Syntheses and Reactions of Enamines from 9-Formylfluorene

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(Received July 12, 1989)

Abstract

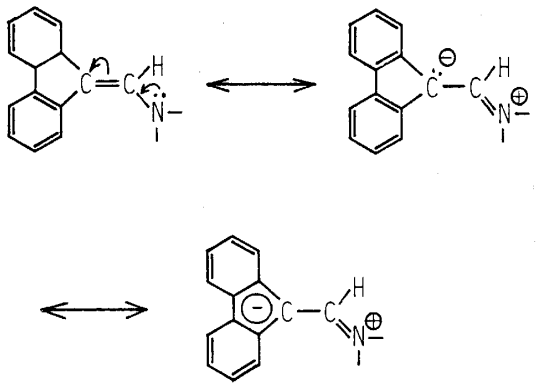
Many enamines **3** from 9-formylfluorene (**1**) were easily prepared by the reaction of **1** with several aliphatic, aromatic, alicyclic and heterocyclic secondary amines **2** in aqueous ethanol at room temperature.

The reaction of 9-morpholinomethylenefluorene (**3i**), a typical **3**, with bromine in dichloroethane gave the corresponding iminium bromide (**4**). The hydrolysis of **4** with water afforded 9-bromo-9-formylfluorene (**6**). 2,2-Biphenylene-1,1-dialkoxyethylene **10** was obtained from 9-bromo-9-formylfluorene dialkyl acetal which was derived from **6** with alkyl orthoformate in alcohols under acidic conditions. Compound **10** was also obtained from **4** via 2,2-biphenylene-1,1-dialkoxy-1-morpholinoethane. Furthermore, the reactions of **3i** with ethyl azidoformate and with *p*-toluenesulfonyl azide were investigated.

1. Introduction

Since stock et al. [1] reported in 1954 that the alkylation and acetylation of carbonyl compornds were carried out via enamine, the reactivities of the enamines have been payed attention, and many studies about the enamines have been undertaken until recent years[2].

However, the investigations on the enamines **3** from 9-formylfluorene (**1**) have scarcely carried out, so far as we know. In the case of the enamines **3**, lone pair on the nitrogen atom can be conjugated with fluorene nucleus by the manner as shown in



Scheme 1

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Scheme 1. Thus, the enamines **3** will be stabilized by delocalization of the partial negative charge on β-carbon atom. Accordingly, the chemical behaviors of **3** will be different from that of usual enamines. In this paper, we wish to report on the syntheses and reactions of **3**.

2. Results and Discussion

2-1 Syneheses of 3

A mixture of 1-equiv of **1** and 2-equiv of secondary amines **2** in C_2H_5OH-H_2O (2 : 1 v/v) was allowed to stand for 10 min at room temperature, and then the solvent was decanted and the residue was heated in 95% ethanol for 0.5-1 h. Derivatives **3** except 9-aminomethylenefluorene (**3a**) and 9-(*N*,*N*-dimethylaminomethylene)-fluorene (**3b**) were easily synthesized by this method. The results are shown in Table 1.

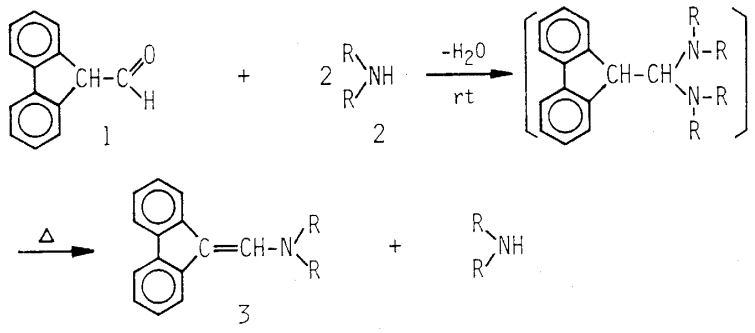
According to the method of Von and Wagner[3], the compounds **3a** and **3b** were

Table 1 Syntheses of Enamines (**3**) from 9-Formylfluorene (**1**) and Secondary Amines (**2**)

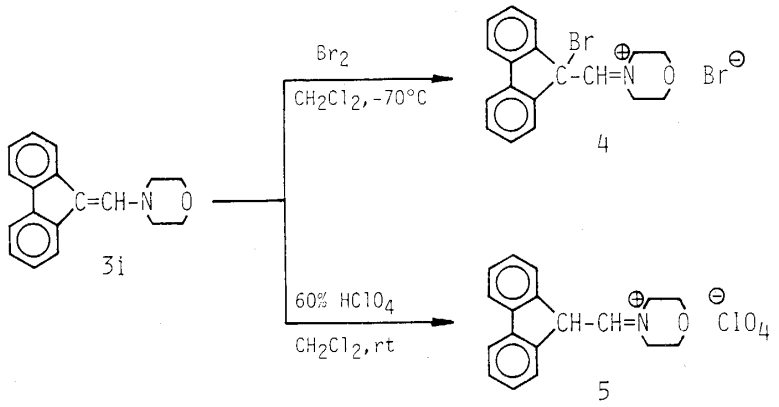
Enamines (3)	2 R	Solvent	Yield (%)	MP (℃) or Bp (℃/mmHg)
3 a[4)a)]	2 H	$C_2H_5OC_2H_5$	51	146-147
3 a[a)]	2 CH_3	$C_2H_5OC_2H_5$	70	72-73
3 c	2 C_2H_5	C_2H_5OH-H_2O (2 : 1)	55	140-142/0.19
3 d	2 CH_2CH_2OH	C_2H_5OH-H_2O (2 : 1)	69	112-114/0.17
3 e	2 C_6H_{11}	C_2H_5OH-H_2O (2 : 1)	47	132-134
3 f	2 Ph	C_2H_5OH-H_2O (2 : 1)	50	139-140
3 g		C_2H_5OH-H_2O (2 : 1)	60	74-75
3 h		$C_2H_5OC_2H_5$[b)] / C_2H_5OH-H_2O (2 : 1)	60 / 75	110-111
3 i		C_2H_5OH-H_2O	85	169-170
3 j		C_2H_5OH-H_2O (2 : 1)	15	129-131

a) Compounds **3 a** and **3 b** were synthesized by the method of Von and Wagner.[3]

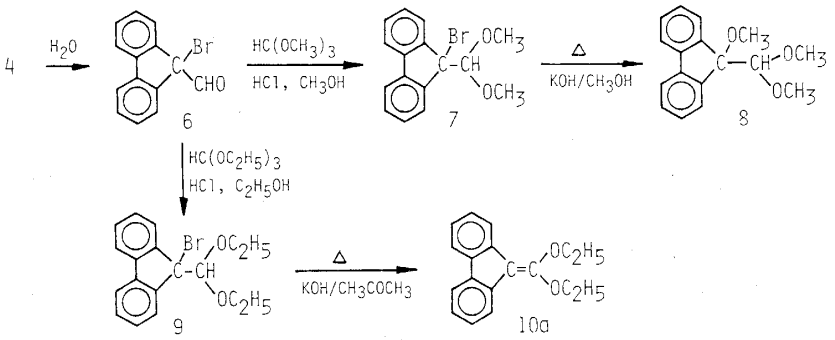
b) Compound **3 h** was prepared by the method of Mannich and Davidsen in ether.[4]



Scheme 2



Scheme 3



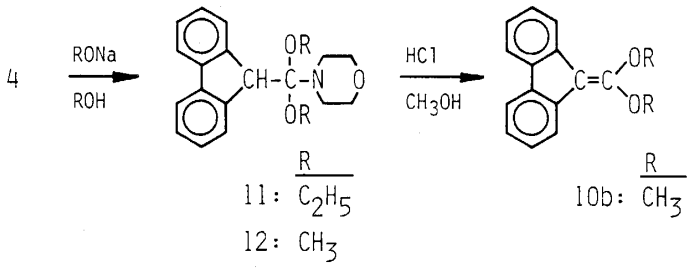
Scheme 4

prepared by bubbling a dry ammonia gas and dimethylamine gas in the solution of **1** in ether, respectively. The compound **3b** was also prepared by use of aqueous dimethylamine (40%) instead of gaseous dimethylamine.

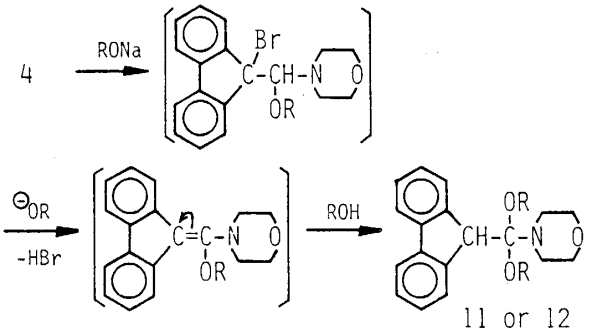
2-2 Reactions of 3

2-2-1 Syntheses and Reactions of Iminium Salts of 3

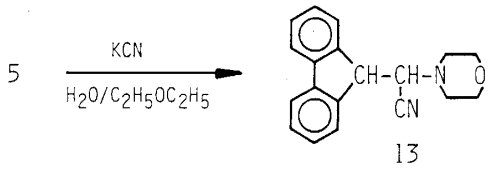
The reactions of 9-morpholinomethylenefluorene (**3i**) with bromine in dichloromethane at -70℃ gave *N*-(9-bromo-9-fluorenylmethylene)morpholinium bromide (**4**), and with 60% perchloric acid in dichloromethane at room temperature gave *N*-(9-fluorenylmethylene)morpholinium perchlorate (**5**), in quantitative yields, respectively.



Scheme 5



Scheme 6

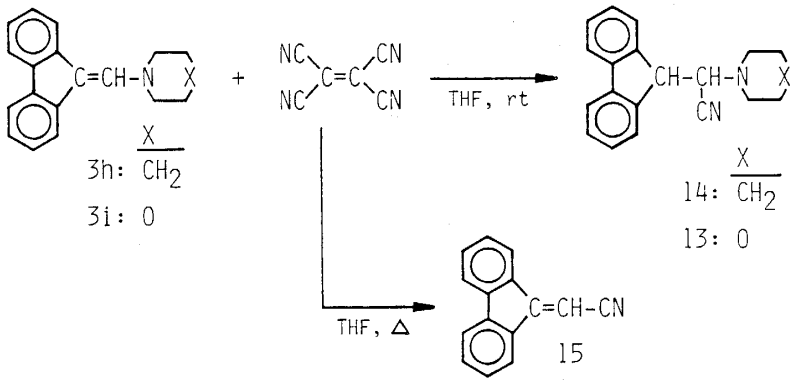


Scheme 7

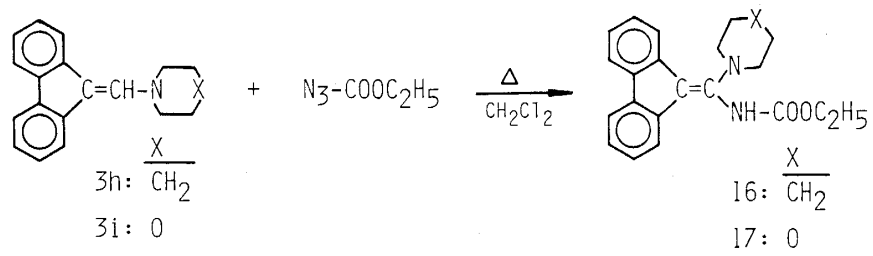
The hydrolysis of **4** with water gave 9-bromo-9-formylfluorene (**6**) in good yield. The reaction of **6** with methyl orthoformate in methanol under acidic conditions gave 9-bromo-9-formylfluorene dimethyl acetal (**7**), and with ethyl orthoformate in ethanol-HCl solution gave 9-bromo-9-formylfluorene diethyl acetal (**9**), respectively. Although the reaction of **7** with methanolic KOH gave 9-formyl-9-methoxyfluorene dimethyl acetal (**8**), the reaction of **9** with aq KOH in acetone gave 2,2-biphenylene-1,1-diethoxyethylene (**10a**) as a dehydrobromination product of **9**.

The treatment of **4** with sodium methoxide in methanol and with sodium ethoxide in ethanol afforded 2,2-biphenylene-1,1-dimethoxy-1-morphlinoethane (**12**) and 2,2-biphenylene-1,1-diethoxy-1-morpholinoethane (**11**), respectively. Compound **12** was also converted into 2,2-biphenylene-1,1-dimethoxyethylene (**10b**) by treatment with aq HCl in methanol.

The reaction mechanism which leads **11** or **12** from **4** can be explain as shown in



Scheme 8



Scheme 9

Scheme 6.

By the way, the reaction of **5** with aq KCN in ether gave quantitatively 2,2-biphenylene-1-cyano-1-morpholinoethane (**13**).

2-2-2 Reactions of 3 with Tetracyanoethylene (TCNE)

Otherwise, the reactions of **3h** and **3i** with TCNE (a strong electrophilc olefin) in THF at room temperature for 24 h gave 2,2-biphenylene-1-cyano-1-piperidinoethane (**14**) and **13**, respectively, instead of an expected cyclobutane products. Furthermore, the reaction of **3i** with TCNE in THF under reflux for 10 h gave 9-cyanomethylenefluorene (15). The above reaction mechanism has not been elucidated clearly.

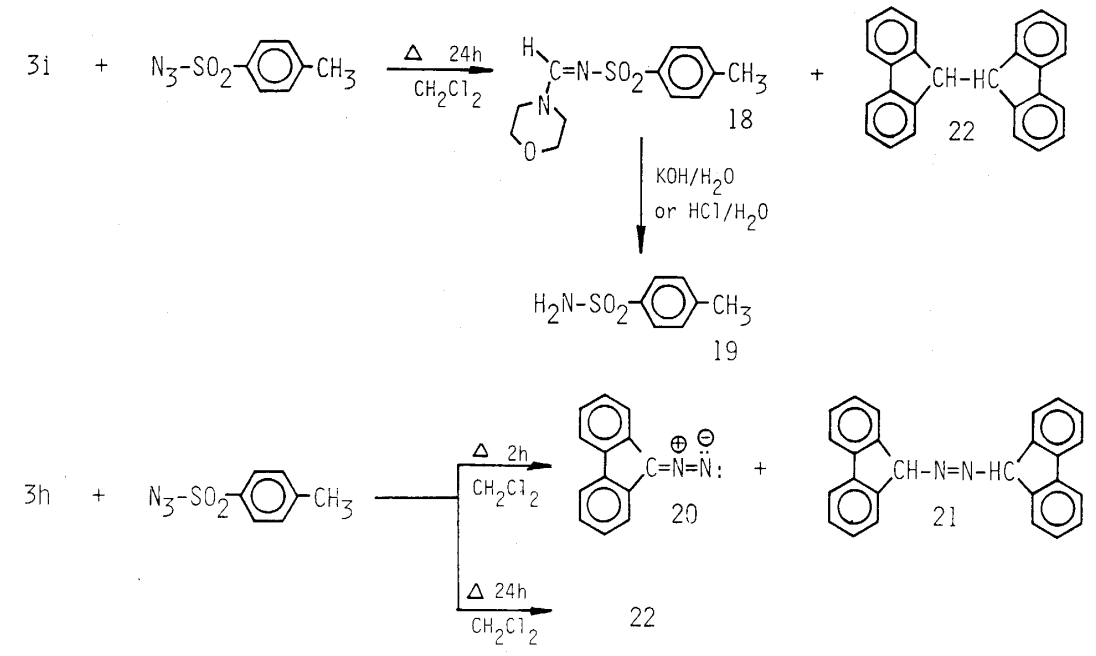
From the results which the reaction of 3 with TCNE gave no addition products, it can be noticed that the enamines **3** should be stabilized by delocalization of the partial negative charge on β-carbon atom, and should be inhibited the addition of TCNE owing to their bulky structures having fluorene and secondary amine moieties.

2-2-3 Reactions of 3 with Ethyl Azidoformate and p-Toluene-sulfonyl Azide

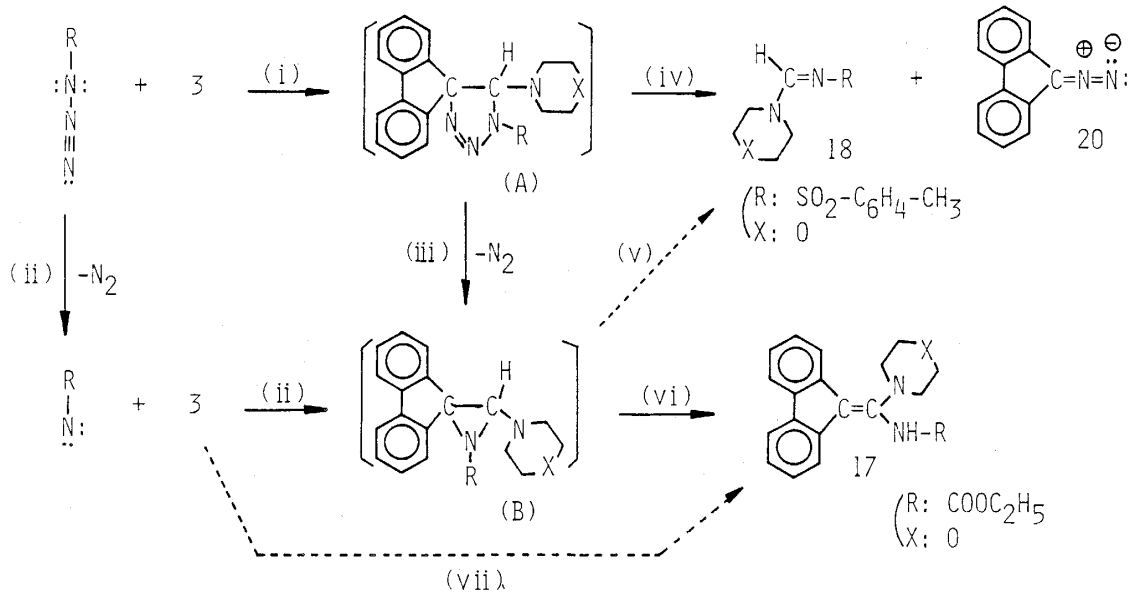
The reactions of enamines with azides have been investigated by several workers[5-7], and in many cases, triazoline derivatives have been isolated as an intermediate. However, there are no reports on the reactions of **3** with azides such as ethyl azidoformate and p-toluenesulfonyl azide as far as we know.

The reactions of **3h** and **3i** with ethyl azidoformate in dichloromethane under reflux for 48h gave, 2,2-biphenylene-1-piperidinoethyl carbamate (**16**) and 2,2-biphenylene-1-morpholinoethyl carbamate (**17**), respectively.

These products **16** and **17** are an insertion product of nitrene N-COOEt into C-H



Scheme 10



Scheme 11

bond of **3**, as a matter of form.

The reaction of **3** i with *p*-toluenesulfonyl azide in dichloromethane under reflux for 24 h or under cooling with ice-bath for 12 h gave both *N*-(morpholinomethylene)-*p*-toluenesulfonamide (**18**). Hydrolysis of **18** was carried out with aq KOH or aq HCl to give *p*-toluenesulfonamide (**19**). On the other hand, the reaction of **3h** with *p*-toluenesulfonyl azide in dichloromethane under reflux for 2 h afforded 9-diazofluorene (**20**) and 9,9′-bifluorenyl (**22**), respectively.

From these experimental results, it can be prosumed that there are several routes

in these reaction processes as shown in Scheme 11. That is, the first route is a path from (i) to (iv) which involves a triazoline intermediate (**A**). The second route is a path from (ii) to (vi) via an aziridine intermediate (**B**). The third route is a path (i) to (Vi) via B. Paths (v) and (vii) can be considered also. However, it is difficult to determine the appropriate routes for these reactions because the intermediates **A** and **B** are not isolated.

3. Experimental

All the melting points are uncorrected. ^{1}H NMR spectra were recorded on a JEOL-MH-100 spectrometer. The IR spectra were measured on a JASO IRA-1 spectrometer.

3-1-1 9-Morpholinomethylenefluorene (3i) ; Tipical Procedure :

To a solution of freshly distilled **1** (31.2 g, 0.16 mol) in ethanol-water (2 : 1 v/v, 450 ml) was added morpholine (27.8 g, 0.32 mol) at room temperature. The mixture was heated for 20 min at 60℃. The reddish oil obtained was decanted and heated in 95% ethanol until the yellow solid was obtained. The solid precipitation was recrystallized from ethanol to give **3i** as yellow crystals ; yield 33 g (85%) ; mp 169-170℃. IR (nujol) : 1620 cm^{-1} (C=C) ; ^{1}H NMR ($CDCl_3$) δ=3.4-3.6 (4H, m, CH_2NCH_2), 3.84-4.04 (4H, m, CH_2OCH_2), 7.24-8.0 (9H, m, =CH and $H_{arom.}$). Found : C, 81.82 ; H, 6.32 ; N, 4.90%. Calcd for $C_{18}H_{17}ON$: C, 82.09 ; H, 6.50 ; N, 5.31%.

9-(N,N-Diethylaminomethylene) fluorene (3c).

Colorless liqued ; IR (neat) : 1620 cm^{-1} (C=C) ; ^{1}H NMR ($CDCl_3$) δ=1.30 (6H, t, j= 7 Hz, $2CH_3$), 3.54 (4H, q, $2CH_2$), 7.2-7.96 (9H, m, =CH and $H_{arom.}$).

9-(N,N-Diethanolaminomethylene) fluorene (3d).

Colorless liquid ; IR (neat) : 1650 cm^{-1} (C=C) ; ^{1}H NMR (CCl_4) δ=2.60-3.24 (4H, m, CH_2NCH_2), 3.6-3.8 (4H, m, CH_2OH), 3.80 (2H, s, 2OH), 7.08-7.76 (9H, m, =CH and $H_{arom.}$).

9-(N,N-Dicyclohexylaminomethylene) fluorene (3e).

Yellow crystals ; IR (unjol) : 1610 cm^{-1} (C=C) ; ^{1}H NMR ($CDCl_3$) δ=0.9-2.1 (20 H, m, $2NCH(CH_2)_5$), 2.4-2.9 (2H, m, 2CH), 7.2-8.2 (9H, m, =CH and $H_{arom.}$).

9-(N,N-Diphenylaminomethylene) fluorene (3f)

Yellow crystals ; IR (nujol) : 1620 cm^{-1} (C=C) ; ^{1}H NMR ($CDCl_3$) δ=6.48-7.8 (19 H, m, =CH and $H_{arom.}$).

9-Pyrrolidinomethylenefluorene (3q).

Yellow crystals ; IR (nujol) : 1610 cm^{-1} (C=C) ; ^{1}H NMR ($CDCl_3$) δ=1.84-2.04 (4H, m, CH_2CH_2), 3.56-3.78 (4H, m, CH_2NCH_2), 7.2-8.0 (9H, m, =CH and $H_{arom.}$). Found : C, 87.53 ; H, 6.71 ; N, 5.92%. Calcd for $C_{18}H_{17}N$: C, 87.40 ; H, 6.92 ; N, 5.66%.

9-Piperazinomethylenefluorene (3j).

Yellow crystals ; IR (nujol) : 1620 cm^{-1} (C=C).

3-1-2 9-Aminomethylenefluorene[4] (3a).

Procedure by the method of Von et al.[3] is described as follows : Into a 40% solution of freshly distilled **1** (9.2 g, 47 mmol) in ether and dioxane was bubbled dry ammonia

gas under ice-bath cooling. The mixture was stirred for 1 h and concentrated in vacuo, leaving a residue which was extracted with hot benzene. The benzene solution was chilled to give **3a** as colorless crystals ; yield 4.7 g (51%) ; mp 146-147℃ (from cyclohexane-benzene). IR (nujol) : 3500 cm^{-1}, 3400 (NH_2), 1640 (C=C) ; ^1H NMR ($CDCl_3$) δ=4.84 (2H, br.s, NH_2), 7.5-8.3 (9 H, m, =CH and $H_{arom.}$).

9-(*N*,*N*-Dimethylaminomethylene)fluorene (3b).

Colorless crystals ; IR (nujol) : 1620 cm^{-1} (C=C) ; ^1H NMR ($CDCl_3$) δ=3.18 (6 H, s, $2CH_3$), 7.1-7.9 (9 H, m, =CH and $H_{arom.}$).

3-1-3 9-Piperidinomethylenefluorene (3h).

Procedure by the method of Monnich et al.[4] is described as follows : To a solution of freshly distilled **1** (8.3 g, 46 mmol) in dry ether (60 ml) was added piperidine (7.8 g, 92 mmol) at 4℃. After stirring for 1.5 h in an ice-bath, the mixure was heated under reflux for 2h. The reaction mixture was concentrated in vacuo, leaving a residue which was recrystallized from cyclohexane to give **3h** as orange crystals ; yield : 6.7 g (60%) ; mp 110-111℃. IR (nujol) : 1620 cm^{-1} (C=C) ; ^1H NMR ($CDCl_3$) δ=1.60 (6 H, br.s, $CH_2CH_2CH_2$), 3.29 (4 H, br.s, CH_2NCH_2), 7.24-8.0 (9 H, m, =CH and $H_{arom.}$). Found : C, 87.31 ; H, 7.32 ; N, 5.35%. Calcd for $C_{19}H_{19}N$: C, 87.07 ; H, 7.59 ; N, 5.46%.

3-2-1 Reaction of 3i with Bromine.

To a solution of **3i** (2.6 g, 0.01 mol) in dichloromethane (70 ml) was added dropwise a solution of bromine (1.6 g, 0.01 mol) in dichloromethane (20 ml) at-70℃ over 20 min. After the addition of all bromine, the mixture was allowed to stand at room temperature. The reaction mixture was concentrated in vacuo to give *N*-(9-bromo-9-fluorenylmethylene)morpholinium bromide (**4**) as orange powder ; yield 4.8 g (98%). IR (nujol) : 1610 cm^{-1} (C=N) ; ^1H NMR ($CDCl_3$) δ=2.54-2.76 (4 H, m, CH_2NCH_2), 3.60-3.80 (4 H, m, CH_2OCH_2), 4.80 (1 H, s, CH), 7.7-7.1 (8 H, m, $H_{arom.}$).

3-2-2 Reaction of 3i with 60% $HClO_4$.

To a solution of **3i** (5.2 g, 0.03) in dichloromethane (100 ml) was added dropwise perchlorc acid (60%, 4.95 g, 0.04 mol) at room temperature. The solution was stirred for 1 h at same temperature to give *N*-(9-fluorenylmethylene) morpholinium perchlorate (**5**) as white powder ; yield 7 g (98%) ; mp 205-210℃ (dec.). IR (nujol) : 1660 cm^{-1} (C=N), 1100 (ClO_4).

3-2-3 Hydrolysis of 4.

To a fresh solution of **4** (4.8 g, 0.01 mol) in dichloromethane (90 ml) was added cold water (100 ml) at - 5℃, and the mixure was stirred vigorously 5 h. The orange layer was separated, washed twice with water and dried with $MgSO_4$. The solution was concentrated in vacuo, leaving 9-bromo-9-formylfluorene (**6**) as yellow oil ; yield 2.5 g (96%) ; bp 95 C/0.25 mmHg (dec.). IR (neat) : 1720 cm^{-1} (C=O) ; ^1H NMR (CCl_4) δ=7.0-7.5 (8 H, m, $H_{arom.}$), 9.14 (1 H, s, CHO).

3-2-4 Dialkoxylation of 4 ; Synthesis of Dimethyl Acetal and Diethyl Acetal :

a) To a solution of **6** (5 g, 0.028 mol) in methanol (25 ml) was added methyl orthoformate and conc. HCl (0.2 ml). The mixture was refluxed for 10 min and cooled quickly. The crude product was precipitated and recrystallized from methanol to give 9-bromo-9-formylfluorene dimethyl acetal (**7**); yield 4.2 g (71%); mp 131-133℃. IR (nujol): 1110 cm^{-1}, 1060 (COC); ^1H NMR ($CDCl_3$) δ=3.38 (6H, s, $2CH_3$), 4.56 (1H, s, CH), 7.2-7.8 (8H, m, $H_{arom.}$).

b) To a solution of **6** (9 g, 0.033 mol) in ethanol was treated with ethyl orthoformate (14.8 g, 0.1 mol) and conc. HCl (0.2 ml). The mixture was worked up as described for the preparation of **7** to give 9-bromo-9-formylfluorene diethyl acetal (**9**); yield 7.5 g (66%); mp 136-138℃. IR (nujol): 1115cm^{-1}, 1100, 1050 (COC); ^1H NMR ($CDCl_3$) δ=1.07 (6H, t, J= 7 Hz, $2CH_3$), 3.2-3.7 (4H, m, $2CH_2$), 4.55 (1H s, CH), 6.95-7.6 (8H, m, $H_{arom.}$).

3-2-5 Reaction of 7 with KOH-CH_3OH

To a solution of **7** (1.6 g, 5 mmol) in methanol (60 ml) was added KOH (1 g), and the mixture was refluxed for 8h. The reaction mixture was poured into water (100 ml) and extracted with ether. The ether solution was dried with $MgSO_4$ and concentrated in vacuo, leaving a residue which was chromatographed on alumina using benzene as eluent to give 9-formyl-9-methoxyfluorene (**8**) as yellow oil; yield 1.0 g (74%). IR (neat): 1100 cm^{-1}, 1075 (COC); ^1H NMR ($CDCl_3$) δ=2.78 (3H, s, OCH_3), 3.26 (6H, s, $CH(OCH_3)_2$), 4.46 (1H, s, CH), 7.1-7.6 (8H, m, $H_{arom.}$).

3-2-6- Dehydrobromination of 9 with KOH-CH_3COCH_3.

To a solution of **9** (1.6 g, 5 mmol) in acetone (30 ml) was added aq KOH (0.56 g/H_2O 4 ml), and the mixure was refluxed for 5h. The reaction mixture was worked up as described for the preparation of **8** to give 2,2-biphenylene-1,1-diethoxyethylene (**10a**) as yellow oil; yield 0.8 g (60%). IR (neat): 1650 cm^{-1} (C=C), 1190, 1100, 1070 (COC); ^1H NMR (CCl_4) δ=1.36 (6H, t, J=6Hz, $2CH_3$), 3.84-4.10 (4H, m, $2CH_2$), 7.0-7.9 (8H, m, $H_{arom.}$).

3-2-7 Reaction of 4 with base; Synthesis of 2,2-biphenylene-1,1-dialkoxy-1-morpholinoethane (11 and 12).

a) To a solution of **4** (11.5 g, 27 mmol) in abs. ethanol (40 ml) was added sodium ethoxide (6.8 g, 0.1 mol) under a N_2 atmosphere, and the mixture was refluxed for 2 h. The reaction mixture was concentrated in vacuo and extracted with ether, and washed with water. The ether solution was dried with $MgSO_4$ and concentrated leaving a residue which was chromatographed on alumina using benzene-petroleum benzine (1 : 1) as eluent to give 2,2-biphenylene-1-diethoxy-1-morpholinoethane (**11**) as colorless crystals; yield 4.4 g (46%); mp 93-95℃. IR (nujol): 1120 cm^{-1}, 1100, 1060 (COC); ^1H NMR ($CDCl_3$) δ=1.00 (6H, t, J= 6 Hz, $2CH_3$), 2.5-2.7 (4H, m, CH_2NCH_2), 3.28 (4H, q, $2CH_2$), 3.6-3.8 (4H, m, CH_2OCH_2), 3.72 (1H, s, CH), 7.2-7.72 (8H, m, $H_{arom.}$).

b) To a solution of **4** (8.7 g, 0.02 mol) in abs. methanol (40 ml) was added sodium methoxide (5.4 g, 0.1 mol) under a N_2 atmosphere, and the mixture was refluxed for 2h. The reaction mixture was worked up as described for the preparation of **11** to give

2,2-biphenylene-1,1-dimethoxy-1-morpholinoethane (**12**) as colorless crystals; yield 2.4 g (42%); mp 176-178℃. IR (nujol): 1120 cm^{-1}, 1080 (COC); ^1H NMR ($CDCl_3$) δ =2.44-2.58 (4H, m, CH_2NCH_2), 3.20 (6H, s, $2CH_3$), 3.52-3.66 (4H, m, CH_2OCH_2), 4.54 (1H, s, CH), 7.1-7.6 (8H, m, $H_{arom.}$).

3-2-8 Reaction of 12 with aq HCl.

A mixture of a solution of **12** (1 g, 3 mmol) in methanol (50 ml) and aq HCl (conc. HCl 1 ml/H_2O 10 ml) was stirred for 12 h at room temperature. The reaction mixture was worked up as described for the preparation of **11** to give 2,2-biphenylene-1,1-dimethoxyethylene (**10**) as yellow oil; yield 0.4 g (55%). IR (neat): 1640 cm^{-1} (C=C), 1110, 1090, 1065 (COC); ^1H NMR ($CDCl_3$) δ=3.35 (6H, s, $2CH_3$), 7.1-7.6 (8H, m, $H_{arom.}$).

3-2-9 Reaction of 5 with aq KCN.

To a solution of **5** (3.0 g, 8.3 mmol) in water (30 ml) was added dropwise a solution of KCN (1.08 g, 17 mmol) in ether (30 ml), the mixture was stirred for 8h at room temperature. The ether layer was separated and the aqueous phese was extracted with ether. The combined ether solution was dried with $MgSO_4$, and concentrated in vacuo, leaving a residue which was recrystallized from methanol to give 2,2-biphenylene-1-cyano-1-morpholinoethane (**13**) as colorless crystals; yield 2.4 g (99%); mp 160-162℃. IR (nujol): 2200 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ= 2.46-2.70. 2.82-3.06 (4H, two m, CH_2NCH_2), 3.24 (1H, d, J=11 Hz, CHCN), 3.85 (4H, t, J= 6 Hz, CH_2OCH_2), 4.13 (1H, d, CH), 7.1-8.0 (8H, m, $H_{arom.}$); MS m/e 290 (M^+). Found: C, 78.58; H, 6.17; N, 9.59%. Calcd for $C_{19}H_{18}ON_2$: C, 78.62; H, 6.20; N, 9.59%.

3-3-1 Reaction of 3h and 3i with TCNE at room temperature.

a) A mixture of **3h** (2.5 g, 9.8 mmol), tetracyanoethylene (1.28 g, 10 mmol), and tetrahydrofuran was stirred for 24 h at room temperature. The solution was filtered, and the filtrate was concentrated in vacuo, leaving a residue which was chlromatographed on alumina using benzene-petroleum benzin (1 : 1 v/v) as eluent to give 2,2-biphenylene-1-cyano-1-piperidinoethane (**14**) as yellow crystals; yield 0.55 g (29%); mp 135-137℃ (from ethanol). IR (nujol): 2200 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ=1.54-1.92 (6H, m, $CH_2CH_2CH_2$), 2.36-2.67, 2.80-3.08, (4H, two m, CH_2NCH_2), 3.16 (1H, d, J=11 Hz, CHCN), 4.13 (1H, d, CH), 7.2-8.0 (8H, m, $H_{arom.}$); MS m/e 288 (M^+). Found: C, 83.61; H, 6.52; N, 9.42%. Calcd for $C_{20}H_{20}N_2$: C, 83.33; H, 6.94; N, 9.72%.

b) Compound **13** was obtained; yield 31%; mp 160-161℃.

3-3-2 Reaction of 3i with TCNE under reflux.

A mixture of **3i** (1.3 g, 5 mmol), tetracyanoethylene (0.65 g, 5 mmol), and tetrahydrofuran (20 ml) was heated under reflux for 10 h. The reaction mixture was worked up as described for the preparation **14** to give 9-cyanomethylenefluorene (**15**) as yellow crystals; yield 0.4 g (41%); mp 103-105℃. IR (nujol): 2200 cm^{-1} (CN); ^1H NMR δ=6.04 (1H, s, =CH), 7.2-8.4 (8H, m, $H_{arom.}$).

3-4-1 Reaction of 3 h and 3 i with Ethyl Azidoformate.

a) To a solution of **3 h** (2 g, 7.6 mmol) in dichloromethane (30 ml) was added ethylazidoformate (1.15 g, 10 mmol). After refluxing for 48 h, the reaction mixture was concentrated in vacuo, leaving a residue which was chromatographed on alumina using benzene as eluent to yield two fractions. Eluting first was 9,9′-bifluorenyl (**22**) as colorless crystals; yield 0.3 g (24%); mp 239-240.5℃. ^{1}H NMR ($CDCl_3$) δ=4.78 (2 H, s, 2 CH), 6.8-7.6 (16H, m, $H_{arom.}$); MS m/e 330(M^+). Eluting second was 2,2-biphenylene-1-piperidinoethenyl carbamate (**16**) as yellow crystals; yield 1.0 g (37%); mp 115-116.5℃. IR (nujol): 3330 cm^{-1} (NH), 1725 (CO), 1610 (C=C), 1210(COC); ^{1}H NMR ($CDCl_3$) δ=0.9-1.04 (6 H, m, $CH_2CH_2CH_2$), 1.34 (3 H, t, J= 7 Hz, CH_3), 2.6-3.2 (4 H, m, CH_2NCH_2), 4.19 (2 H, q, J= 7 Hz, CH_2CH_3), 5.70 (1 H, s, NH), 7.1-7.8 (8 H, m, $H_{arom.}$).

b) The reaction of **3 i** with ethyl azidoformate as above gave 2,2-biphenylene-1-morpholinoethenyl carbamate (**17**) as yellow crystal; yield 1.3 g (37%); mp 163-164℃. IR (nujol): 3320 cm^{-1} (NH), 1720 (CO), 1610 (C=C), 1210 (COC); ^{1}H NMR ($CDCl_3$) δ=1.32 (3 H, t, J= 7 Hz, CH_3), 2.7-3.4 (8 H, m, CH_2NCH_2 and CH_2OCH_2), 4.18 (2 H, q, CH_2CH_3), 5.58 (1 H, s, NH), 7.0-7.8 (8 H, m, $H_{arom.}$).

3-4-2 Reaction of 3 i with p-Toluenesulfonyl Azide under reflux and under cooling.

a) A mixture of **3 i** (2.0 g, 7.6 mmol), *p*-toluenesulfonyl azide (1.9 g, 10 mmol), and dichloromethane (30 ml) was refluxed for 24 h. The solution was concentrated in vacuo, leaving a residue which was recrystalized from benzene-petroleum benzin to give-*N*-(morpholinomethylene)-*p*-toluenesulfonamide (**18**) as colorless crystals; yield 1.2 g (60%); mp 171-172℃. IR (nujol): 1610 cm^{-1} (C=N), 1340, 1140 (SO_2); ^{1}H NMR($CDCl_3$) δ=2.40 (3 H, s, CH_3), 3.48 (2 H, t, J= 6 Hz, NCH_2), 3,65 (4 H, s, CH_2OCH_2), 3.74 (2 H, t, CH_2N), 7.22 (2 H, d, J= 8 Hz, 2,6-H), 7.72 (2 H,d, 3,5-H), 8.15 (1 H, s, N=CH).

The filtrate was concentrated to give a residue which was chromatographed on alumina using benzene-petroleum benzine (1 : 1 v/v) as eluent, giving **22** (0.3 g, 23%).

b) A mixture of **3 i** (2 g, 7.6 mmol) and p-toluenesulfonyl azide (1.9 g, 10 mmol) in dichloromethane (30 ml) was stirred for 24 h under-ice-bath cooling. The reaction mixture was conducted in a manner to that described above, giving **18** (1.0 g, 50%).

3-4-3 Hydrolysis of 18.

a) A mixture of **18** (0.35 g, 1.3 mmol) in water (20 ml) was heated at 80℃ for 3 h and allowed to stand at room temperature, giving *p*-toluenesulfonamide (**19**) as colorless needles; yield 0.2 g (90%); mp 135-137℃. IR (nujol): 3330 cm^{-1}, 3230 (NH_2), 1500, 1300 (SO_2).

b) The reaction of **18** (0.35 g, 1.3 mmol) and aq HCl (conc. HCl 2 ml/H_2O) 20 ml) was conducted in a manner similar to that described above, giving **19** (0.18 g, 80%).

3-4-4 Reaction of 3 h with p-Toluenesulfony Azide under reflux.

a) To a solution of **3 h** (2.0 g, 7.6 mmol) in dichloromethane (30 ml) was added

p-toluenesulfony azide (1.9 g, 10 mmol). The mixture was refluxed for 2 h, concentrated in vacuo, leaving a residue which was chromatographed on alumina using benzene-petroleum benzine (1 : 1 v/v) as eluent to yield two fractions. Eluting first was 9-diazofluorene **(20)** as red brown powder ; yield 0.2 g (10%) ; mp 90-92℃ (dec.). IR (nujol) : 2020 cm^{-1} (N=N=C) ; MS m/s 192 (M^+). Eluting second was 9,9′-azofluorene **(21)** as brown power ; yield 0.3 g (22%) ; mp 192-195℃ (dec.). IR (nujol) : 2020 cm^{-1} (N=N) ; MS m/e 358 (M^+).

b) The reaction of **3h** (2 g, 7.6 mmol) and *p*-toluenesulfonyl azide (1.9 g, 10 mmol) in dichloromethane for 24 h under refluxing (as described above) gave **22** (0.4 g, 32%).

Reference

1) G. Stork, R. Terrell, and J. Szmuszkovicz, *J. Am. Chem. Soc.*, **76**, 2029 (1954).
2) As areview, "Enamines : Synthesis, Structure, and Reactions", ed by A. G. Cook, Maecel Dekker, New York (1969).
3) I. Von and E. C. Wagner, *J. Org. Chem.*, **9** 155 (1944).
4) W. Wislicenus and K. Rutz, *Ber.*, **43**, 2719 (1910).
5) R. Fusco, G. Bianchetti, D. Pocar, and R. Ugo, *Chem. Ber.*, **96**, 802 (1963).
6) R. Huisgen, G. Szeimies, and L. Mobius, *Chem. Ber.*, **100**, 2494 (1967).
7) M. E. Munk and Y. K. Kim, *J. Am. Chem. Soc.*, **86**, 2213(1964).