Allene Oxide Intermediates: Vinylidene Carbene Addition to Carbonyl Compounds

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Solutions of fluorenylidene carbene (**10**) have been generated by treatment of 9-(aminomethylene)-fluorene (**9**) with *n*-butyl nitrite. This vinylidene carbene forms a 1:1 adduct with azobenzene, and with acetone pivaldehyde and tolualdehyde it forms 1:2 adducts containing the 5-fluorenylidene-1,3-dioxolane ring system. Evidence for the intermediacy of an allene oxide (**3**) is presented.

Les solutions de carbène fluorinylidène (**10**) ont été obtenues en traitant l'aminométhylène-9 fluorène (**9**) par le nitrite de *n*-butyle. Ce vinylidène carbène forme un adduit 1:1 avec l'azobenzène et avec l'acétone, le pivaldéhyde et le tolualdéhyde des adduits 1:2 contenant le système cyclique fluorenylidene-5 dioxolane-1,3. L'intermédiaire alleneoxyde (**3**) a été mis en évidence. [Traduit par le journal]

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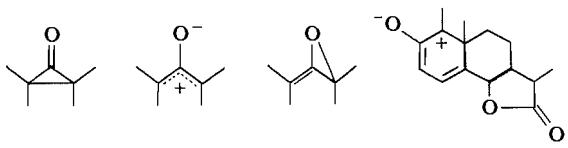
Introduction

The three isomeric systems: cyclopropanone (**1**), oxyallyl (**2**), and allene oxide (**3**) have attracted attention for a long time as reactive intermediates, and in recent years substituted cyclopropanones (1) and allene oxides (2) have been synthesized. However, there is only one report of an isolation of an oxyallyl system by Fisch and Richards (3), who suggest the structure **4** for the unstable blue non-paramagnetic species obtained in a frozen glass by radiation of lumisantonin; and for this one case, evidence is weak.



1 **2** **3** **4**

Concerning the experimental thermodynamic stabilities of the three systems, all that is known so far is that 1,1-di-*tert*-butylallene-1,2-oxide[3] (4*a*) and 1,3-di-*tert*-butylallene oxide (2) are less stable than the corresponding cyclopropanones, since both can be thermally isomerized to the cyclopropanone; whereas 1,1,3-tri-*tert*-butylallene-1,2-oxide (4*b*) is very stable thermally and has not been isomerized. Theoretical calculations were first carried out by Burr and Dewar (5) in 1954 using the LCAO method, and oxyallyl was predicted to be less stable than cyclopropanone. Next came a contradictory result by Hoffmann (6) in 1968 using an extended Hückel method, which indicated that oxyallyl should be 60 kcal more stable than allene oxide which should be 7 kcal more stable than cyclopropanone. Then in 1970, Dewar and coworkers (7) confirmed the 1954 result using the newer MINDO/2 method giving cyclopropanone 78 kcal more stable than oxyallyl.

Obviously much more experimental data relevant to the relative stabilities of the isomers (**1–3**) are called for, and high in priority is the synthesis of more examples. One approach is to attempt to synthesize substituted examples of each of the three isomers by carefully selecting stabilizing substituents.

The work reported in this paper was initiated in order to synthesize system **5** and its isomers **6**, **7**, and **8**, and then to investigate their relative stabilities and the possibility of interconversion. This particular system was chosen because the allene oxide **5** might prove to be more stable than the cyclopropanone **7** in contrast to the *tert*-butyl substituted systems. The reasons for this suggestion are firstly that molecular models of **5** show less steric crowding than those of **7** for most R substituents, and secondly that the extra conjugation in **5** might stabilize it relative to **7**. This latter idea is backed up by the fact that the enol **13***a* in acetonitrile solvent contains none of its *aldo* tautomer detectable by n.m.r. (8). The oxyallyl system **6** might also be appreciably stabilized if R'' is a carbonium ion stabilizer such as *p*-tolyl.

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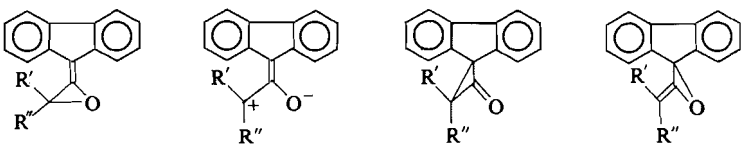
[3]In this case it is not proven whether the *tert*-butyl groups are attached to the 1- or 3-carbon atom.



5 6 7 8

	a	*b*	*c*	*d*	*e*	*f*
R′ =	CH_3	H	H	*t*-Bu	CH_3	H
R″ =	CH_3	*t*-Bu	*p*-Tolyl	*t*-Bu	Ph	CCl_3

The synthetic approach to **5** was based on Curtin *et al*'s (9) synthesis of the methylenecyclopropane **11** by treating the enamine **9** with isoamyl nitrite in the presence of 2,3-dimethyl-2-butene. The presumed (9) reaction sequence is initial formation of a diazonium salt followed by loss of nitrogen and a proton to give the carbene **10** which then adds to the alkene to give **11** (see Scheme 1). If one simply replaces the alkene in this synthesis by any other doubly-bonded molecule represented by the general formula X=Y, then on paper one has a general synthesis of compounds of general formula **14**. If X=Y is a carbonyl compound, the product should be an allene oxide, **5**.

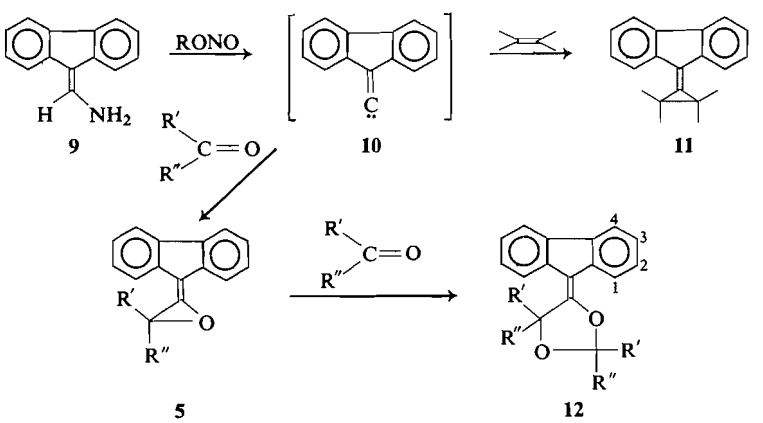
This paper reports attempts at this method of synthesis of allene oxides.

Results and Discussion

Numerous different sets of conditions were tried for the reaction between 9-(aminomethylene)-fluorene, *n*-butyl nitrite, and various doubly-bonded molecules. The first part of the reaction, the generation of the carbene **10** with loss of nitrogen was followed by measurement of the volume of gas evolved. The rate was found to be very sensitive to the composition of the medium. For example, while more than 50% of the expected volume of nitrogen is evolved within an hour when the solvent is benzene at 35 °C, no appreciable reaction is observed when the solvent is ether under the same conditions. It was found in general most satisfactory to dispense with the solvent except for solids and reactants in short supply. The temperature generally was raised slowly until at least 50% of the quantitative volume of gas had evolved. The products were then separated by column chromatography.

The following ketones and aldehydes were used as the doubly-bonded reactant: di-*tert*-butyl ketone, acetone, acetophenone, pivaldehyde, tolualdehyde, and chloral. In no case was a stable 1:1-adduct with the carbene **10** obtained. However, in three cases 1:2-adducts having structures **12***a*, *b*, and *c* were isolated as stable crystalline compounds.

The structures were assigned from the spectra of three compounds which are given in tabular form in Table 1. In the p.m.r. spectra, the aliphatic protons of compounds **12***a*, *b*, and *c* occurred at the expected chemical shifts with expected intensity and multiplicity. There was



9 10 11 5 12

SCHEME 1

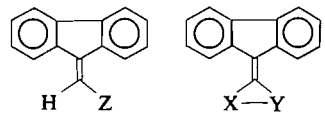
TABLE 1. P.m.r. and u.v. data

Compound	P.m.r. δ(p.p.m.)*	U.v. λ_{max}(nm)(ε)†
12*a*	‡8.0–8.2 (qt) 1H (Ar)	283 (18 600)
	7.6–7.9 (m) 3H (Ar)	294 (20 400)
	7.2–7.4 (m) 4H (Ar)	317 (14 300)
	1.91 (s) 6H (Me)	331 (14 800)
	1.66 (s) 6H (Me)	
12*b*	‡8.0–8.2 (qt) 1H (Ar)	290 (15 500)
	7.5–7.8 (m) 3H (Ar)	293 (infl) (15 400)
	7.1–7.4 (m) 4H (Ar)	318 (infl) (14 100)
	5.23 (s) 1H (*tert* H)	315 (15 400)
	4.74 (s) 1H (*tert* H)	
	1.18 (s) 9H (*t*-Bu)	
	1.07 (s) 9H (*t*-Bu)	
12*c*	§8.2–8.4 (qt) 1H (Ar)	287 (infl) (20 400)
	6.9–7.9 (m) 15H (Ar)	299 (21 300)
	6.55 (s) 1H (*tert* H)	318 (17 400)
	6.44 (s) 1H (*tert* H)	331 (20 400)
	2.37 (s) 1H (Me)	
	2.44 (s) 1H (Me)	
13*a*	‖8.1–8.3 (qt) 1H (Ar)	282 (16 900)
	7.1–8.0 (m) 9H	293 (18 600)
	(Ar + OH + vinyl H)	316 (9700)
		325 (infl) (9000)

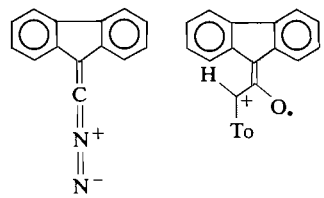
*Relative to internal TMS; s, singlet; d, doublet; qt, quartet; m, multiplet.
†Solvent: 95% EtOH.
‡Solvent: CCl_4.
§Solvent: $CHCl_3$.
‖Solvent: CH_3CN.

no indication of geometric isomers in **12***b* and *c*, so it is assumed that the isolated compounds are the least hindered *trans* isomers. The aromatic multiplet has a revealing feature for each of **12***a*, *b*, and *c*: a one-proton quartet,[4] is isolated at unusually low field around δ 8.0–8.4 p.p.m. This is interpreted as originating from the proton on C-1 of **12**, which is deshielded by the neighboring oxygen atom of the enol ether. The postulate is corroborated by the observation of a similar quartet for 9-(hydroxymethylene)-fluorene (**13***a*) at δ 8.1–8.3 p.p.m. In the u.v. spectra, four bands characteristic of the fluorenylidene chromophore appear around 285, 295, 315, and 330 nm for all three compounds and the enol **13***a*, whereas compounds containing the fluorene chromophore normally do not absorb above 310 nm. The mass spectra of **12***a*, *b*, and *c* show the expected molecular ions, and the i.r. spectra have no contradictory features.

[4]This quartet has four main peaks spaced approximately equidistantly and of similar intensities, and each shows a further poorly-resolved fine structure.



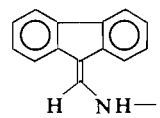
13 **14**



15 **16**

a, Z = OH; *b*, Z = N=CHTo;

c, X—Y = PhN—NPh;

d, Z = 

The structures of the products are compatible with intermediate formation of the desired allene oxide followed by its cycloaddition to a further molecule of carbonyl compound. Evidence for the intermediacy of a 1:1 adduct is the analogy to Curtin's work in which a 1:1 adduct (**11**) was isolated, and the following experimental evidence. During column chromatography over silica gel of the product mixture from the reaction between 9-(aminomethylene)-fluorene, acetophenone, and *n*-butyl nitrite, after all the acetophenone had been eluted, a later fraction had a p.m.r. spectrum showing the ratio of aliphatic to aromatic protons exactly right for the allene oxide **5***e* and yet the peaks corresponded to a 50/50 mixture of acetophenone and an unidentified aromatic hydrocarbon product (which must contain a multiple of eight hydrogen atoms). The hydrocarbon product was dark and polymeric in form and resisted attempts to purify it. It is only possible to explain the above observations in terms of decomposition of the chromatographic fraction in question; and it is possible that this fraction contained the allene oxide, which decomposed on work-up to acetophenone and the carbene **10**, which subsequently decomposed to the unidentified product. An alternative mechanism involving a carbonyl

ylid intermediate instead of **5** cannot however be ruled out, and Martin *et al.* (10) believe such a mechanism to occur during 1:2 adduct formation between dichlorocarbene and benzaldehyde. Evidence on this point could be obtained if the fluorenylidene-1,3-dioxolane products (**12**) would undergo reverse cycloaddition to give back the 1:1 adduct transiently, which could then add to an alkene to give a product, the structure of which would distinguish between the two mechanisms. Along this line **12***b* was heated at 200° for 1 h with dimethylfumarate, but starting material was recovered quantitatively. It is of interest, however, that in the mass spectrometer, **12***c* shows a 50% peak of mass 296 corresponding to the radical ion **16** of the 1:1 adduct, which must arise by loss of a tolualdehyde fragment from the molecule. Likewise **12***a* has a prominent peak *m/e* 234 (4%) corresponding to loss of an acetone fragment, but for **12***b* the peak due to loss of pivaldehyde (*m/e* 274 (4%)) is not prominent; instead a strong peak at 291 (15%) is observed by preferential loss of a *tert*-butyl group. A further uncertainty about the mechanism of the formation of **12** is the fact that it is not experimentally established whether or not the carbene **10** is an intermediate. One can equally well arrive at the products via the diazo intermediate **15** (11) which might then add to the carbonyl reactant before it loses a molecule of nitrogen. However if the carbene **10** is generated, its addition to two molecules of carbonyl compound is reasonable by analogy to other work (10, 12).

After having looked at cycloadditions to the C=O double bond, it was of interest to find out whether a C=N double bond would behave in the same way. Experimentally, neither *N*-phenyl- or *N*-methyl-*p*-tolualdimine yielded products of the desired type. Instead of the new compound *N*-(fluorenylidenemethyl)-*p*-tolualdimine (**13***b*) was obtained in both cases. This product was still obtained if the butyl nitrite was omitted in the reaction conditions. Its formation can be rationalized in terms of addition of 9-(aminomethylene)-fluorene across the double bond of the imine, followed by elimination of aniline or methylamine. The structure of **13***b* is supported by its ready hydrolysis with acid to **9** and tolualdehyde; in fact it was very difficult to isolate in good yield because of its instability to acids and bases. In the absence of catalysts, solutions of **13***b* remain unchanged when heated at 250° for half an hour.

Next to be looked at was the cycloaddition of carbene **10** to N=N double bonds. Azobenzene was treated with 9-(aminomethylene)-fluorene and *n*-butyl nitrite to yield a white crystalline substance m.p. 238–239° having correct elemental analysis and molecular weight (from mass spectroscopy) for the desired product **14***c*. The p.m.r. spectrum showed a complex multiplet between δ 5.7 and 8.2 p.p.m. Since absorption up-field of δ 6.5 p.p.m. is difficult to explain in terms of structure **14***c*, it is thought that **14***c* may have been formed initially, but rearranged intramolecularly to give a product containing a pyrrole ring. The u.v. spectrum is compatible with this idea since it shows a shoulder at 317 nm (ε 9600) indicating more conjugation than in fluorene.

Although adducts were successfully isolated in the cases reported above, yields were low and these positive results were only obtained after numerous variations in the conditions. The inherent difficulty of the reaction is that there exist numerous alternative side-reactions which the reactants can undergo. Most of the products isolated by column chromatography were non-crystalline, but three crystalline side-products were often isolated: the secondary amine **13***d*, 9,9′-biformyl-9,9′-bifluorenyl (**17**) and fluorenone. **13***d* has been suggested by Curtin *et al.* (9) to arise from insertion of the carbene **10** in the NH bond of **9**. He also proposed that **17** could be formed by initial nitrosation of the 9- carbon atom of 9-(aminomethylene)-fluorene followed by loss of nitric oxide to give a radical which dimerizes to give the imine of **17** and thence **17** itself by hydrolysis during work-up. Fluorenone might arise by autoxidation of **9** during work-up for which there are analogies in the literature (13).

Conclusion

Evidence is presented for the intermediacy of allene oxides **5** or their isomers **6**, **7**, and **8**, when 9-(aminomethylene)-fluorene (**9**) is treated with *n*-butyl nitrite in the presence of aldehydes and ketones. The intermediate would then add a further molecule of aldehyde or ketone to give the 1:2 adducts (**12**). It is suggested that further attempts to isolate a stable allene oxide of type **5** should be tried by using different aldehydes and ketones, since the concentration of **5** in the reaction vessel should depend directly on the relative rates of conversion of **10** to **5** and **5** to **12**, and both these rates should depend on the steric

and electronic effects of R′ and R″, the substituents on the aldehyde or ketone.

Experimental

Melting points were determined on a Meltemp apparatus and are uncorrected. I.r. spectra were obtained on a Beckman model IR5A spectrophotometer in Nujol mulls unless otherwise stated. U.v. spectra were run on a Unicam SP800 spectrophotometer at 25 °C in 1 cm cells. P.m.r. spectra were recorded on a Varian A60A spectrometer using an internal TMS standard. Mass spectra were run on a Varian-Mat CH-7 spectrometer. Microanalyses were performed by A. B. Gygli, Microanalysis Laboratories Limited, Toronto. The following experimental results are selected as examples from the many varied conditions used.

*9-(Hydroxymethylene)-fluorene (**13a**)*

The method used was similar to that of Wislicenus and Waldmuller (14). A mixture of 6.3 g potassium methoxide, 15 g fluorene, 6.7 g ethyl formate, and 75 ml dry ether was refluxed for 4 h over a steam bath. The mixture was cooled and then extracted with 75 ml of water. The water layer was washed with several small portions of ether and then acidified with dilute sulfuric acid. The oil which separated was extracted with ether, and the ether solution washed with dilute sodium bicarbonate solution and then water. The resulting solution was dried over anhydrous magnesium sulfate. Removal of drying agent and evaporation of the ether left a residue of 16.5 g crude product which was distilled under reduced pressure to give 9 g (51%) 9-(hydroxymethylene)-fluorene. I.r.: 3300, 1710, 1681, 1449, 781 cm^{-1}. U.v. and p.m.r.: see Table 1. This compound is a skin irritant, and contact with the hands should be carefully avoided.

*9-(Aminomethylene)-fluorene (**9**)*

The method used was similar to that of Von and Wagner (15). A solution of 12.5 g freshly distilled 9-(hydroxymethylene)-fluorene in 35 ml of dry benzene was placed in an ice bath and dry ammonia gas was passed in for 4 h. Evaporation of the solvent yielded a pale yellow solid, which was extracted with boiling 25% benzene in petroleum ether (b.p. 90–100 °C) mixture. One gram of the secondary amine **13***d* was left undissolved: m.p. 315–317 °C; i.r. 1645, 1274, 769, 719 cm^{-1}. The solution was evaporated to yield 9-(aminomethylene)-fluorene: m.p. 145–147°; i.r. 3472, 3356, 1661, 1285, 775, 734 cm^{-1}; p.m.r. δ 8.1–7.1 p.p.m. (multiplet) 9H (aromatic and vinyl) 5.5 p.p.m. (broad) 2H (NH_2).

*2,2,4,4-Tetramethyl-5-fluorenylidene-1,3-dioxolane (**12a**)*

Butyl nitrite, 8.24 g, was added to a refluxing solution of 9-(aminomethylene)-fluorene, 10.80 g in acetone, 200 ml under an atmosphere of nitrogen. After refluxing for 24 h the solvent was removed *in vacuo* to give 12.2 g of red oil. This was separated by quantitative t.l.c. using 2 mm thickness of Merck Kieselgel G and 15% *n*-hexane in benzene as the solvent. A u.v. lamp was used to visualize the bands. A band having $R_f = 0.3$ yielded 1.2 g of gum which on crystallization from acetone twice gave crystals (0.4 g) of 9,9′-biformyl-9,9′-bifluorenyl (**17**), m.p. 214–215° (lit. (9) m.p. 215–217°); p.m.r. ($CHCl_3$-*d*) δ 9.83 (singlet) 2H (CHO), 7.6–7.0 p.p.m. (multiplet) 16H (aromatic). Evaporation of the mother liquor followed by recrystallization of the gum from hexane yielded 5.0 mg of fluorenone, m.p. 81–82°; i.r. 1718, 1597, 1299, 919, 736; p.m.r. ($CHCl_3$-*d*) 7.8–7.2 p.p.m. (multiplet) (aromatic) identical with authentic sample. A chromatographic band having $R_f = 0.5$ yielded 0.34 g of gum which was crystallized from petroleum ether (b.p. 40–60 °C) to yield 0.17 g (1%) colorless crystals of 2,2,4,4-tetramethyl-5-fluorenylidene-1,3-dioxolane. This was further purified by vacuum sublimation at 90 °C: m.p. 145–146°; i.r. (KBr disk) 1613, 1370, 1263, 1163, 971, 917, 736 cm^{-1}; p.m.r. and u.v. see Table 1; m.s. base peak *m/e*: 206, parent peak (10%) *m/e*: 292.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.21; H, 6.91.

Reaction between 9-(Aminomethylene)-fluorene, n-Butyl Nitrite, and Acetophenone

n-Butyl nitrite (1.33 g) was added to a solution of 1.99 g 9-(aminomethylene)-fluorene and 1.56 g acetophenone in 200 ml benzene. After being kept at room temperature for 2 h, the solution was warmed to 60 ± 5° for 12 h. The solvent was then removed by a current of nitrogen to yield a red oil, which was poured onto a silica gel (Woelm activity 1) chromatographic column. Elution with benzene – *n*-hexane mixtures of increasing polarity yielded first acetophenone, then a very small amount of gum showing only aromatic protons in its p.m.r. spectrum, and next 150 mg of a gum which appeared to be a 50/50 mixture of acetophenone and an eight-proton aromatic compound.

*2,4-Di-tert-butyl-5-fluorenylidene-1,3-dioxolane (**12b**)*

To a solution of 3.2 g 9-(aminomethylene)-fluorene in 20 ml pivaldehyde was added 2.4 g of *n*-butyl nitrite. The reaction was carried out under nitrogen in a closed system connected to a gas burette. Eighty percent of the calculated volume of nitrogen expected based on 9-(aminomethylene)-fluorene was evolved after 12 h at room temperature. The excess pivaldehyde was evaporated *in vacuo* and the resulting oil chromatographed through a column of neutral alumina (Woelm activity 1). Elution with benzene – petroleum ether (b.p. 60–80°) of increasing polarity yielded 310 mg (5%) of 2,4-di-*tert*-butyl-5-fluorenylidene-1,3-dioxolane. It was recrystallized twice from petroleum ether (b.p. 60–80°): m.p. 150–151°; i.r. 1650, 1183, 1093, 980, 767, 732 cm^{-1}; p.m.r. and u.v. (see Table 1); mass spectra base peak *m/e*: 191, parent peak (15%) *m/e*: 348.

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.73; H, 8.08. Found: C, 82.82; H, 8.00.

*2,4-Di-p-tolyl-5-fluorenylidene-1,3-dioxolane (**12c**)*

n-Butyl nitrite (390 mg) was added to a solution of 490 mg 9-(aminomethylene)-fluorene and 4.33 g *p*-tolualdehyde in 200 ml benzene. The reaction mixture was kept at room temperature for 2 h, at 60 ± 5° for 12 h, and then the solvent was evaporated in a current of dry air to give a red oil which was separated by column chromatography over silica-gel (Woelm activity 1). Elution with *n*-hexane – benzene mixtures yielded 87 mg (8.3%) of 2,4-di-*p*-tolyl-5-fluorenylidene-1,3-dioxolane. It was recrystallized twice from petroleum ether (b.p. 60–80°), m.p. 213–214°; i.r. (KBr disc) 1653, 1198, 1176, 813, 769, 731 cm^{-1}; p.m.r. and u.v. see Table 1; mass spectra base peak *m/e*: 268, parent peak (7%) *m/e*: 416.

Anal. Calcd. for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.44; H, 5.86.

N-(Fluorenylidenemethyl)-p-tolualdimine (13b)

n-Butyl nitrite (580 mg) was added to a solution of 3.05 g *N*-phenyl-*p*-tolualdimine and 500 mg 9-(aminomethylene)-fluorene in 200 ml of benzene. After keeping the reaction mixture at room temperature for 2 h and then warming it to 60 ± 5° for 12 h, the solvent was removed by passing a current of dry air to give a red oil which was separated by column chromatography over silica-gel (Woelm activity 1). The fraction eluting with benzene (60%) – *n*-hexane (40%) solvent yielded 30 mg of yellow crystalline *N*-(fluorenylidenemethyl)-*p*-tolualdimine. It was purified by vacuum sublimation at 100° and recrystallization from ether: m.p. 146–147°; i.r. 1538, 1166, 966, 813, 778, 730 cm^{-1}; p.m.r. (CCl_4) δ 8.8–8.5 (quartet) 1H (C-1 aromatic proton), 8.14 (singlet) 1H (aldiminic CH), 7.8–6.9 (multiplet) 12H (aromatic and vinyl), 2.33 p.p.m. (singlet) 3H (methyl); u.v. λ_{max} (95% ethanol) 236 (ε 44 000), 261 (ε 36 000), 271 (ε 36 000), 375 (ε 36 000) nm; mass spectra parent peak *m/e*: 295.

Anal. Calcd. for $C_{20}H_{17}N$: C, 89.57; H, 5.84; N, 4.59. Found: C, 89.62; H, 6.07; N, 4.52.

Reaction between 9-(Aminomethylene)-fluorene, n-Butyl Nitrite, and Azobenzene

A solution of 2.14 g 9-(aminomethylene)-fluorene, 2.06 g azobenzene, and 1.16 g *n*-butyl nitrite in 250 ml dry ether was refluxed for 40 h. Since the i.r. spectrum showed that much 9-(aminomethylene)-fluorene remained, the solvent ether was distilled from the reaction mixture and 200 ml of the solvent benzene added. Azobenzene (210 mg) and 280 mg butyl nitrite were also added. After refluxing for a further 58 h, the i.r. spectrum of the mixture showed only a small NH band. The solvent was removed *in vacuo* to give a red oil. Column chromatography over silica-gel (Woelm activity 1) yielded 230 mg (5.8%) of a white crystalline compound eluted with 40% benzene in *n*-hexane. It was recrystallized from chloroform twice: m.p. 238–239°; i.r. (KBr disc) 1491, 1449, 773, 735, 699 cm^{-1}; p.m.r. ($CHCl_3$-*d*) δ 8.2–5.7 p.p.m. (multiplet); u.v. λ_{max}(CCl_4) 294 (ε 17 200), 305 (ε 17 600), 316 (inflection) (9600) nm; mass spectra base peak *m/e*: 77, parent peak (83%) *m/e*: 358.

Anal. Calcd. for $C_{26}H_{18}N_2$: C, 87.12; H, 5.06; N, 7.82. Found: C, 87.29; H, 5.20; N, 7.73.

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