm ($\log\varepsilon$): 247 (4.7), 362 (3.7). Mass spectrum *m/e*: 530 (M^+).

*Reduction of **5a** with Sodium Borohydride.* A solution of 1.3 g of **5a** in 16 m*l* of ethanol-dioxane mixture (1 : 1) was stirred with 0.5 g of sodium borohydride at room temperature for 1.5 hr. To the reaction mixture was added 50 m*l* of water. The resulting solution was then extracted with 100 m*l* of diethyl ether. The extract was dried over anhydrous sodium sulfate and then evaporated to leave a reddish oily residue. The residue was chromatographed on alumina using benzene as an eluent to obtain 0.56 g (58%) of 1-(9-acridinyl)-2-(*p*-*N*,*N*-dimethylanilino)ethane (**7**), which on recrystallization from petroleum ether (bp 45—60°C) gave orange prisms, mp 131—132°C.

Found: C, 80.79; H, 6.81; N, 12.03%. Calcd for $C_{22}H_{23}N_3$: C, 80.90; H, 6.79; N, 12.31%. IR cm^{-1}: ν_{NH} 3280.

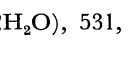
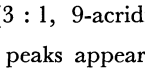
NMR (in $CDCl_3$) δ ppm: 2.8 (6H, singlet, $N(CH_3)_2$), 3.5 (2H, triplet, CH_2, J=6 Hz), 3.8 (2H, triplet, CH_2, J= 6 Hz), 3.55 (1H, singlet, NH), 6.6—8.4 (21H, multiplet, aromatic protons).

Mass spectrum *m/e*: 341 (M^+).

*Reaction of **4** with **2e**.* A solution of 1.0 g of **4** and 1.4 g of **2e** in 20 m*l* of ethanol containing 0.1 m*l* of HCl was stirred at room temperature for 24 hr. Filtration gave 0.31 g (18%) of 2 : 2 adduct **8e**, which on recrystallization from chloroform afforded pale yellow prisms, mp 212—213°C (decomp.).

Found: C, 72.80; H, 4.18; N, 7.93%. Calcd for $C_{42}H_{30}N_4O_2Cl_2$: C, 72.54; H, 4.32; N, 8.08%.

UV λ_{max} nm ($\log\varepsilon$): 253 (4.2), 520 (4.1).

The mass spectrum of **8e** did not show a parent peak (M^+), but major fragment peaks at *m/e* 656, 658, 660 (9 : 6 : 1, M^+-2H_2O), 531, 533 (M^+-2H_2O- Cl-  -N), 316, 318 (3 : 1, 9-acridinyl-CH=N-  -Cl^+), 315, 317, and other peaks appeared in the spectrum.

The filtrate was evaporated *in vacuo* to leave a residue, which was chromatographed on alumina using chloroform as an eluent to give 10 mg of oxazetidine **5e**, mp 191°C (decomp.), as violet prisms, together with a large amount of tar.

Found: C, 72.66; H, 4.33; N, 8.00%. Calcd for $C_{21}H_{15}N_2OCl$: C, 72.54; H, 4.32; N, 8.08%.

Mass spectrum *m/e*: 346, 348 (3 : 1, M^+), 330, 332 (M^+-O), 316, 318 (M^+-CH_2O).

22) N. S. Drozdov and E. V. Yavorskaya, *Zh. Obshch. Khim.*, **30**, 3421 (1960).

Similarly, the reaction of 1.0 g of **4** with 1.2 g of **2d** in 20 m*l* of ethanol containing 0.1 m*l* of HCl afforded 0.3 g (20%) of 2 : 2 adduct **8d**, mp 172—173°C, as pale yellow prisms.

Found: C, 81.03; H, 5.09; N, 8.90%. Calcd for $C_{42}H_{32}N_4O_2$: C, 80.76; H, 5.12; N, 8.97%.

Mass spectrum *m/e*: 588 (M^+-2H_2O), 497 (M^+-2H_2O-PhN), 282 (9-acridinyl-CH=N-Ph^+), 281.

Reduction of ***8d*** *with Sodium Ethoxide.* A solution of 3.0 g of **8d** in 20 m*l* of ethanol was stirred with 0.5 g of sodium at room temperature for 12 hr. Filtration afforded 0.4 g (23%) of 2,4-di(9-acridinyl)butyraldehyde-*N*-phenylanil (**10**), which on recrystallization from pyridine gave yellow prisms, mp 296—297°C.

Found: C, 85.66; H, 5.27; N, 9.13%. Calcd for $C_{36}H_{27}N_3\cdot 1/2C_5H_5N$: C, 85.55; H, 5.48; N, 8.95%. IR cm^{-1}: $\nu_{C=N}$ 1660.

NMR (in CF_3COOH) δ ppm: 3.5, 5.6 (each 2H, multiplet, CH_2), 7.3—8.8 (23H, multiplet, aromatic (21H) and two methine protons).

Mass spectrum *m/e*: 501 (M^+), 309 (M^+—9-acridinylmethyl, base peak), 295 (9-acridinyl-$\overset{+}{C}$HCH=NPh), 206 (9-acridinyl-$CH_2CH_2^+$).

The filtrate was concentrated *in vacuo* to leave a residue, which was chromatographed on alumina using benzene as an eluent to give 10 mg of azobenzene and 0.25 g (11%) of 1-anilino-1,3-di(9-acridinyl)propane (**9**). Recrystallization of **9** from pyridine afforded yellow prisms, mp 214—215°C.

Found: C, 85.79; H, 5.28; N, 8.76%. Calcd for $C_{35}H_{27}N_3$: C, 85.86; H, 5.56; N, 8.58%. IR cm^{-1}: ν_{NH} 3280.

NMR (in $CDCl_3$) δ ppm: 2.9, 3.5 (each 2H, multiplet, CH_2), 4.5 (1H, multiplet, NH), 6.0 (1H, multiplet, $\rangle$CH), 6.5—8.7 (21H, multiplet, aromatic protons).

Mass spectrum *m/e*: 489 (M^+), 397 (M^+—PhNH), 297 (M^+—9-acridinyl-CH_2^+), 283 (9-acridinyl-CH=$\overset{+}{N}$HPh, base peak), 206 (9-acridinyl-$CH_2CH_2^+$).

Hydrolysis of ***10***. After 0.1 g of **10** in 4 m*l* of ethanol–concentrated potassium oxide aqueous solution (1 : 1) was stirred at 90°C for 30 min, filtration afforded 70 mg of crystals. The crystals were washed with diethyl ether to leave 60 mg (75%) of yellow crystals, which on recrystallization from benzene gave 1,3-di(9-acridinyl)propane (**11**), mp 201—202°C, as yellow prisms.

Found: C, 87.70; H, 5.53; N, 7.03%. Calcd for $C_{29}H_{22}N_2$: C, 87.40; H, 5.57; N, 7.03%. Mass spectrum *m/e* 398 (M^+).

NMR spectrum (in CF_3COOH) δ ppm: 2.7 (2H, multiplet, CH_2), 4.5 (4H, multiplet, CH_2), 7.9—8.9 (16H, multiplet, aromatic protons).

The ether-washings were concentrated to give a trace amount of pale yellow crystals, whose IR spectrum showed the bands ascribable to ν_{OH} and $\nu_{C=O}$ at 3400 and 1700 cm^{-1}, respectively. However, the carboxylic acid could not be isolated in pure state.

Preparation of ***11***. A mixture of 3.0 g of 9-methylacridine, 0.5 g of paraformaldehyde and 1.5 g of dimethylamine hydrochloride in 25 m*l* of ethanol was refluxed for 2 hr. The reaction mixture was neutralized with aqueous sodium hydroxide to give brown oily substance, which solidified on trituration with diethyl ether. The solid was recrystallized from benzene to afford 0.75 g (72%) of **11**. mp 201—202°C.

Reaction of ***8d*** *with Triethylphosphite.* A solution of 1.0 g of **8d** in 5 m*l* of triethylphosphite was refluxed for 10 hr. The reaction mixture was concentrated *in vacuo* and the residue was allowed to stand overnight to give 0.25 g (32%) of 2,3-di(9-acridinyl)-1-phenylpyrroline (**12d**), which on recrystallization from benzene afforded orange prisms, mp 276—277°C.

Found: C, 86.79; H, 4.91; N, 8.08%. Calcd for $C_{36}H_{25}N_3$: C, 86.54; H, 5.04; N, 8.41%.

NMR (in CF_3COOH) δ ppm: 4.7 (2H, multiplet, CH_2), 7.0—9.3 (23H, multiplet, aromatic (21H), $\rangle$CH and =CH).

Mass spectrum *m/e*: 499 (M^+), 497 (M^+-H_2, base peak), 422 (M^+—Ph), 420, 406 (497^+—PhN), 393 (497^+—PhN=CH), 312 (M^+—9-acridinyl), 295 (M^+—9-acridinyl-CH=CH), 281 (9-acridinyl-C≡$\overset{+}{N}$Ph), 205 (9-acridinyl-CH=CH_2^+), 204.

The filtrate was further concentrated to leave a residue, which was chromatographed on alumina using chloroform as an eluent to give 0.1 g of azobenzene and tar.

Similarly, treatment of 0.5 g of **8e** with 3 m*l* of triethylphosphite yielded 0.12 g (38.5%) of pyrroline **12e**, mp 292—293°C, as orange prisms and a small amount of *p,p'*-dichloroazobenzene, mp 189°C (lit,[23] mp 187°C).

Found: C, 81.07; H, 4.19; N, 7.65%. Calcd for $C_{36}H_{24}N_3Cl$: C, 80.79; H, 4.49; N, 7.87%.

Mass spectrum *m/e*: 533, 535 (3 : 1, M^+).

Hydrolysis of ***8d***. A solution of 0.5 g of **8d** in 10 m*l* of 20% aqueous hydrochloric acid was stirred at 90°C for 10 min. The reaction mixture had been cooled and neutralized with ammonium hydroxide to precipitate crystals. Recrystallization from benzene afforded 0.17 g (40%) of **12e**, mp 292—293°C.

*2,3-Di(9-acridinyl)-1-phenylpyrrole (****13d****).* A solution of 0.5 g of pyrroline **12d** in 3 m*l* of triethylphosphite was refluxed for 15 hr. The reaction mixture was concentrated *in vacuo* to give 0.3 g (60%) of crystals. Recrystallization from benzene afforded **13d**, mp 280—281°C, as orange yellow prisms. The pine reaction color test of **13d** was positive.

Found: C, 86.90; H, 4.46; N, 8.26%. Calcd for $C_{36}H_{23}N_3$: C, 86.92; H, 4.62; N, 8.45%. Mass spectrum *m/e*: 497 (M^+). NMR (in CF_3COOH) δ ppm: 7.3—9.1 (multiplet, aromatic protons).

23) E. Bamberger, *Ann. Chem.*, **382**, 95 (1911).