gave 95 mg (7%) of 2-phenyl-4,5-di-*p*-tolyl-1,2,3-triazole (**8d**); mp 144–145 °C (mixture melting point).

No other product could be isolated from this run.

B. In Benzene. A solution of **1d** (1.008 g, 4 mmol) in benzene (650 mL) was irradiated under nitrogen atmosphere for 0.5 h. Workup of the mixture, as in the earlier case, by chromatography over silica gel and elution with petroleum ether gave 0.12 g (9%) of the triazole **8d**; mp 144–145 °C (mixture melting point).

Irradiation of 3-Phenyl-4-*p*-tolylsydnone (1d) with *p*-Toluic Acid. A mixture of **1d** (0.51 g, 2 mmol) and *p*-toluic acid (0.3 g, 2.1 mmol) was dissolved in methanol (200 mL), and the solution was irradiated for 1 h under a nitrogen atmosphere. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over silica gel. Elution with petroleum ether gave 3 mg (9%) of the triazole **8d**; mp 145–146 °C (mixture melting point).

Subsequent elution of the column with a mixture (1:1) of benzene and petroleum ether gave 25 mg (6%) of α,β-di-*p*-toluylphenylhydrazine (**16d**).

Photooxygenation of 3-Methyl-4-phenylsydnone (1e). A solution of 3-methyl-4-phenylsydnone (**1e**) (0.88 g, 4 mmol) in methanol (450 mL) containing a small amount (0.01 g) of Rose Bengal was irradiated for 1 h, under oxygen bubbling. Removal of the solvent under vacuum gave a viscous mass, which was dissolved in methylene chloride (100 mL) and subsequently extracted with sodium bicarbonate. The aqueous layer, on acidification with dilute hydrochloric acid, gave 0.11 g (10%) of benzoic acid (**12b**); mp 120–121 °C (mixture melting point).

The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum to give a product which was subsequently recrystallized from a mixture (1:1) of benzene and petroleum ether to give 65 mg (5%) of α,β-dibenzoylhydrazine (**16e**); mp 144–146 °C (mixture melting point).[26]

Photolysis of 3-Methyl-4-phenylsydnone (1e). A benzene solution of 3-methyl-4-phenylsydnone (**1e**) (1.06 g, 6 mmol in 450 mL) was irradiated for 2 h, under a nitrogen atmosphere. Removal of the solvent under vacuum gave a product mixture which was subsequently chromatographed over silica gel. Elution of the column with a mixture (1:1) of benzene and petroleum ether gave 0.1 g (10%) of 4-methyl-2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (**5e**) after recrystallization from petroleum ether: mp 105–106 °C; IR spectrum (KBr) ν_{max} 3104 (ν_{C-H}, aromatic), 2924 (ν_{C-H}, aliphatic), 1774 ($\nu_{C=O}$), 1616, 1600, 1576, 1494, 1454, 1426, 1390, 1349, 1285, 1018, 1008, 988 cm^{-1}; NMR spectrum ($CDCl_3$) δ 3.45 (s, 3 H, CH_3 protons), 7.60 (m, 5 H, aromatic protons).

Anal. Calcd for $C_9H_8N_2O_2$: C, 61.35; H, 4.54; N, 15.93. Found: C, 61.44; H, 4.85; N, 15.9.

Attempted Photooxygenation of 3-Phenylsydnone (1a). A solution of 3-phenylsydnone (0.648 g, 4 mmol) in methanol (450 mL) was mixed with a small quantity (0.01 g) of Rose Bengal, and the resulting solution was irradiated under oxygen bubbling for 2 h. Removal of the solvent under vacuum gave a brown residue, which was chromatographed over silica gel. Elution with different solvents did not give rise to any identifiable product.

Photooxygenation of *C*-Biphenylene-N^{α}-(4-Chlorophenyl)-N^{β}-cyanoazomethine Imine (19). To a benzene solution of *C*-biphenylene-N^{α}-(4-chlorophenyl)-N^{β}-cyanoazomethine imine (**19**) (0.6 g, 1.8 mmol, in 700 mL) was added a methanol solution of Rose Bengal (0.03 g in 30 mL), and the resultant mixture was irradiated for 2 h, under oxygen bubbling. Removal of the solvent under vacuum gave a viscous residue, which was chromatographed over neutral alumina. Elution with petroleum ether gave 0.26 g (78%) of 9-fluorenone (**21**), mp 84–86 °C (mixture melting point), after recrystallization from ethyl alcohol.

No other product could be isolated from this run.

Acknowledgments. The authors thank the Department of Science and Technology of the Government of India, Indian Institute of Technology, Kanpur, India, and the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support for this work.

Registry No. **1a**, 120-06-9; **1b**, 3815-83-6; **1c**, 3815-77-8; **1d**, 70702-63-5; **1e**, 35431-71-1; **5e**, 879-60-7; **8b**, 27653-10-7; **8c**, 18411-23-9; **8d**, 10591-73-8; **12b**, 65-85-0; **16b**, 5455-22-1; **16c**, 70702-64-6; **16d**, 70749-44-9; **16e**, 21150-15-2; **17**, 15424-14-3; **18**, 18039-45-7; **19**, 5825-75-2; **21**, 486-25-9.

(26) A. Michaelis and E. Hadanck, *Ber. Dtsch. Chem. Ges.*, **41**, 3289 (1908).

(27) C. Engler and H. Heine, *Ber. Dtsch. Chem. Ges.*, **6**, 638 (1873).

Cycloadditions of Ketenes with *N*-Fluorenylidenealkylamine and -arylamine Oxides. Synthesis of Spirooxazolidinones and Spiroisoxazolidinones[1]

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The cycloadditions of several *N*-fluorenylidenearylamine and -alkylamine oxides (**1** and **2**) with cyclopentamethyleneketene, *tert*-butylcarbethoxyketene, and *tert*-butylcyanoketene were investigated. In general, the *N*-aryl derivatives afforded spirooxazolidinones (**3**) while the *N*-alkyl derivatives gave spiroisoxazolidinones (**4**). ^1H NMR and ^{13}C NMR studies of **3** and **4** were carried out to substantiate their structures. A mechanistic scheme which accounts for all of the observed cycloaddition products is proposed.

Our previous interest in the reactions of ketenes with *N*-aryl-[2a] and *N*-alkylimines,[2b] ketenimines,[2c] and azines[2d] led us to examine the cycloadditions of ketenes and nitrones. As we had developed a convenient method for the synthesis of *N*-methyl nitrones,[3] we initially studied the cycloaddition of *N*-fluorenylidenemethylamine oxide with *tert*-butylcyanoketene. We then extended these investigations to other N-substituted nitrones and other ketenes as well.

N-Aryl nitrones (**1a–c**) were prepared in 78–91% yields by the oxidation of the corresponding imines with *m*-chloroperbenzoic acid in methylene chloride. Nitrone **1d**

(1) Presented in part at the 174th National Meeting of the American Chemical Society, Chicago, Ill., August 1977.

(2) (a) A. S. Gomes and M. M. Joullié, *J. Heterocycl. Chem.*, **6**, 729 (1969); (b) J. M. Bohen and M. M. Joullié, *J. Org. Chem.*, **38**, 2652 (1973); (c) Z. Lysenko and M. M. Joullié, *ibid.*, **41**, 3925 (1976); (d) J. E. Semple and M. M. Joullié, *ibid.*, **43**, 3066 (1978).

(3) M. Abou-Gharbia and M. M. Joullié, *Synthesis*, **5**, 318 (1977).

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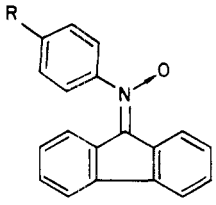
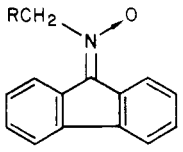


1a, R = CH_3
b, R = OCH_3
c, R = F
d, R = CF_3



2a, R = H
b, R = CH_3
c, R = C_6H_5

was obtained in 40% yield by this procedure; the yield could be increased to 60% when 48% peracetic acid was used as the oxidizing agent in the presence of an ammonium chloride/ammonium hydroxide buffer. *N*-Fluorenylidenemethylamine *N*-oxide (**2a**) was obtained in 90% yield via the reaction of *N*-fluorenylideneaniline and *N*-methylhydroxylamine-*O*-sulfonic acid at 0 °C.[3]

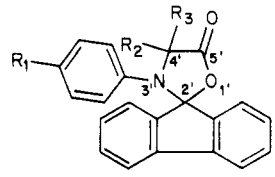
An important consideration in examining the cycloadditions of ketenes and nitrones is the purity of the nitrone, especially when these compounds are synthesized by the oxidation of imines. Syntheses of this type are known to afford oxaziridines.[4] However, when the products are unstable as, for example, *N*-phenyl- or 2,3-diaryloxaziridines,[5,6] nitrones are isolated instead. Since oxaziridines, in contrast to nitrones, oxidize iodide ion quantitatively,[7] iodometric titrations allow the detection of even trace quantities of oxaziridines and were used to establish the purity of the starting materials. In addition to the iodometric titrations, the purity of the nitrones was confirmed by spectroscopic techniques (UV, ^1H NMR, ^{13}C NMR).

The infrared spectra of both **1** and **2** showed absorptions at 1600–1550 cm^{-1} characteristic of >C = N stretching and 1260–1200 cm^{-1} typical of =N→O stretching. The ultraviolet spectra of both **1** and **2** showed the same characteristic maxima exhibited by **2a**, which was prepared by an alternate method. The ^1H NMR spectra of the nitrones exhibited a characteristic absorption for H-1 of the fluorene ring (δ 8.0–8.6) at lower field than the remaining aromatic protons (presumably due to its proximity to the negatively charged oxygen).[8] Finally, the ^{13}C chemical shift of the C-9 is typical of nitrones and appears around 144.4–145.1 ppm. Representative spectroscopic data for nitrones are shown in Table I.

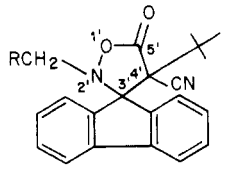
The ketenes studied were cyclopentamethyleneketene,[9] *tert*-butylcarbethoxyketene,[10] and *tert*-butylcyanoketene.[11]

Results and Discussion

The reactions of *N*-fluorenylideneaniline oxides (**1a–d**) with the three cited ketenes in boiling benzene or toluene afforded spirooxazolidinones (**3a–f**) in 52–78% yields. *N*-Fluorenylidenemethylamine *N*-oxide (**2a**), on the other hand, reacted with *tert*-butylcyanoketene under similar conditions to afford spiroisoxazolidinone **4a** in 72% yield. To establish the generality of these reactions, compounds **2b** and **2c** were prepared and treated with *tert*-butylcyanoketene. The expected spiroisoxazolidinones (**4b,c**) were obtained in 65 and 62% yields, respectively.



3a, R_1 = CH_3, R_2 = R_3 = $(CH_2)_5$
b, R_1 = CH_3, R_2 = *t*-Bu, R_3 = $CO_2C_2H_5$
c, R_1 = CH_3, R_2 = *t*-Bu, R_3 = CN
d, R_1 = OCH_3, R_2 = *t*-Bu, R_3 = CN
e, R_1 = F, R_2 = *t*-Bu, R_3 = CN
f, R_1 = CF_3, R_2 = *t*-Bu, R_3 = CN



4a, R = H
b, R = CH_3
c, R = C_6H_5

Distinction between structures **3** and **4** was achieved by ^{13}C NMR analysis. It appeared reasonable to assume that the ^{13}C chemical shift of the 9 carbon in fluorenes would be dependent on the substituents at this position. We therefore examined the ^{13}C chemical shifts of various 9-substituted fluorenes and compared these values to that of C-9 in fluorene itself (Table II). Incremental changes in chemical shifts were induced by the introduction of pertinent substituents. By adding the sum of the substituent contributions to the chemical shift of C-9 in fluorene, we predicted that the chemical shifts of the respective spiro carbons in the title compounds would differ by approximately 20 ppm. Experimentally determined chemical shift differences (18–19 ppm) were remarkably consistent with this prediction. The ^{13}C NMR chemical shifts of the spiro carbon (C-9), carbonyl carbons (C-5′), and quaternary carbons (C-4′) of compounds **3a–f** and **4a–c** are given in Table III.

The ^1H NMR spectra of compounds having a *tert*-butyl group also proved important in distinguishing between the isomeric spirooxazolidinones and spiroisoxazolidinones. The resonance of a *tert*-butyl group geminal to an electron-withdrawing group (CO_2Et or CN) usually appears at approximately 1.25 ppm. In compounds **4a–c**, the chemical shifts of the *tert*-butyl groups are seen at approximately 0.8 ppm. This divergence may be ascribed to the proximity of the *tert*-butyl group to the fluorene nucleus in the spiroisoxazolidinones and the resulting effect of the fluorene diamagnetic ring current.

An interesting phenomenon was observed in the low-temperature ^{13}C NMR spectrum of **3c** which exhibited four different resonances for C-20, C-21, C-23, and C-24 of the *N*-phenyl group (Figure 1), an effect attributable to restricted rotation of the *N*-phenyl group as a result of its interaction with the *tert*-butyl substituent on C-11. This observation was additionally supported by ^1H NMR temperature studies on **3c**. The broadened AA′BB′ pattern obtained for the protons of the *N*-phenyl group at ambient temperature undergoes considerable change as the temperature is decreased. Consistent with our structural assignments, the ^1H NMR and ^{13}C NMR spectra of **4a–c** exhibited no temperature dependence.

To obtain additional evidence for our structural assignments, we investigated the chemical behavior of some of our products. The reduction of **3a** with lithium aluminum hydride for 18 h afforded 9-fluorenol in 73% yield (Scheme I). The formation of this compound could be

(4) W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).
(5) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **23**, 651 (1958).
(6) M. Lamchen, "Mechanisms of Molecular Migrations", B. S. Thyagarajan, Ed., Wiley, New York, 1968, p 9.
(7) E. Schmitz, *Adv. Heterocycl. Chem.* **2**, 92 (1963).
(8) K. Kinko and S. Hiroshi, *Bull. Chem. Soc. Jpn.*, **42**, 3306 (1969).
(9) C. W. Smith and D. G. Norton "Organic Syntheses", Collect. Vol. 4, Wiley, New York, 1963, p 348.
(10) M. S. Newman and E. A. Zueck, *J. Org. Chem.*, **27**, 1436 (1962).
(11) W. Weyler, W. G. Duncan, and H. W. Moore, *J. Am. Chem. Soc.*, **97**, 6187 (1975).

Table I. Spectroscopic Data of Selected Nitrones

compd	R	IR (KBr) ν(C=N), ν(N→O), cm^{-1}	UV (CH_3OH) λ, nm	^{1}H NMR ($CDCl_3$) δ(H-1)	^{13}C NMR δ(C-9)
1c	p-FC_6H_4	1540, 1250, 1220	245, 265, 270, 310, 340, 355	8.60-8.80	144.4
2a	H	1550, 1290, 1200	241, 260, 269, 300, 332, 346	8.60-8.80	145.1

Table II. ^{13}C NMR Chemical Shifts for C-9 in Substituted Fluorenes

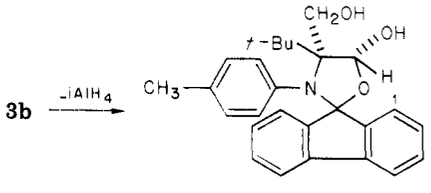
R	δ(C-9)	Δ, ppm
H	36.9	0
Me	42.4	5.5
Br	45.9	9.0
CO_2Et	53.3	16.6
CO_2H	53.4	16.5
NH_2	58.1	21.2
OH	75.1	38.2

Table III. ^{13}C NMR Spectral Data for Spirooxazolidinones and Spiroisoxazolidinones

compd	δ(C-9)	δ[C-5′ (3′)]	δ(C-4′)
3a	101.8	175.8	60.7
3b	102.4	170.5	61.9
3c	102.7	166.7	61.8
3d	102.7	166.7	68.3
3e	102.7	166.4	68.1
3f	102.8	166.1	67.9
4a	83.7	166.9	62.3
4b	82.7	166.5	61.8
4c	82.9	166.8	61.8

explained by the intermediacy of an unstable dihydro derivative, **5**, which decomposed to fluorenone, the latter species then being reduced to 9-fluorenol. Taylor[12a] observed a similar phenomenon in the reduction of 3′-isopropyl-4′,4′-dimethylfluorene-9-spiro-2′-oxazolidin-5′-one with lithium aluminum hydride. An unstable derivative resulting from reduction of the ester carbonyl was isolated in 40% yield and found to undergo facile conversion to fluorenone in the presence of aqueous acid or base or upon chromatography on silica gel. The reduction of 3′-methyl-4′,4′-diphenylfluorene-9-spiro-2′-oxazolidin-5′-one with the same reagent afforded 3′-methyl-4′,4′-diphenyl-5′-hydroxyfluorene-9-spiro-2′-oxazolidine which appeared to be in equilibrium with its ring–chain tautomer.[12b]

Our isolation of a stable cis diol (**6**), in 67% yield, from



6

the reduction of **3b** supported the intermediacy of a dihydro derivative in the hydride reductions of **3a** and other spirooxazolidinones. The CHOH and CH_2OH groups in **6** were assigned an α configuration on the basis of the low-field ^{1}H NMR shift of H-1 in the fluorene nucleus and the low-field ^{13}C NMR shift of C-1 as a result of their proximity to the respective hydroxyl groups. The reactions of dimethylketene with *N*-fluorenylidenealkylamine *N*-oxides in ethyl acetate were reported by Taylor[13] to afford spiro β-lactams **9** and spirooxazolidinones **10**. Similar

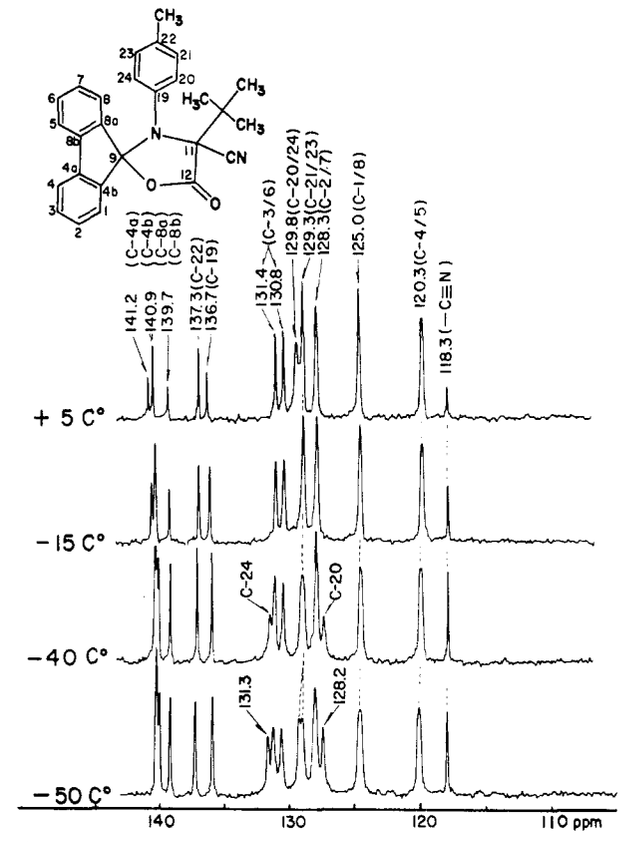
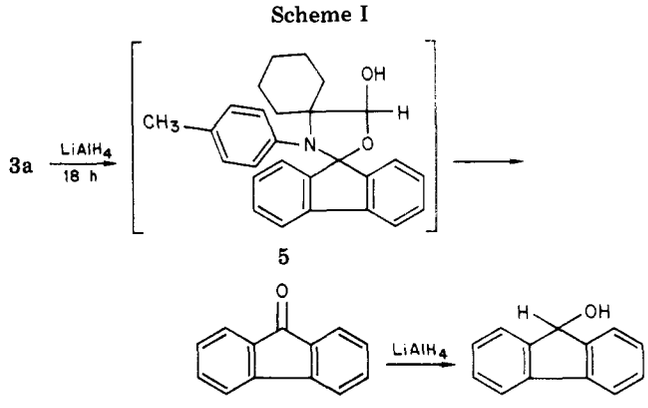


Figure 1.

Scheme I

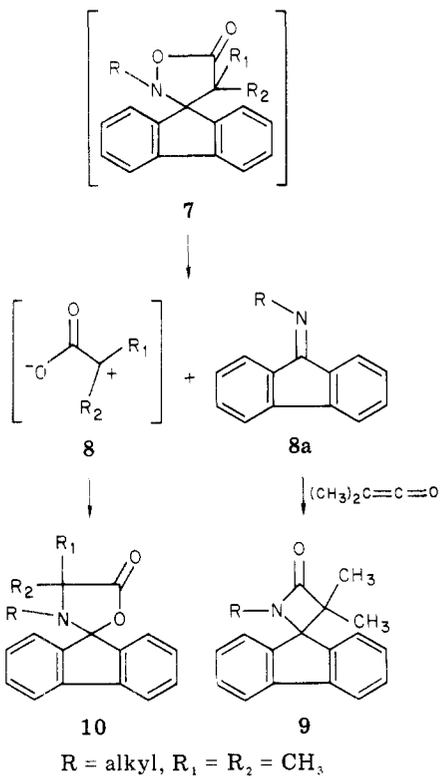


results were obtained with diphenylketene and the same nitrones in benzene.[12a,b] *N*-Methyl nitrone afforded five compounds: fluorenone azine (1%), a spiroazetidinone (19%), a spirooxazolidinone (8%) and two additional products which were not further identified. *N*-Ethyl nitrone also afforded a spiroazetidinone (60%) and spirooxazolidinone (12%) but *N*-isopropyl nitrone gave only the latter product (91%). Structural assignments were based on mass spectral fragmentation data and chemical evidence. To explain these results, Taylor proposed a mechanism (Scheme II) involving a zwitterion (**8**) and an imine (**8a**) believed to result from the decomposition of the expected 1,3-cycloaddition product, a presumably unstable spiroisoxazolidinone (**7**). It is interesting to note that with both dimethyl- and diphenylketene, the proportions of the spirooxazolidinones and β-lactams varied

(12) (a) R. N. Pratt, D. P. Stokes, and G. A. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 498 (1975); (b) A. F. Gettins, D. P. Stokes, and G. A. Taylor, *ibid.* 1849 (1977).

(13) A. F. Gettins and G. A. Taylor, *J. Chem. Soc., Chem. Commun.*, 1146 (1972).

Scheme II



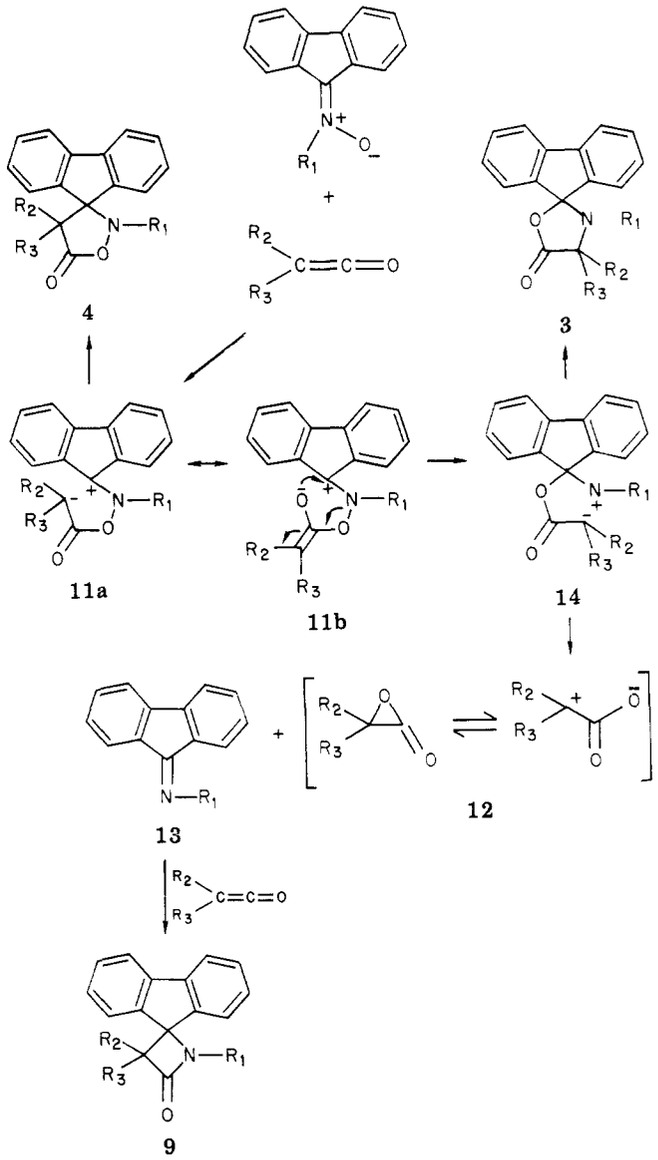
R = alkyl, $R_1 = R_2 = CH_3$

widely with changes in the *N*-alkyl substituents: 1:1 for *N*-Me, 1:2 for *N*-Et, and 4.5:1 for *N*-isopropyl. The ratios are independent of the initial proportions of ketene and nitrone. Taylor attributed this variation in ratios to steric rather than electronic effects of the *N*-alkyl groups.[12b]

Our results on the reactions of *tert*-butylcyanoketene with *N*-alkyl nitrones in toluene contrast significantly with those of Taylor. While Taylor obtained spirooxazolidinones (**10**) from *N*-alkyl nitrones, we exclusively obtained spiroisoxazolidinones (**4a–c**) in good yields. Taylor also isolated spiro β-lactams (**9**) while we were unable to detect similar products under a variety of experimental conditions, including low temperatures and the presence of either a radical inhibitor or an excess of ketene. On the other hand, the reactions of *tert*-butylcyanoketene with *N*-aryl nitrones in toluene afforded exclusively spiroisoxazolidinones (**3a–f**).

Our results can be very simply explained in terms of known ketene chemistry (Scheme III). The reactions are believed to involve nucleophilic attack of the nitrones on the ketenes to afford a delocalized zwitterion whose major contributing resonance form may be represented by **11a** or **11b** depending on the substituents (R_2 and R_3). Substituents which stabilize a carbanion should favor **11a** whereas electron-donating substituents should favor **11b**. If the major contributing form is **11a**, cyclization would be expected to occur readily to give a spiroisoxazolidinone (**4**), the reaction involving nucleophilic attack on a very stable benzylic cation. In accord with this premise, spiroisoxazolidinones have been obtained with *tert*-butylcyanoketene but not with dimethyl- or diphenylketene, the cyano group being more effective than phenyl or alkyl groups in the stabilization of a carbanion. Steric effects should also be important in this ring closure as we have established from spectroscopic studies that there are significant steric interactions between the C-4′ substituents and the fluorene ring. Steric effects may, in fact, be a principal reason why this cyclization has only been observed with *N*-alkyl nitrones.

Scheme III



When R_2 and R_3 are phenyl groups, resonance form **11b** should be the major contributing structure as the result of extension of delocalization. In this case, cyclization is suppressed in favor of a sigmatropic rearrangement which affords a zwitterion capable of undergoing ring closure to spirooxazolidinone compounds (**3**) observed by both Taylor and ourselves. The cleavage of a nitrogen–oxygen bond has precedent in the sigmatropic rearrangement first postulated by Hassall and Lippman[14] and is, therefore, not unexpected. The nitrenium ion in **14** should be better stabilized by aromatic than aliphatic N substituents, a point which is consistent with the better yields obtained with *N*-aryl nitrones. This stabilization could also account for the variation in the ratios of spirooxazolidinones and β-lactams with the type of *N*-alkyl group present in the nitrone, isopropyl groups affording the best yield of spirooxazolidinones. This argument appears more reasonable than a steric argument[12b] which should, in fact, give opposite results.

The preceding mechanism not only explains our results but those of Taylor as well.

Stabilization of the carbanion center in **14** is also important. When cyano or carbethoxy groups are present,

(14) C. H. Hassall and A. E. Lippman, *J. Chem. Soc.*, 1059 (1953).

cyclization to spirooxazolidinones **3a–f** occurs exclusively. With dimethyl or diphenyl groups, elimination to an imine (**13**) and a presumed α-lactone intermediate (**12**) would be preferred. The latter species could exist in equilibrium with a 1,3 zwitterion such as the one postulated by Taylor. Analogous deoxygenation reactions were first observed between dimethyl- or diphenylketene and heteroaromatic *N*-oxides.[15a-c] The addition of these ketenes to heteroaromatic *N*-oxides was believed to afford a zwitterion which could undergo internal nucleophilic displacement to afford a labile α-lactone and the deoxygenated product. Although trapping or isolation of such a lactone has not been accomplished, support for its existence may be found in recent work by Schaumann and Behrens, who have identified several α-thiolactones from the reactions of thioketenes with nitrones of the 1-pyrroline 1-oxide type.[16]

We therefore believe that zwitterion 8 arises via the well-precedented deoxygenation reaction shown in Scheme III rather than the decomposition of a spiroisoxazolidinone (**7**) as postulated by Taylor. There is no support for the invocation of **7** as an intermediate since all available evidence from known spiroisoxazolidinones show them to be rather stable. Although we have prepared a series of spiro β-lactams from fluorenylidene imines and *tert*-butylcyanoketene,[17] we could not detect any spiro β-lactams in the reactions that afforded compounds **4a–c**. We therefore believe that the mechanism shown in Scheme III represents the best explanation for the observed results and is consistent with literature background on these reactions.

Experimental Section

All melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord 137-B. The ^{1}H NMR spectra were determined on Varian A-60, HR-220, and HA-100 spectrometers. ^{13}C NMR spectra were determined on JEOL-PS 100 and Bruker 20 spectrometers. Mass spectra were obtained on a Finnigan Model F-3300 with data system 600 mass spectrometer, with an ionizing potential of 70 eV. Elemental analyses were performed by Robertson Laboratory.

Materials. The imines were prepared from the commercially available fluorenone following reported procedures.[18,19] Cyclopentamethyleneketene was prepared in 60% yield from α-bromocyclohexanecarboxylic acid bromide following Smith conditions.[9] *tert*-Butylcarbethoxyketene[10] and *tert*-butylcyanoketene were prepared following reported procedures.[11]

General Procedure for the Preparation of *N*-Aryl Nitrones. A small excess of *m*-chloroperbenzoic acid (0.022 mol) in 40 mL of methylene chloride was added with stirring and cooling (0–5 °C) to a solution of the appropriate imine (0.02 mol) in 10 mL of methylene chloride. After the addition of the peroxy acid, the reaction mixture was stirred for 5 h at 0–5 °C. *m*-Chlorobenzoic acid was removed by filtration, and the filtrate was washed twice with a Na_2CO_3 solution and finally with water. After the filtrate was dried over anhydrous Na_2SO_4, the organic layer was evaporated and the residue was recrystallized from the appropriate solvent.

***N*-Fluorenylidene-*p*-toluidine *N*-Oxide (1a).** This compound was prepared by the general procedure, using 5.3 g (0.02 mol) of *N*-fluorenylidene-*p*-toluidine. Compound **1a** was recrystallized from methylene chloride–pentane (1:1) to afford 5.1 g (91% yield): mp 164–165 °C; IR (KBr) ν_{max} 1510, (C=N), 1250 (N→O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.5 (s, 3 H), 6.72–8.7 (m, 12 H). Anal. Calcd for $C_{20}H_{15}NO_2$: C, 84.19; H, 5.30; N, 4.91. Found: C, 84.04; H, 5.53; N, 4.77.

***N*-Fluorenylidene-*p*-anisidine *N*-Oxide (1b).** The general procedure was followed, using 5.7 g (0.02 mol) of *N*-fluorenylidene-*p*-anisidine. The product (**1b**) was recrystallized from 95% ethanol to afford 5.1 g (85% yield): mp 169–171 °C; IR (KBr) ν_{max} 1520 (C=N), 1225 (N→O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.55 (s, 3 H), 6.55–7.95 (m, 12 H). Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 80.00; H, 5.08; N, 4.48.

***N*-Fluorenylidene-*p*-fluoroaniline *N*-Oxide (1c).** The general procedure was followed, using 5.4 g (0.02 mol) of *N*-fluorenylidene-*p*-fluoroaniline. The product (**1c**) was recrystallized from methylene chloride to afford 4.5 g (78% yield): mp 203–205 °C; IR (KBr) ν_{max} 1630, 1510 (C=N), 1230 (N→O) cm^{-1}. Anal. Calcd for $C_{19}H_{12}FNO$: C, 78.87; H, 4.18; N, 4.84. Found: C, 78.74; H, 4.37; N, 5.11.

***N*-Fluorenylidene-*p*-(trifluoromethyl)aniline *N*-Oxide (1d).** To a stirred solution of 6.4 g (0.02 mol) of *N*-fluorenylidene-*p*-(trifluoromethyl)aniline were added 1 mL of ammonium hydroxide, 1 g of ammonium chloride in 50 mL of methylene chloride, and 9 mL (0.02 mol) of 48% peracetic acid over a period of 15 min. The solution was stirred at 0–5 °C for 10 h and then filtered and washed first with sodium bisulfite solution and then with sodium carbonate solution followed by water. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The residual yellow needles were recrystallized from 95% ethanol to afford 4 g (61% yield) of **1d**: mp 154–155 °C; IR (KBr) ν_{max} 1600, 1550 (C=N), 1310 (N→O) cm^{-1}. Anal. Calcd for $C_{20}H_{12}F_3NO$: C, 70.79; H, 3.56; N, 4.12. Found: C, 71.00; H, 3.64; N, 4.26.

***N*-Fluorenylidenemethylamine *N*-Oxide (2a).** *N*-Methylhydroxylamine-*O*-sulfonic acid (0.7 g, 0.0055 mol) was added slowly over a period of 10 min at 0–10 °C to a stirred solution of *N*-fluorenylideneaniline (1.2 g, 0.005 mol) in 50 mL of methanol. The resulting mixture was stirred for 1 h at that temperature and then diluted with ice water. The solution was extracted with methylene chloride, and the extract was dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to afford a yellow solid which was recrystallized from 95% ethanol to yield 0.9 g (90% yield) of **2a**: mp 143–145 °C (lit.[12] mp 145–146 °C).

***N*-Fluorenylideneethylamine *N*-Oxide (2b).** Zinc dust (55 g, 0.84 mol) was added over a period of 2 h to a stirred mixture of nitroethane (25 g, 0.33 mol), 12 g of ammonium chloride, and 160 mL of water. The mixture was filtered and the filtrate was acidified with dilute hydrochloric acid and evaporated under reduced pressure to a viscous liquid. A solution of 15 g (0.08 mol) of fluorenone in 250 mL of ethanol was added to this residue, and the mixture was stirred with an excess of solid $NaHCO_3$ until gas evolution ceased (2 h). The solution was filtered, boiled for 3 days, and evaporated to dryness. The residue was extracted with 150 mL of chloroform, and the extract was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was recrystallized from 20 mL of ethanol to afford 8.30 g (47% yield) of **2b** as yellow needles: mp 85–87 °C (lit.[12] mp 87–88 °C).

***N*-Fluorenylidenebenzylamine *N*-Oxide (2c).** The general procedure was followed, using 5.4 g (0.02 mol) of *N*-fluorenylidenebenzylamine. The product was recrystallized from ethanol to afford 3.62 g (63% yield): mp 118–120 °C; IR (KBr) ν_{max} 1550 (C=N), 1200 (N→O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.70 (s, 2 H), 7.1–7.75 (m, 12 H), 8.7–9 (m, 1 H). Anal. Calcd for $C_{20}H_{15}NO$: C, 84.19; H, 5.30; N, 4.91. Found: C, 84.29; H, 5.48; N, 4.80.

Reaction of Cyclopentamethyleneketene with 1a. 3′-*p*-Tolyldispiro[cyclohexane-1′,4′-oxazolidine-2′,9′(9*H*)-fluorene]-5′-one (3a). Nitrone **1a** (2.85 g, 0.01 mol) was added to a cyclopentamethyleneketene in a bis(2-methoxyethyl) ether solution [prepared from 5.00 g (0.01 mol) of α-bromocyclohexanecarboxylic acid bromide and 1.50 g (0.02 mol) of zinc]. The mixture was warmed at 50 °C on a water bath for 30 min. Evaporation of the ether solution afforded a white solid which was recrystallized from a methanol–chloroform (1:1) solution to yield 2 g (52% yield) of **3a**: mp 188–189 °C; IR (KBr) ν_{max} 1775 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1–2.4 (m, 10 H), 2.14 (s, 3 H), 6.63–6.93 (m, 4 H), 7.10–7.74 (m, 8 H). Anal. Calcd for $C_{27}H_{25}NO_2$:

(15) (a) T. Koenig, *Tetrahedron Lett.*, 3127 (1965); (b) R. N. Pratt, D. P. Stokes, G. A. Taylor, and S. A. Procter, *J. Chem. Soc. C*, 1472 (1971); (c) R. N. Pratt and G. A. Taylor, *ibid.*, 1653 (1968).
(16) E. Schaumann and U. Behrens, *Angew. Chem., Int. Ed. Engl.*, **16**, 722 (1977).
(17) M. Abou-Gharbia, T. T. Su, and M. M. Joullié, *J. Pharm. Sci.*, **67**, 956 (1978).
(18) M. E. Taylor and T. L. Fletcher, *J. Org. Chem.*, **21**, 523 (1956).
(19) M. E. Taylor and T. L. Fletcher, *J. Org. Chem.*, **26**, 940 (1961).

C, 82.00; H, 6.27; N, 3.54. Found: C, 81.85; H, 6.53; N, 3.56.

Reaction of *tert*-Butylcarbethoxyketene with 1a. 4′-*tert*-Butyl-5′-oxo-3′-*p*-tolylspiro[fluorene-9,2′-oxazolidine-4′-ethyl carboxylate] (3b). *tert*-Butylcarbethoxyketene (0.85 g, 0.005 mol) was added to 1.4 g (0.0048 mol) of **1a** in 5 mL of dry toluene. The mixture was refluxed on an oil bath for 3 h. The solvent was removed by distillation under reduced pressure and the residue was recrystallized from an ethanol–petroleum ether (1:4) solution to yield 1.2 g (55%) of **3b**: mp 159–161 °C; IR (KBr) ν_{max} 1775 (C=O) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 1.21 (s, 9 H), 1.32 (t, 3 H), 2.06 (s, 3 H), 4.46 (q, 2 H), 6.68–6.76 (m, 4 H), 7.23–7.63 (m, 8 H). Anal. Calcd for $C_{29}H_{29}NO_4$: C, 76.45; H, 6.42; N, 3.07. Found: C, 76.28; H, 6.46; N, 2.90.

Reaction of *tert*-Butylcyanoketene with 1a. 4′-*tert*-Butyl-5′-oxo-3′-*p*-tolylspiro[fluorene-9,2′-oxazolidine]-4′-carbonitrile (3c). To a solution of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (0.2 g, 0.001 mol) in 20 mL of dry toluene was added 9.57 g (0.002 mol) of **1a** over a period of 5 min, with stirring. The solution was heated for 2 h. The toluene was removed under reduced pressure and the resulting brown oil was solidified upon trituration with 50% ethanol. The solid was recrystallized from 75% ethanol to yield 0.55 g (68.4% yield) of **3c**: mp 189–190 °C; IR (KBr) ν_{max} 1778 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9 H), 2.15 (s, 3 H), 6.52–8.3 (m, 12 H); MS *m/e* 408 (M^+, *m/e*(calcd) 408). Anal. Calcd for $C_{27}H_{24}N_2O_2$: C, 79.39; H, 5.92; N, 6.86. Found: C, 79.63; H, 6.06; N, 6.76.

4′-*tert*-Butyl-5′-oxo-3′-*p*-anisylspiro[fluorene-9,2′-oxazolidine]-4′-carbonitrile (3d). The general procedure described for **3c** was followed, using 0.6 g (0.002 mol) of **1b**. The product was recrystallized from 50% ethanol to yield 0.61 g (72% yield): mp 171–173 °C; IR (KBr) ν_{max} 1770 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9 H), 3.25 (s, 3 H), 6.4–8.2 (m, 12 H); MS *m/e* 424 (M^+, *m/e* (calcd) 424). Anal. Calcd for $C_{27}H_{24}N_2O_3$: C, 76.39; H, 5.69; N, 6.60. Found: C, 76.12; H, 5.80; N, 6.60.

4′-*tert*-Butyl-5′-oxo-3′-(*p*-fluorophenyl)spiro[fluorene-9,2′-oxazolidine]-4′-carbonitrile (3e). The procedure described for **3c** was followed, using 0.57 g (0.002 mol) of **1c**. Addition of 50% ethanol to the reaction mixture afforded a white solid which was recrystallized from 70% aqueous ethanol to give 0.64 g (78% yield) of **3e**: mp 150–151 °C; IR (KBr) ν_{max} 1800 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 9 H), 6.55–8.1 (m, 12 H). Anal. Calcd for $C_{26}H_{21}FN_2O_2$: C, 75.70; H, 5.13; N, 6.79; F, 4.60. Found: C, 75.56; H, 5.32; N, 6.68; F, 4.45.

4′-*tert*-Butyl-5′-oxo-3′-*p*-(trifluoromethyl)phenylspiro[fluorene-9,2′-oxazolidine]-4′-carbonitrile (3f). The reaction was carried out as described for **3c** using 0.67 g (0.002 mol) of **1d**. Addition of absolute ethanol to the reaction mixture afforded a buff solid which was recrystallized from 95% ethanol to yield 0.6 g (65%) of **3f**: mp 169–170 °C; IR (KBr) ν_{max} 1800 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9 H), 7.3–8.0 (m, 12 H). Anal. Calcd for $C_{27}H_{21}F_3N_2O_2$: C, 70.11; H, 4.57; F, 12.32; N, 6.05. Found: C, 70.35; H, 4.74; F, 12.04; N, 6.22.

Reaction of *tert*-Butylcyanoketene with 2a. 4′-*tert*-Butyl-5′-oxo-2′methylspiro[fluorene-9,3′-isoxazolidine]-4′-carbonitrile (4a). The reaction was carried out as described for **3c**, using 0.4 g (0.002 mol) of **2a**. Addition of petroleum ether to the reaction mixture gave a white solid which was recrystallized from 50% ethanol to yield 0.47 g (72% yield) of **4a**: mp 178–180 °C; IR (KBr) ν_{max} 1775 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 9 H), 2.4 (s, 3 H), 7.3–8.4 (m, 8 H). Anal. Calcd for $C_{21}H_{20}N_2O_2$: C, 75.88; H, 6.06; N, 8.43. Found: C, 75.73; H, 6.13; N, 8.14.

4′-*tert*-Butyl-5′-oxo-2′-ethylspiro[fluorene-9,3′-isoxazolidine]-4′-carbonitrile (4b). The reaction was carried out as for **3c**, using 0.45 g (0.002 mol) of **2c**. Addition of 50% ethanol to the reaction mixture gave a buff solid which was recrystallized from 50% ethanol to yield 0.45 g (65% yield) of **4b**: mp 161–162 °C; IR (KBr) ν_{max} 1770 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (s, 9 H), 0.98–1.25 (t, 3 H), 1.9–2.7 (m, 2 H), 7.20–7.70 (m, 7 H) 8.20–8.40 (m, 1 H). Anal. Calcd for $C_{22}H_{22}N_2O_2$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.10; H, 6.25; N, 7.89.

4′-*tert*-Butyl-5′-oxo-2′-benzylspiro[fluorene-9,3′-isoxazolidine]-4′-carbonitrile (4c). The reaction was carried out as described for **3c**, using 0.56 g (0.002 mol) of **2c**. Addition of 50% ethanol to the reaction mixture gave a white solid which was recrystallized from 50% ethanol to afford 0.64 g (80% yield) of **4c**: mp 183–184 °C; IR (KBr) ν_{max} 1770 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (s, 9 H), 3.1–3.8 (q, 2 H), 7.3–7.8 (m, 13 H). Anal. Calcd for $C_{27}H_{24}N_2O_2$: C, 79.39; H, 5.92; N, 6.86. Found: C, 79.62; H, 6.15; N, 6.81.

Reduction of 3a with Lithium Aluminum Hydride. Compound **3a** (0.3 g, 0.001 mol) was added to a suspension of 0.5 g of $LiAlH_4$ in 50 mL of dry ether, and the mixture was stirred under reflux for 18 h. Excess hydride was decomposed with water, the ether solution was filtered and washed with dilute HCl followed by water, and the organic layer was dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure afforded a white solid which was recrystallized from ether–petroleum ether (1:1) to afford 0.13 g (72% yield) of 9-fluorenol: mp 146–148 °C (lit.[20] mp 151–152 °C); IR (KBr) ν_{max} 3400 (OH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.1 (broad, 1 H), exchanged with D_2O), 5.45 (s, 1 H), 7.77 (m, 8 H). Anal. Calcd for $C_{13}H_{10}O$: C, 85.68; H, 5.53. Found: C, 85.49; H, 5.48.

Reduction of 3b with Lithium Aluminum Hydride. The reduction was carried out as described for **3a**, using 0.2 g (0.004 mol) of **3b** and 0.2 g of $LiAlH_4$. Removal of ether under reduced pressure afforded a white solid which was recrystallized from ether to yield 0.13 g (67% yield) of **6**: mp 191 °C; IR (KBr) ν_{max} 3300 (OH) cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 1.00 (s, 9 H), 2.00 (s, 3 H), 3.2 (s, 1 H, exchanged with D_2O), 4.08–4.2 (m, 3 H after D_2O q, 2 H), 6.00 (d, 1 H, J = 6 Hz after D_2O appeared as a singlet), 6.7 (q, 4 H), 7.0–8.4 (m, 8 H); MS *m/e* 415 (M^+ *m/e* (calcd) 415). Anal. Calcd for $C_{27}H_{29}NO_3$: C, 78.00; H, 7.00; N, 3.36. Found: C, 77.67; H, 7.10; N, 3.67.

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Registry No. 1a, 66783-82-2; **1b**, 66783-83-3; **1c**, 66783-84-4; **1d**, 66783-85-5; **2a**, 33226-81-2; **2b**, 39656-21-8; **2c**, 70765-97-8; **3a**, 66783-75-3; **3b**, 66783-76-4; **3c**, 66783-78-6; **3d**, 70765-98-9; **3e**, 70765-99-0; **3f**, 66783-77-5; **4a**, 66783-79-7; **4b**, 66783-80-0; **4c**, 70766-00-6; **6**, 70766-01-7; *N*-fluorenylidene-*p*-toluidine, 10183-83-2; *N*-fluorenylidene-*p*-anisidine, 5455-02-7; *N*-fluorenylidene-*p*-fluoroaniline, 390-41-0; *N*-fluorenylidine-*p*-(trifluoromethyl)aniline, 68161-28-4; *N*-methylhydroxylamine-*O*-sulfonic acid, 3400-11-1; *N*-fluorenylideneaniline, 10183-82-1; nitroethane, 79-24-3; fluorenone, 486-25-9; *N*-fluorenylidenebenzylamine, 70766-02-8; cyclopentamethyleneketene, 22589-13-5; *tert*-butylcarbethoxyketene, 51552-63-7; 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone, 29342-21-0; *tert*-butylcyanoketene, 29342-22-1; fluoren-9-ol, 1689-64-1; fluorene, 86-73-7; 9-methylfluorene, 2523-37-7; 9-bromofluorene, 1940-57-4; ethyl fluorene-9-carboxylate, 26878-12-6; fluorene-9-carboxylic acid, 1989-33-9; fluoren-9-amine, 525-03-1.

(20) W. Wislicenus and W. Mocker, *Ber. Dtsch. Chem. Ges.*, **46**, 2772 (1913).