Nitrosation Reactions of Primary Vinylamines. Possible Divalent Carbon Intermediates[1]

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2,2-Diphenylvinylamine (I) with isoamyl nitrite in boiling benzene or cyclohexene gives diphenylacetylene (III) in a yield as high as 85%. Aminomethylenefluorene (II), in benzene under similar conditions, gives the bis(fluorenylidenemethyl)amine (V). In cyclohexene, however, the product from II is the methylenecyclopropane derivative, 9-(bicyclo[4.1.0]hept-7-ylidene)fluorene (VI) in yields as high as 80%. The structure of VI is established by reduction with lithium aluminum hydride to the hydrocarbon VII which could be oxidized to the 9-hydroxyfluorene VIII which was synthesized independently by the reaction of bicyclo[4.1.0]hept-7-yllithium (IX) with fluorenone. Reaction of amine II with isoamyl nitrite and tetramethylethylene in boiling benzene gives 2,2,3,3-tetramethyl-1-fluorenylidenecyclopropane (X) but in only 10% yield. The amine I with nitrosyl chloride in methylene chloride or ether gives diphenylacetylene (III), cis- and trans-α-chlorostilbene (cis- and trans-XIII), α-chlorodiphenylacetaldehyde (XIV), nitric oxide, and benzophenone. Attempts to intercept the diazonium ion from the amine I by carrying out the nitrosyl chloride reaction at low temperatures and adding β-naphthol or its sodium salt before the reaction comes to room temperature have thus far proved unsuccessful. The reaction of the amine II with nitrosyl chloride gives as the major products 9,9'-biformyl-9,9'-bifluorenyl (XV) (60%) and nitric oxide (50%) together with small amounts (5%) of 9-chlorophenanthrene (XVI) and possibly traces (≤0.1%) of 9-chloromethylenefluorene (XVII). Diphenylacetaldehyde imine, the tautomer of I, rearranges extensively to I on standing in ethanol. The bearing of this observation on the methods of synthesis of the two tautomers is discussed. α-Chlorodiphenylacetaldehyde (XIV) is obtained from diphenylacetaldehyde either with sulfuryl chloride or with thionyl chloride. The latter reaction is of interest in connection with the conversion previously reported of 9-hydroxymethylenefluorene to the dimeric aldehyde XV.

In view of the contrast[4] between the alkyl diazonium ion with its inferred exceedingly great reactivity and the aryl diazonium ion, readily isolated as its salts, the behavior of structurally intermediate compounds is of interest. Two ways of altering the carbon skeleton of "aliphatic" amines so as to retard the loss of N_2 from the diazonium ion suggest themselves. The first approach, placement of the amine group at the bridgehead of a bicyclic system, has led to the successful coupling with β-naphthol of an "aliphatic" diazonium salt.[5] Work directed toward the second approach,

placement of the amine group on a carbon atom of a carbon–carbon double bond, is the subject of the present investigation. The reactions of two vinylamines, 2,2-diphenylvinylamine (I) and 9-(aminomethylene)fluorene (II), with nitrosyl chloride and with isoamyl nitrite are described.
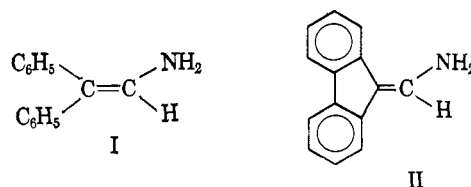
Diphenylvinylamine (I) was prepared by Krabbe, Seher, and Polzin[6] from the reaction of diphenylacetaldehyde with ammonia in methanol solution. Witkop,[7] on the other hand, failed to repeat the earlier synthesis and observed that the reaction of diphenylacetaldehyde with ammonia in diethyl ether solution gave the insoluble diphenylacetaldehyde imine, the tautomer of I. We have determined that in ether solution the imine is formed as previously reported and that in methanol the vinylamine I is formed as was found by Krabbe, Seher, and Polzin. Furthermore, spectral evidence suggested that diphenylacetaldehyde imine isomerized to its tautomer I. (Absorption at 283 mμ characteristic of I developed over a period of many hours when the imine tautomer was dissolved in ethanol solution, whereas the spectrum of I during this time remained unchanged.) It seems likely, therefore, that the imine is the kinetically favored product in ether or in an alcohol solvent and that it rearranges to the more stable tautomer I in the hydroxylic solvents. Survival of the imine in the reaction carried out in ether would, of course, be assisted by its insolubility. Aminomethylenefluorene (II) was obtained from ammonia and 9-formylfluorene in anhydrous ether solution. Both the synthesis and the structure determination had been reported by earlier investigators.[8]

Reactions of the Vinylamines I and II with Isoamyl Nitrite. Although the reactions of the two amines with nitrosyl chloride could be carried out at lower temperatures and appeared to offer more chance of access to the corresponding diazonium ions, another reagent, isoamyl nitrite in boiling benzene or ether, gave simpler product mixtures which are of greater synthetic interest and these will be discussed first. The use of ethyl and amyl nitrite to diazotize aniline in ethanol solution was reported by Griess[9] in 1865,

(1) Taken from the Ph.D. Theses of J. A. Kampmeier, 1960, and B. R. O'Connor, 1964, submitted to the University of Illinois.
(2) National Science Foundation Fellow, 1958–1960.
(3) National Science Foundation Fellow, 1960–1964.
(4) H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961.

(5) D. Y. Curtin, B. H. Klanderman, and D. F. Tavares, *J. Org. Chem.*, **27**, 2709 (1962).
(6) W. Krabbe, A. Seher, and E. Polzin, *Ber.*, **74**, 1892 (1941).
(7) B. Witkop, *J. Am. Chem. Soc.*, **78**, 2873 (1956).
(8) W. Wislicenus and R. Russ, *Ber.*, **43**, 2719 (1910); E. C. Wagner and F. D. Miller, *J. Org. Chem.*, **16**, 279 (1951).
(9) P. Griess, *J. Chem. Soc.*, **3**, 298 (1865).

and the reactions of nitrite esters with aromatic[10,11a] or aliphatic[11b] amines have been found to give products suggestive of diazonium ion (or diazotate) intermediates, followed by carbonium ion, radical, benzyne, or carbene depending on the system studied. Nitrite esters as diazotizing agents in nonpolar or neutral media could be expected to show unusual behavior in diazotization reactions because of the high basicity and nucleophilicity of the counterion RO^- produced, at least in a formal sense, concurrently with the diazonium ion as in I-D.

When diphenylvinylamine (I) was dissolved in boiling benzene and isoamyl nitrite added, diphenylacetylene (III) formed in 50–85% yield; reaction was complete in 3 to 5 hr. Infrared absorption at 1665 and 1278
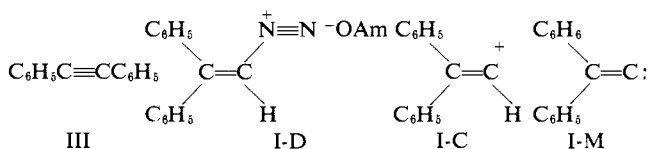
cm.$^{-1}$ suggested the presence of benzophenone, but no other product was isolated.[12] The mechanism for the rearrangement of amine I with isoamyl nitrite can reasonably be formulated in terms of a diazonium ion pair I-D (or the related covalently bonded diazotate) followed by the carbonium ion I-C or the divalent carbon intermediate I-M.[13] Rearrangement of a phenyl group from one doubly bound carbon atom to the other is reminiscent of the Beckmann rearrangement with its migration from doubly bound carbon to nitrogen. The rearrangement of 2,2-diarylvinyl halides with strong bases[14,15] involves a similar net structural change but may be quite remote from the point of view of mechanism. The reaction of 5,5-diphenyl-3-nitroso-2-oxazolidone (IV) with 50% sodium hydroxide at 0°

IV
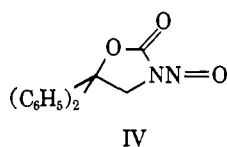
has been shown[16] to lead to the rapid evolution of nitrogen and the formation of diphenylacetylene (III) in nearly quantitative yield. Although a reaction sequence involving the diazonium ion I-D and carbonium ion I-C were proposed, the detailed mechanism of the reaction has not been established.

Whatever the mechanism of the conversion of the amine I to diphenylacetylene (III), it was of interest

to examine the reaction of isoamyl nitrite with the vinylamine II whose rearrangement should be greatly retarded by the restraint imposed by the bond between the two benzene rings. Reaction of the aminomethylenefluorene (II) with isoamyl nitrite in boiling benzene (under nitrogen) gave the divinylamine V in yields of 30–35%. This substance is a by-product in the synthesis of the vinylamine II from the aldehyde precursor and ammonia.[8,17] The structure of the divinylamine V was assigned by Kuhn and Neugebauer.[18]

V
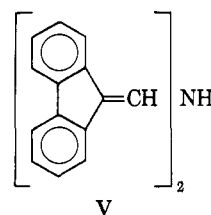
The possible involvement of an intermediate II-M with divalent carbon in the formation of the divinylamine V from vinylamine II and isoamyl nitrite suggested the desirability of carrying out the reaction of II with isoamyl nitrite in cyclohexene, an often used

II–M   VI

VII   VIII
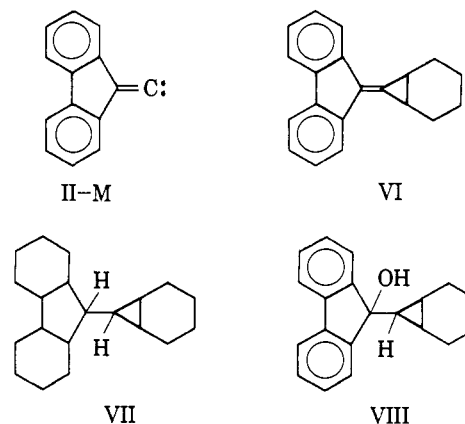
trapping agent for suspected divalent carbon intermediates.[13] When the reaction was allowed to proceed under reflux in a nitrogen atmosphere for 8 to 15 hr., 9-(bicyclo[4.1.0]hept-7-ylidene)fluorene (VI) was indeed obtained in yields of 55 to 80%. The structure of VI was confirmed by reduction with lithium aluminum hydride to the hydrocarbon VII, and oxidation of VII to the alcohol VIII by a procedure developed by Sprinzak[19] for the conversion of other 9-alkylfluorenes to the 9-alkyl-9-hydroxyfluorenes. The alcohol VIII was synthesized independently by reaction of the lithium reagent IX from 7-chlorobicyclo[4.1.0]heptane[20] with fluorenone.[21]

IX

(10) V. Meyer and G. Ambuhl, *Ber.*, 8, 1073 (1875); E. Bamberger, *ibid.*, 27, 668 (1894); S. Huang, *Hua Hsueh Hsueh Pao*, 25, 171 (1959); *Chem. Abstr.*, 54, 4489h (1959); J. I. G. Cadogen, *J. Chem. Soc.*, 4257 (1962).

(11) (a) M. Stiles, private communication; L. Friedman and F. N. Logullo, *J. Am. Chem. Soc.*, 85, 1549 (1963); (b) L. Friedman and F. D. Mendicino, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., 1963, p. 86Q.

(12) The formation of III from I under other diazotizing conditions has been observed independently by W. M. Jones (private communication).

(13) See J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964.

(14) T. L. Jacobs, "Organic Reactions," Vol. 5, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 40 ff.
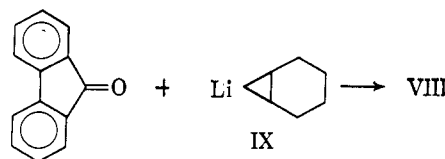
(15) See ref. 13, p. 83 ff.

(16) See M. S. Newman and A. E. Weinberg, *J. Am. Chem. Soc.*, 79, 2814 (1957), and references cited therein to this and other examples of the reaction.

(17) I. Von and E. C. Wagner, *J. Org. Chem.*, 9, 155 (1944).

(18) R. Kuhn and F. A. Neugebauer, *Monatsh.*, 94, 1 (1963).

(19) Y. Sprinzak, *J. Am. Chem. Soc.*, 80, 5449 (1958).

(20) G. L. Closs and L. E. Closs, *ibid.*, 82, 5723 (1960).

(21) Only one of the two probable stereoisomeric alcohols VIII was obtained. No direct evidence is available concerning the configuration but consideration of steric strain suggests that the compound is probably the isomer with the tetramethylene bridge *trans* to the fluorenyl group on the cyclopropane ring.

The reaction of the vinylamine II with isoamyl nitrite in the presence of tetramethylethylene in boiling benzene solution occurred in an analogous fashion, but the product X was produced in only 9% yield.

X   XI   XII
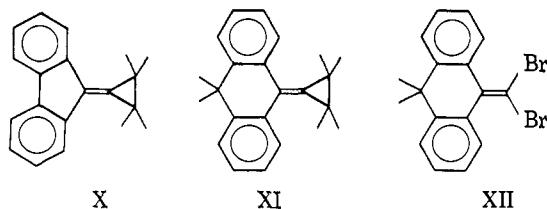
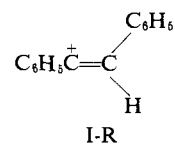Although the mechanisms of these reactions of vinylamines with isoamyl nitrite must await investigation, it is an attractive possibility that both in the diphenylvinyl and in the fluorenyl systems divalent carbon intermediates I-M and II-M are involved. The double-bonded divalent carbon atom has been reviewed by Hine.[22] It may be noted that a product XI, structurally related to the tetramethylcyclopropane X, has been obtained in 8% yield from the vinylidene bromide XII and phenyllithium in ether containing tetramethylethylene at −44°.[23] As Hine has pointed out,[24] the alkaline decomposition of the diphenyl-nitrosooxazolidone IV, studied by Newman and his associates,[16] may involve the same divalent carbon intermediate I-M as can be postulated for the conversion of the amine I to diphenylacetylene (III). The constraint added by the bond between the two phenyl rings in the fluorene system can, of course, explain the failure of the amine II to undergo rearrangement just as well in terms of a divalent carbon mechanism as by a carbonium ion mechanism.

Reactions of the Amines I and II with Nitrosyl Chloride. The reaction of diphenylvinylamine (I) with nitrosyl chloride was carried out in methylene chloride under a variety of conditions. Addition of a solution of nitrosyl chloride (30% molar excess) in methylene chloride to the amine in the same solvent at 25° with no attempt to exclude atmospheric oxygen gave two sets of products as shown below. Amounts of products obtained are reported as mole per cent based on amine employed. Results (shown in parentheses) of similar reactions carried out with nearly equimolar amounts of reagents at 0° in a nitrogen atmosphere were essentially the same. The formation of the three
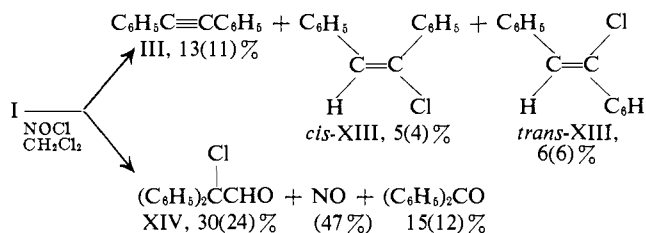
products with rearranged carbon skeleton (III, cis-XIII, and trans-XIII) is readily explained in terms of a carbonium ion rearrangement from the ion I-C, formed by loss of nitrogen from the diazonium ion, to the ion I-R. Closely related vinyl cations have been proposed

(22) See ref. 13, Chapter 5; see also M. Tanabe and R. A. Walsh, *J. Am. Chem. Soc.*, **85**, 3522 (1963); H. Günther and A. A. Bothner-By, *Chem. Ber.*, **96**, 3112 (1963); and H. Hartzler, *J. Am. Chem. Soc.*, **86**, 526 (1964).
(23) C. G. Carlson, Ph.D. Thesis, University of Illinois, 1963.
(24) See ref. 13, pp. 89 and 90.

I-R

as intermediates in the addition of trifluoroacetic acid to acetylenes[25] and in the solvolysis of α-bromostyrene and certain of its *para*-substituted derivatives.[26] Removal of a proton from the ion I-R leads to the acetylene III. Addition of chloride ion to the ion I-R leads to either of the two chlorides, cis- and trans-XI. The formation of the stereoisomeric chlorides in nearly equal amounts is of particular interest. The equilibrium constant for their interconversion has been estimated[27] as about 50 at 200–240°, trans-XI being the more stable. The difference in stability is probably even greater at room temperature, and since the three products are inferred to be stable under the reaction conditions their relative amounts are kinetically controlled. The nearly random formation of the three products is readily explained in terms of competing reactions of the intermediate I-R chloride ion pair if the reactions are highly exothermic and the transition states resemble the initial states,[28] in this perspective three slightly differently oriented I-R chloride ion pairs. Although the possibility cannot be rigorously excluded that the migration of a phenyl ring occurs by fragmentation of the ion I-C into phenylacetylene and a phenyl cation followed by readdition, such a mechanism seems highly unlikely since gas phase chromatography of several product mixtures showed no indication of the presences of even traces of phenylacetylene or chlorobenzene which would have been expected if the fragments became kinetically independant. In addition, a search for 2,2-diphenylvinyl chloride, the product of replacement without rearrangement, showed that a maximum of 2% could have been formed.

That the chlorine atom incorporated in three of the products originates from nitrosyl chloride rather than from the methylene chloride solvent is confirmed by the observation that when N_2O_4 was employed as the nitrosating agent in methylene chlorine at 0°, there was obtained diphenylacetylene in 10% yield together with 25% of benzophenone but no chlorinated products cis-XIII, trans-XIII, and XIV.

Attempts to intercept the diazonium intermediate I-D by addition of nitrosyl chloride to the amine I at −70° followed by a methanol solution of the sodium salt of β-naphthol gave no isolable azo compound. When β-naphthol in methylene chloride was added to a solution containing amine I and nitrosyl chloride at −78°, no azo compound was isolated and the yields of the replacement products III and XIII were not appreciably different from those obtained without the addition of β-naphthol. We conclude that the diphenylvinyl system does not provide the combined stabilization of the diazonium ion I-D and destabilization of the carbonium ions I-C and I-R formed by loss of nitrogen which are requisite for the isolation of

(25) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **85**, 2865 (1963).
(26) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964).
(27) T. W. J. Taylor and A. R. Murray, *J. Chem. Soc.*, 2078 (1938).
(28) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

stable diazonium intermediates, at least under the conditions employed here.

The formation in the reaction of nitrosyl chloride with vinylamine I of the chloroaldehyde XIV and nitric oxide in a ratio of approximately 1:2 is clearly to be ascribed to a competing reaction, probably independent of the one just considered. It is with reference to this reaction that the behavior of the fluorenylamine II with nitrosyl chloride is of primary interest. With reaction conditions comparable to those employed with the diphenylamine I, the major products from II were 9,9'-biformyl-9,9'-bifluorenyl (XV) and nitric oxide as shown below. Amounts of products formed are reported as mole per cent of vinylamine employed except in the case of the dimeric aldehyde XV where this quantity is doubled to give the mole per cent of fluorene units accounted for. The amounts of aldehyde XV formed were estimated from the n.m.r. spectrum of the reaction mixture; the aldehyde could be isolated in an amount containing 31–35% of the fluorene units in the initial amine II. 9-Chlorophenanthrene (XVI)

XV, 59(61)%

XVI, 5%   +   NO (48)%   XVII, <0.1%
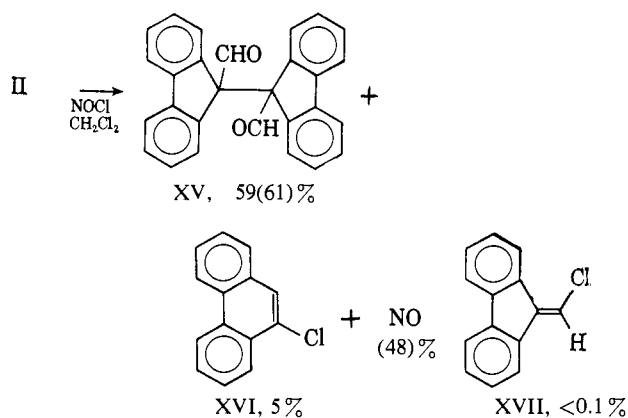
was isolated to the extent of 5 mole % and though the gas phase chromatography gave some indication of the formation of 9-chloromethylenefluorene (XVII), the product of replacement of the nitrogen function without rearrangement, it was not present to the extent of more than about 0.1 mole %. Results, indicated in parentheses, at 0° in a nitrogen atmosphere were not substantially different from those obtained when the reaction was carried out at 25° in the presence of oxygen.

The aldehyde XV had been reported previously as the product of the reaction of 9-(hydroxymethylene)-fluorene (XVIII) with thionyl chloride in diethyl ether.[29]


XVIII
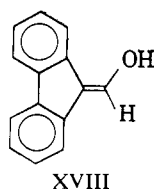
The reactions leading to nitric oxide, of nitrosyl chloride with amines, as exemplified by the reactions of I and II appear to be rare if not unprecedented. Control experiments with cyclohexylamine and n-propylamine showed that a maximum of 3% of nitric oxide could have been formed. The divergence in behavior of the

(29) E. J. Greenhow, A. S. Harris, and E. N. White, J. Chem. Soc., 3116 (1954).

vinylamines I and II might be explained in a variety of ways. As a working hypothesis the following scheme can be considered. Initial attack of nitrosyl chloride should occur at either a nitrogen atom or at the doubly bound carbon atom of the vinylamine to give ion A,

A   B   C
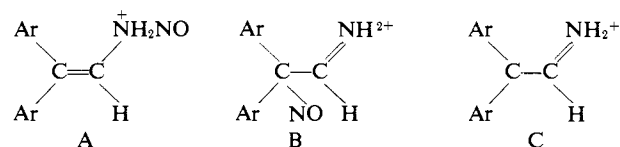
the customary diazotization intermediate,[30] or B. It seems plausible that the added stabilization of the ion radical C provided by the carbon unsaturation might make its formation from A by homolytic fragmentation competitive with the processes which normally lead A to the diazonium ion. Homolytic fragmentation of B can lead to the same ion radical C. This formulation leads to the conclusion that the ion radical C, when Ar = phenyl, reacts with nitrosyl chloride[31] to yield the chloroimmonium salt D which on hydrolysis, either by traces of water present in the reaction mixture or

D   E
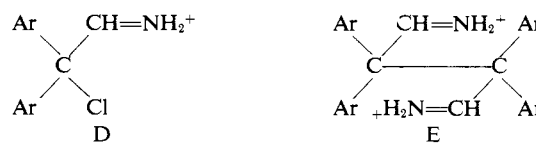
during the work-up, produces the chloro aldehyde XIV. Alternatively, the intermediate C, when Ar–C–Ar = fluorenyl, presumably because of its increased stability, can accumulate in solution sufficiently to dimerize to the immonium salt E of the dialdehyde XV. It should be noted that the experimentally observed ratio of nitric oxide to chloro- aldehyde in the reaction of amine I is about 2:1 and that in the reaction of amine II the ratio of nitric oxide to dimeric aldehyde XV is nearly 1:1 as required by this formulation. A reaction of amine I with nitrosyl chloride initiated at −78° and allowed to warm to room temperature gave substantially the same amounts of rearrangement products (III, cis-XI, and trans-XI) as were found in reactions initiated at higher temperatures but a marked reduction (to 5%) of chloro aldehyde XIV; a corresponding decrease in the amount of nitric oxide produced left the nitric oxide:chloro aldehyde ratio still approximately equal to 2. The mechanism considered above for the formation of dimer XV suggested the desirability of carrying out the reaction of the fluorenylamine II with nitrosyl chloride (at 0° under nitrogen) with the order of addition of reagents inverted. By addition of the amine to the nitrosyl chloride solution it might be possible to cause the ion radical C to react with nitrosyl chloride to form chloro aldehyde rather than the dimeric aldehyde XV. At the same time the amount of aldehyde XV is decreased, the amount of nitric oxide formed should increase. Although the anticipated decrease in dimeric aldehyde (from 50 to 35%) was observed, the amount of nitric oxide produced remained constant. This experiment, of course, provides no test of the proposed intermediacy of the ion radical C

(30) E. Müller, H. Haiss, and W. Rundel, Chem. Ber., 93, 1541 (1960).
(31) Analogy is provided by the known reaction of triphenylmethyl radical with nitrosyl chloride to form triphenylmethyl chloride and triphenylnitrosomethane [W. Schlenk, L. Mair, and C. Bornhardt, Ber., 44, 1169 (1911)].

since it is not known that the radical (with Ar–C–Ar = fluorenyl) would react with nitrosyl chloride sufficiently rapidly to be intercepted in this way.

The cleavage product, benzophenone, which was found in all reaction mixtures from amine I and nitrosyl chloride may well have been formed by more than one path. The chloro aldehyde XIV was found to be converted to benzophenone on standing in the atmosphere or even during gas phase chromatography. The reaction of aliphatic amines with nitrosyl chloride under conditions comparable to those used here customarily leads to appreciable amounts of the alcohol formed by replacement[32]; the product from amine I should be the enol form of diphenylacetaldehyde which is known to undergo autoxidation to benzophenone.[33]

The formation of 9-chlorophenanthrene (XVI) from vinylamine II, although in small yield, is particularly striking if it is considered that the rearranged chloride XVI predominated over the unrearranged chloride XVII by a factor of at least 20. Whether the rearrangement of the phenyl group occurred as a conventional concerted 1,2-phenyl migration (in spite of the fact that in the transition state the phenyl ring cannot achieve the ideal orientation perpendicular to the path of migration) or by a two-step cleavage and readdition of the phenyl ring is uncertain. There is a possible analogy to the Beckmann rearrangement of fluorenone oxime and related substances where similar steric considerations prevail Thus fluorenone oxime rearranges to chlorophenanthradene on treatment with phosphorus pentachloride but only at a much higher temperature than is required for benzophenone oxime which has no comparable restraint on the orientation of the phenyl rings.[34] Similarly, although benzophenone hydrazone gives benzanilide when treated with nitrous acid,[35] fluorenone hydrazone fails to undergo analogous rearrangement.[36] A study by Huisgen, Witte, and Ugi[37] on the effect of ring size on the rates of rearrangement of the series of oxime picrates XIX gave relative first-order rate constants

XIX
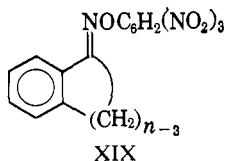
of 2×10^7, 9×10^4, and 1 for the compounds with $n =$ 8, 7, and 6. When n was 5 the rate was too slow to be measured.

The reaction of the fluorenyl aldehyde enol XVIII with thionyl chloride to give the dimeric aldehyde XV[29] is of interest because of its possible relationship to the reaction leading to the formation of XV from the amine II and nitrosyl chloride. Thus, fragmentation of a sulfinic ester chloride XX would lead to a formylfluorene radical F, the molecule SO, and a chlorine atom. Dimerization of F leads to the aldehyde XV and reaction of F with a chlorine atom would lead to
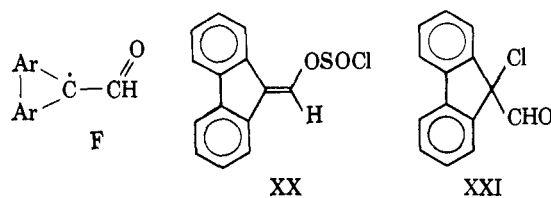
the α-chloro aldehyde XXI analogous to XIV. Although the chloro aldehyde XXI was not isolated in pure form, its presence in considerable amount in the reaction mixture from XVIII and thionyl chloride was suggested by infrared and n.m.r. examination of the oil remaining after the relatively insoluble dimer XV was filtered. The diphenyl chloro aldehyde XIV was isolated from reaction of diphenylacetaldehyde with thionyl chloride. Sulfur monoxide, a postulated product of these reactions, appears not to have been completely characterized, but it has long been suspected to be a product of certain reactions of thionyl chloride.[38]

Experimental[39]

2,2-Diphenylvinylamine (I). To 200 ml. of methanol, saturated with anhydrous ammonia, stirred, and cooled in an ice–water bath, was added over 15–30 min. 25 g. (0.13 mole) of diphenylacetaldehyde[40] in 50 ml. of methanol. Ammonia was then bubbled through the reaction mixture at room temperature for 12 hr. The precipitate was collected, washed, and recrystallized from absolute ethanol. The pale yellow needles (6.0 g., 24%) had m.p. 116–125° dec. After sublimation at 90–100° (0.03 mm.) the m.p. was 113–119° dec. The m.p. of 142° reported previously[6] was never observed. The ultraviolet spectrum (ethanol) with λ_{max} 283 mμ (ϵ 15,000) was used as the principal criterion of purity. N,N-Dimethyl-2,2-diphenylvinylamine,[41] m.p. 82.8–84.3°, prepared for comparison had λ_{max} 305 mμ (ϵ 15,400). The infrared spectrum of I (10% chloroform solution) showed a strong absorption at 1650 and doublet at 3400 and 3500 cm.$^{-1}$. The n.m.r. showed the vinyl proton absorption as a triplet centered at τ 3.32. (The N,N-dimethyl derivative of I had strong infrared absorption at 1617 cm.$^{-1}$ and a singlet vinyl proton at τ 3.85.)

Anal. Calcd. for $C_{14}H_{13}N$: C, 86.1; H, 6.7; N, 7.2. Found: C, 85.8; H, 6.7; N, 7.2.

(32) B. H. Klanderman, Ph.D. Thesis, University of Illinois, 1963.
(33) See, for example, J. W. Huffman and R. P. Elliott, *Chem. Ind.* (London), 650 (1963).
(34) L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, 11, 1 (1960).
(35) D. E. Pearson, K. N. Carter, and C. M. Greer, *J. Am. Chem. Soc.*, 75, 5905 (1953).
(36) C. L. Arcus and G. C. Barrett, *J. Chem. Soc.*, 2089 (1960).
(37) R. Huisgen, J. Witte, and I. Ugi. *Chem. Ber.*, 90, 1844 (1957).

(38) See D. J. Meschi and R. J. Myers, *J. Am. Chem. Soc.*, 78, 6220 (1956); A. C. Poshkus and J. E. Herweh, *ibid.*, 84, 555 (1962); H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *ibid.*, 84, 4772 (1962); Y. Okumura, *J. Org. Chem.*, 28, 1075 (1963).
(39) Melting points are corrected. Microanalyses and molecular weights (with a Mechrolab vapor pressure osmometer Model 301A) were provided by Mr. J. Nemeth and his associates. Infrared spectra were obtained with a Perkin-Elmer Model 137 Infracord or by Mr. Dick Johnson and his associates with Perkin-Elmer Models 21 and 521 spectrophotometers; n.m.r. spectra were recorded by Mr. B. Shoulders, Mr. O. W. Norton, and Mr. Dick Johnson and associates with Varian Model V-4300B or Model A-60 instruments. The n.m.r. data are reported in p.p.m. from tetramethylsilane as an internal standard taken as 10 (τ-scale). Ultraviolet spectra were obtained with a Cary Model 14M and a Bausch and Lomb Spectronic 505 spectrometer. Vapor phase chromatographic analyses were made with an Aerograph Model A-350-B dual column chromatograph with helium as the carrier gas and with injector and detector block temperatures usually about 25° higher than the column temperature. Spectra are recorded in the Ph.D. theses of ref. 1 and are available from University Microfilms, Ann Arbor, Mich.
(40) S. Daniloff and E. Venus-Danilova, *Ber.*, 59, 1032 (1926); D. J. Reif and H. O. House, *Org. Syn.*, 38, 26 (1958).
(41) A. Seher, *Arch. Pharm.*, 284, 371 (1951).

The N-acetyl derivative of I prepared by acetylation with acetic anhydride had, when recrystallized from ligroin, m.p. 162–164° (lit.[42] m.p. 162–163°).

N-Phenyl-N'-(2,2-diphenylvinyl)urea, m.p. 235–236°, was obtained from reaction of I with phenyl isocyanate at room temperature and purification by washing with petroleum ether (b.p. 70–90°).

Anal. Calcd. for $C_{21}H_{18}N_2O$: C, 80.2; H, 5.8; N, 8.9. Found: C, 80.1; H, 5.9; N, 8.9.

N,N-Bis(2,2-diphenylvinyl)amine, m.p. 136–141° dec. when recrystallized from ethanol (lit.[43] m.p. 144–146°), crystallized from the mother liquor remaining from the preparation of vinylamine I when it was allowed to stand and was also obtained when anhydrous hydrogen bromide was passed into a solution in dry ether of amine I, and the precipitate thus formed was recrystallized from ethanol.

Diphenylacetaldimine,[7] prepared from 2.0 g. of diphenylacetaldehyde in 20 ml. of ether saturated with ammonia, had m.p. 88–89° (lit.[7] m.p. 89°). A solution of the imine in absolute ethanol (1.0×10^{-4} M) had an initial absorbance at 283 mμ of 0.03. The absorbance rose to 0.22 in 68 hr. and to a limiting value of 0.65 in 408 hr. The amine I, on the other hand, showed no appreciable change in intensity at this wave length during the first 46 hr. and had decreased only 4% after 173 hr. No equilibrium constant can be estimated since the imine and vinylamine approached different limiting absorbances, possibly owing to disappearance of imine in part by a path other than tautomerization.

9-Hydroxymethylenefluorene (XVIII) (9-Formylfluorene). Reaction[44] of 43 g. (0.26 mole) of fluorene with ethyl formate gave, after acidification, extraction with ether, and evaporation of the ether, 35 g. of product which was used for the synthesis of the vinylamine II without further purification. Crystallization from carbon tetrachloride gave pale yellow plates, m.p. 117–123°, which in a potassium bromide disk showed only weak absorption at 1700 cm.⁻¹ but strong absorption at 1665, 1195, and 1175 cm.⁻¹. It is concluded that both the solid and dioxane solution contained mostly the enol form in disagreement with the assignment of the aldehyde form previously made to the solid.[44] The n.m.r. of the dioxane solution showed the hydroxylic proton absorption as a broadened singlet at τ 1.0. This shifted to τ −1.3 in dimethyl sulfoxide. A yellow oil, b.p. 104–106° (0.1 mm.), remaining from the crystallization of the enol was shown by the infrared (strong absorption at 1710 cm.⁻¹ as well as 3300 and 1675 cm.⁻¹) and the n.m.r. (doublets at τ 0.9, J = 2–3 c.p.s.; and τ 5.5, J = 2–3 c.p.s.) to be a mixture of aldehyde and enol forms contaminated with fluorenone. The aldehyde had previously been described[44] as a yellow oil, b.p. 169–172° (2 mm.).

9-(Aminomethylene)fluorene (II), m.p. 149–151° when purified by sublimation, was prepared by the method of Von and Wagner[17] in a yield of 70–75% after one recrystallization from benzene–petroleum ether (b.p. 60–90°). It was accompanied occasionally by a small

(42) W. Krabbe, H. H. Böhlk, and K. H. Schmidt, Ber., 71, 64 (1938).
(43) W. Krabbe and K. H. Schmidt, ibid., 72, 381 (1939).
(44) W. Wislicenus and M. Waldmuller, ibid., 42, 785 (1909).

amount of the secondary amine V, m.p. 310–312°, recrystallized from hot nitrobenzene (lit.[8,17] m.p. 316–317°).

The N-acetyl derivative, prepared from amine II and acetic anhydride and recrystallized from benzene, had m.p. 213–214° (lit.[17] m.p. 205–206°).

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.7; H, 5.6; N, 6.0. Found: C, 81.9; H, 5.5; N, 5.9.

Reaction of 2,2-Diphenylvinylamine (I) with Isoamyl Nitrite. To 1.0 g. (0.0051 mole) of amine I in 85 ml. of benzene was added 0.6 g. (0.005 mole) of isoamyl nitrite[45] (n^{25}D 1.3890). The reaction mixture became yellow but no gas was evolved until the solution was warmed to 70°. At that temperature the solution bubbled and gradually became orange. After 30 min. at 70–75°, 0.2 g. (0.0016 mole) of isoamyl nitrite was added and refluxing continued overnight. Evaporation of solvent and volatile products left 1.1 g. of red oil with maxima in the ultraviolet spectrum characteristic of diphenylacetylene (263, 271, 278, 287, and 296 mμ). Chromatography of 0.74 g. of product on alumina (elution with Skellysolve B (hexane)–benzene (75:25) yielded 0.38 g. (62% yield based on I) of white solid, m.p. 56–58°, with an infrared spectrum identical with that of authentic diphenylacetylene. Gas phase chromatographic analysis of a portion of the crude product on an 8-ft. Carbowax 20M (20% on Chromosorb) column at 215° showed two components with the retention times of diphenylacetylene and benzophenone. A quantitative estimate with gas phase chromatography using acenaphthene as an internal standard indicated 72% of diphenylacetylene and 15% of benzophenone. Other reactions carried out with variations in conditions gave similar results which are summarized in Table I. Reactions were carried out until spectra of aliquots showed no amine I remained.

Table I

Reacn. condn. I (g.); AmONO/I; ml. of solvent; reflux time (hr.); atmosphere	Yield, %——, Diphenylacetylene (III)	Benzophenone	Method of analysis
1.0; 3; 85ᵃ; 8; air	72	15	G.p.c.
	62	..	Isolation, m.p. 57–58°
1.2; 1.5; 60ᵃ; 3 or	52	..	λmax at 296 mμ
22ᵇ; N₂	57	Trace	G.p.c.
2.0; 2; 100ᶜ; 18;	85	..	Ultraviolet
N₂	73	..	Isolation, m.p. 57–58°
0.4; 2; 70ᵈ; 33;	50	..	Ultraviolet
N₂			

ᵃ Benzene. ᵇ G.p.c. analysis of aliquots showed 52% of III after 3 hr., 54 after 5.5 hr.; 57% after 22 hr. ᶜ Cyclohexene. ᵈ Ether.

Reaction of 9-(Aminomethylene)fluorene (II) with Isoamyl Nitrite in Benzene. Isoamyl nitrite[45] (1.4 g., 0.012 mole) was added to 2.0 g. (0.0096 mole) of amine II in 100 ml. of benzene under reflux. The reaction mixture became orange and, in a few minutes, bright red. The insoluble solid, filtered after 5 hr., amounted to 0.60 g. (31%) of golden yellow fibers, m.p. 310° dec., which showed no melting point depression when mixed with the divinylamine[17] V obtained as a by-

(45) W. A. Noyes, Org. Syn., 16, 8 (1938).

product in the preparation of II. The ultraviolet-visible spectrum was identical with that of divinyl-amine V with maxima at 290 mμ (ϵ 17,000), 301 (16,000), 415 (65,000), and 436 (77,000).

Reaction of Amine II with Isoamyl Nitrite in Cyclohexene. 9-(Bicyclo[4.1.0]hept-7-ylidene)fluorene (VI). Isoamyl nitrite[45] (3.5 g., 0.03 mole) was added to 4.0 g. (0.021 mole) of amine II in 200 ml. of freshly distilled cyclohexene under reflux. After 15 hr. the solvent was removed leaving 6.5 g. of orange solid.[46] A quantitative estimate of the yield of VI, made by comparing the absorbance in the ultraviolet spectrum of the reaction mixture with plots of absorbance *vs.* concentration of purified VI at the wave lengths of maxima at 314, 285, 256, and 230 mμ, gave values of 90–95%. Chromatography on alumina (elution with Skellysolve B (hexane)–benzene) and crystallization from ethanol gave 3.8 g. (80%) of VI, m.p. 125–126°. Recrystallization from ethanol of a sample from a reaction carried out in a similar way gave m.p. 126–127°. The ultraviolet spectrum (ethanol) had maxima at 230 mμ (ϵ 54,500), 246 (29,000), 256 (45,000), 275 (17,000), 285 (21,500), 301 (17,500), and 314 (21,500), in good agreement with the spectrum reported[47] for 9-ethylidenefluorene.

A solution of amine II in benzene heated under reflux for 48 hr. at 75° without the isoamyl nitrite gave essentially unchanged starting material as shown by the infrared and ultraviolet spectra.

Anal. Calcd. for $C_{20}H_{18}$: C, 93.0; H, 7.0; mol. wt., 258. Found: C, 92.8, 93.1; H, 6.9, 7.1; mol. wt. (benzene), 260.

Reaction of Amine II with Isoamyl Nitrite in Tetramethylethylene–Benzene. 9-(Tetramethylcyclopropylidene)fluorene (X). Isoamyl nitrite (1.2 g., 0.010 mole) was added to a solution of 1.4 g. (0.0073 mole) of amine I in a mixture of 50 ml. of tetramethylethylene[48] (b.p. 71–74°, n^{26}D 1.4070) and 20 ml. of benzene under reflux in a nitrogen atmosphere. After 18 hr. the solvent was removed to give 3.53 g. of red oil of which 3.4 g. was chromatographed on alumina. Elution with Skellysolve B (hexane) yielded 0.17 g. (9%) of white solid whose ultraviolet spectrum had seven maxima with relative intensities similar to those of the cyclohexene adduct VI. Recrystallization of 0.070 g. from 95% ethanol gave 0.040 g. of white needles, m.p. 178–180°. The ultraviolet spectrum in ethanol had maxima at 229 mμ (ϵ 53,000), 246 (29,000), 254 (44,000), 275 (17,000), 285 (19,500), 300 (16,500), and 313 (21,500).

Anal. Calcd. for $C_{20}H_{20}$: C, 92.3; H, 7.7; mol. wt., 260. Found: C, 92.0; H, 7.7; mol. wt. (benzene), 246. The n.m.r. spectrum showed a complex multiplet at τ 2.6 and a singlet at τ 8.60.

(46) An observation which we hope to pursue further was made during a reaction of 0.82 g. of amine II with a 100% excess of isoamyl nitrite and a 300% excess of cyclohexene in 40 ml. of benzene under nitrogen at 75°. After about 3.5 hr. crystals began to be deposited, and after 8 hr. a considerable quantity of yellow needles had appeared. They had redissolved at the end of 24 hr. when the ultraviolet spectrum of the mixture indicated that 20% of the product VI had accumulated. Another equivalent of isoamyl nitrite was added and the reaction continued for 24 hr. longer, at which time the ultraviolet analysis indicated that 30% of VI had formed.

(47) E. J. Greenhow, D. McNeil, and E. N. White, *J. Chem. Soc.*, 986(1952).

(48) G. K. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 140 (1936).

Reduction of VI with Lithium Aluminum Hydride. 9-(Bicyclo[4.1.0]hept-7-yl)fluorene (VII). To 0.175 g. (0.0046 mole) of lithium aluminum hydride suspended in 25 ml. of ether distilled from lithium aluminum hydride was added slowly 1.68 g. (0.0065 mole) of the bicyclic olefin VI in 30 ml. of dry ether. After 3.5 hr. of refluxing, the reaction mixture was hydrolyzed with crushed ice and acidified with dilute sulfuric acid; the organic layer was separated, washed, and dried over magnesium sulfate. Removal of the solvent left 1.6 g. of white solid VII, m.p. 85–88°. Recrystallization from 95% ethanol gave 1.24 g. (73%) of VII, m.p. 88.5–89.5°. A similar reduction carried out in tetrahydrofuran for 3 hr. at room temperature and decomposed with Dry Ice gave only a trace of an acidic fraction but a 37% yield of VII (purified by chromatography on alumina, elution with Skellysolve B–benzene, 90:10), m.p. 86–90°, was obtained and recrystallized from ethanol to give m.p. 88.5–90°. There was no melting point depression when the two samples were mixed. The ultraviolet spectrum in ethanol had λ_{max} 264 mμ (ϵ 16,500), 289 (5900), and 301 (9200), in good agreement with the literature values[47] for 9-methylfluorene.

The n.m.r. spectrum showed, in addition to the complex aromatic and cyclohexane proton absorptions present in the olefin VI, a doublet centered at τ 6.28 (J = 12 c.p.s.) and a complex pattern between τ 9.15 and 9.65, each with an area corresponding to one proton. To simplify the n.m.r. spectrum, the reduction of VI was carried out with lithium aluminum deuteride in tetrahydrofuran to give VII deuterated at the tertiary carbon of the cyclopropane ring, m.p. 87–90°; mixture melting point with VII showed no depression. The n.m.r. spectrum of the deuterated compound showed a singlet at τ 6.23 (instead of the doublet at 6.28) and the complex pattern at τ 9.15–9.65 had disappeared. A similar reduction of the olefin VI in tetrahydrofuran followed by decomposition of the reaction mixture with deuterium oxide (>99% D) gave a product, m.p. 88.5–90°, whose n.m.r. spectrum showed no doublet at τ 6.28, and the complex pattern "simplified" to a quartet (with broad peaks, however) centered at τ 9.3.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.3; H, 7.7; mol. wt., 260. Found: C, 92.4; H, 7.8; mol. wt. (benzene), 250.

Reaction of Bicyclo[4.1.0]hept-7-yllithium with Fluorenone. 9-Hydroxy-9-(bicyclo[4.1.0]hept-7-yl)fluorene (VIII). To 1.2 g. of lithium (0.173 g.-atom) containing 0.8% sodium (and prepared by pounding into thin sheets and coating with copper powder[49]) in 25 ml. of ether (distilled from lithium aluminum hydride) was added with vigorous stirring 9.0 g. (0.07 mole) of 7-chlorobicyclo[4.1.0]heptane[20] over 15 min. The solution was cooled to −20° and stirring continued at −20 to 0° for 5 hr. to give the lithium reagent IX. Fluorenone (6.3 g., 0.035 mole) was added at 0°, and, after 3 hr. of stirring at 0° and 8 hr. at 30°, methanol was added and then saturated aqueous ammonium chloride. Separation of the ether layer followed by washing, drying over anhydrous magnesium sulfate, and evaporation of the ether left 10.9 g. of a brown oil which when washed with pentane gave 3.4 g.

(49) D. Y. Curtin and W. J. Koehl, *ibid.*, **84**, 1967 (1962).

(35%) of pentane-insoluble solid, m.p. 119–123°. Crystallization of 0.66 g. from 95% ethanol (decolorizing carbon) gave 0.45 g. of VIII, m.p. 121–123°. In addition to the characteristic fluorene and cyclohexane proton absorption in the n.m.r. there was a quartet at τ 9.53 (relative area 1) attributed to the unique tertiary hydrogen. The infrared spectrum (10% chloroform solution) had strong absorption at 3600 cm.$^{-1}$ and no significant absorption between 1605 and 1900 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.9; H, 7.3. Found: C, 86.8; H, 7.0.

Oxidation[19] *of the Hydrocarbon VII.* To 1.0 g. (0.0038 mole) of the hydrocarbon VII in 10 ml. of dry pyridine was added 0.2 ml. (0.04 g., 0.0002 mole) of Triton B solution prepared by mixing 10 ml. of 40% Triton B in methanol with 10 ml. of freshly distilled pyridine, removal of the methanol under reduced pressure, and addition of 10 ml. of pyridine. Dry oxygen was passed through the stirred solution for 3 hr. with the occasional addition of more pyridine to replace losses by evaporation. After the addition of 1 g. of sodium bisulfite in 10 ml. of water, the mixture was stirred for 2 hr. and poured into 50 ml. of water. Extraction with ether, washing of the ether extracts with 10% aqueous ferrous ammonium sulfate and water, drying over magnesium sulfate, and removal of the ether left 0.73 g. of yellow oil which was chromatographed (thin layer) by elution on silica gel G with benzene–Skellysolve B, 25:75. Development with 1% potassium permanganate was used to locate the product which was recovered from the alumina as 0.1 g. of light yellow solid which, crystallized from 95% ethanol (charcoal), amounted to 0.025 g. (2.5%), m.p. 121–123°. Identity with the authentic alcohol VII was established by comparison of the n.m.r. and infrared spectra and by the failure of a mixture to show a melting point depression.

Purification and Standardization of Nitrosyl Chloride. When not otherwise indicated, solutions in methylene chloride or ether were prepared by adding a measured volume of liquefied commercial nitrosyl chloride to the solvent or by bubbling the commercial gas into the solvent at 0°. "Purified nitrosyl chloride" was obtained by refluxing the liquid for 3 hr. with a 1-ft. Vigreux column surrounded by a Dry Ice bath initially at −78° and then distilling the residue twice.[50] Nitrosyl chloride solutions were titrated for total chloride ion after hydrolysis (by addition of a 5-ml. aliquot to excess 1 *N* potassium hydroxide solution). After back-titration to the phenolphthalein end point with 1 *N* nitric acid and buffering with 2 g. of sodium bicarbonate, the solution was titrated to the silver chromate end point with standard 0.10 *N* silver nitrate.

Reaction of Amine I with Nitrosyl Chloride. A number of reactions were carried out initially to establish the nature of the products and to develop suitable analytical methods. As an example, to a slurry of 0.5 g. (0.02 mole) of calcium hydride[51] in 200 ml. of methylene chloride was added 4.0 g. (0.02 mole) of amine I, and the solution was cooled to −78° in a Dry

(50) J. R. Morton and H. W. Wilcox, *Inorg. Syn.*, 2, 126 (1946).
(51) The calcium hydride was added in this run (but not in most others) in the hope that it would scavenge hydrogen chloride formed in the reaction. It seemed to have no effect at all on the reaction.

Ice–acetone bath. (Not all of the amine was soluble at −78°.) A solution of nitrosyl chloride in methylene chloride (50 ml., 0.4 *M* or 0.02 mole) was added rapidly. The mixture was dark green but gradually became yellow on warming to room temperature. In other experiments it was noted that even after 90 min. at −78° gas evolution occurred on warming to −20 to 0°. An aliquot (100 ml.) was withdrawn and evaporated to leave 1.4 g. (4.2 g. corrected to total product) of orange oil which when washed with carbon tetrachloride gave 0.2 g. (14% of product) of a yellow insoluble solid which was not investigated further. Removal of the solvent from the carbon tetrachloride soluble fraction left an oil the ultraviolet spectrum (ethanol) of which showed the characteristic fine structure of diphenylacetylene. Chromatography of 1.3 g. on 85 g. of silica gel (elution with Skellysolve B–benzene, 75:25) gave 0.47 g. (1.27 g. corrected to entire product). An n.m.r. spectrum compared to a spectrum of an authentic mixture suggested the oil consisted primarily of diphenylacetylene (III) and *cis*- and *trans*-chlorostilbenes XIII in a ratio of 1:3:3 (yields of 4, 13, and 14%). Gas phase chromatographic separation at 205° with an 8-ft. column (20% QF-1 on Chromosorb) gave separation into three peaks: *cis*-XIII, retention time 4.2 min.; III, retention time 4.4 min.; and *trans*-XIII, retention time 8.0 min. Under the same conditions the retention times of authentic III and *trans*-XIII were 4.4 and 8.0 min. With an 8-ft. column (20% Carbowax 20M on Chromosorb) at 230°, retention times of the fractions were 8.9, 10.4, and 18.3 min. Authentic III and *trans*-XIII had times of 10.4 and 18.3 min. The *cis*-XIII fraction (8.9 min.) was collected as a clear oil with ultraviolet maxima at 224 mμ (ϵ 18,000) and 270 (11,000), identical with *cis*-XIII, and retention times on the two columns above identical with those of authentic *cis*-XIII under the same conditions. The second fraction from the silica gel chromatography above (eluted with Skellysolve B–benzene, 50:50) amounted to 0.09 g. (0.24 g. corrected, or 5%) of chloro aldehyde XIV, identified by its infrared and n.m.r. spectra in carbon tetrachloride (absorption at 1737, 2710, and 2820 cm.$^{-1}$ and singlets at τ 0.4, area 1, and τ 2.73, area 10). In a reaction similar to that above, except that chromatography was carried out on Florisil, the first fraction when subjected to gas phase chromatography permitted the isolation of *trans*-XIII as a solid, m.p. 50.5–52°, identical with an authentic sample. In another reaction in which the carbon tetrachloride soluble products were not chromatographed but submitted directly to gas phase chromatography (8-ft. column, 20% Carbowax 20M on Chromosorb at 225°), there were six peaks with retention times of 12.0 (*cis*-XIII, 12.0), 13.9 (III, 13.9), 16.9 (benzophenone, 17.0), 20.1 (diphenylacetaldehyde, 20.2), 25.2 (*trans*-XIII, 25.2), and 38.0. The diphenylacetaldehyde was collected; infrared maxima 1725, 2700, and 2800 cm.$^{-1}$ and also 1665 and 1278 cm.$^{-1}$ (absorption of benzophenone).

A control reaction carried out with 2.0 g. (0.01 mole) of diphenylacetaldehyde in 125 ml. of methylene chloride at −78° and 25 ml. (0.01 mole) of 0.36 *M* nitrosyl chloride in methylene chloride at −78° for 2 hr. showed only the aldehydic proton absorption in the n.m.r. (carbon tetrachloride) of diphenylacetalde-

Table II

Reaction conditions I (g.); NOCl/I; ml. solvent; temp. (°C.); time (hr.); atmosphere	Products (mole % of amine I employed)					
	Chlorostilbenes (XIII) cis	trans	Acetylene III	Aldehyde XIV	Benzophenone	Nitric oxide
1.4; 1.3; 125,[a] 25; 10; air	5	6	13	30	15	..
2.0; 0.9; 175,[a] 25; 10; air	..	..	..	20[b]	..	..
1.0; 1.6; 57,[a] 0, 0.25, N$_2$	3	5	10	22	18	45
1.0; 1.8; 110,[a] 0–25; 2.5; N$_2$	5	6	12	27	7	47
2.0; 1.0; 117,[a] 0; 1.3; N$_2$	..	..	..	24	..	47
1.0; 1.2[c]; 80[a]; 0; 1; N$_2$	8	12	7	6	8	40
1.0 1.0; 108[a]; −78; 1.5[d]; air	6	12	3	35	11	..
1.0; 1.0; 108[a]; −78; 1.5[d]; air	5	14	5	26	14[e]	..
1.4; 1.0; 120[a]; −78; 1; air	..	..	..	26	..	..
1.0; 1.04; 53[a]; −78; 0.75[d]; N$_2$	7	13	8	..	9	11
1.0; 1.04; 100[a]; −78; 0.75[d]; N$_2$	8	14	8	..	7	11
1.0; 1.08; 110[a]; −78; 1[d]; N$_2$	8	13	6	5	4	14
1.1; 1.0; 63[a]; −78; 0.75[f]; N$_2$	0	0	5	0	5	19
1.0; 1.0; 108[a]; −78; 0.5[f]; N$_2$	0	0	3	0	12	..
1.2; 0.85; 104[a]; −78; 2[d,g]; N$_2$	2	3	14	..	7	..
0.6; 1.07; 55[h]; −78; 2[d]; air	0	0	3	0	22	..
1.0; 0.98; 108[i]; −78; 10[j]; air	2	1	10	13	20	..
0.63; 1[k]; 55[a]; 0; 3[d]; air	0	0	10	0	25	..

[a] Methylene chloride was the solvent. [b] Isolated as the dinitrophenylhydrazine derivative, m.p. 163–165° dec. [c] Amine I in 50 ml. of methylene chloride added to 31 ml. of 0.19 M nitrosyl chloride (CH$_2$Cl$_2$) over 90 min. [d] Allowed to warm to room temperature after time indicated. [e] Benzoin (5%) also found in the g.p.c. (retention time, 33.6 min). [f] Quenched at −78° with 0.39 g. of n-propylamine. [g] After 5 min., 10 ml. of CH$_2$Cl$_2$ containing 0.72 g. of β-naphthol was added. [h] The solvent (50 ml. of CH$_2$Cl$_2$) contained 2.5 g. of dry pyridine. [i] Anhydrous ether. [j] Allowed to warm to 25° during 10 hr. [k] Dinitrogen tetroxide used instead of nitrosyl chloride.

hyde (doublet τ 0.15), and the absorption at τ −0.5 characteristic of the chloro aldehyde XIV was completely absent.

Quantitative Determination of Products. For more accurate quantitative determinations the original reaction mixture was washed with water, the organic layer dried over anhydrous sodium sulfate, and the resulting oil (approximately equal in weight to the weight of original amine I employed) was used without further manipulation. The amounts of acetylene III, chlorostilbenes XIII, and benzophenone were determined by gas phase chromatography with an 8-ft. column (20% Carbowax 20M on Chromosorb at 225°). A weighed amount of acenaphthene, comparable to the amounts of products, was added to an aliquot (approximately 0.3 g. carefully weighed in each case) and 0.5 ml. of benzene and the mixture were injected. Calibration curves were made by plotting the ratio of weights of components III and XIII to the weight of acenaphthene vs. the ratio of peak areas in chromatographs of standard two-component mixtures, and the curves so obtained were used to obtain amounts of products from the unknown mixtures. Retention times were benzene, 2 min.; acenaphthene, 7 min.; cis-XIII, 10 min.; III, 12 min.; benzophenone, 14 min.; and trans-XIII, 21 min. The slight sensitivity of the relative amounts of the three products (III and the XIII isomers) to the drastic changes in temperature, order of mixing of reagents, and work-up procedure indicates that they were not being interconverted to a major extent. Chloro aldehyde XIV was determined on the original mixture from the n.m.r. spectrum. A weighed amount of 2,6-dimethoxybenzaldehyde, τ −0.5, was added to a solution of an aliquot in methylene chloride. The ratio of the area of the CHO absorption of XIV at τ +0.2 to that of the standard gave the amount of XIV. The results are presented in Table II.[52] The nitric oxide was determined by entrainment in a nitrogen

(52) Detailed data are presented in the thesis of ref. 1.

stream bubbled through a bottle packed with glass helices containing 100 parts by volume of 95% sulfuric acid and two parts by volume of 70% nitric acid.[53] The nitrosylsulfuric acid thus formed was converted by dilution with water to nitrous acid which was oxidized with excess standard potassium permanganate. The unreacted permanganate was reduced by excess standard ferrous sulfate which was back titrated with permanganate solution. A blank, determined with the sulfuric–nitric acid solution, was used to correct the amount of permanganate consumed (the blank amounted to about 25% of the total permanganate consumed which limits the accuracy of the method). Results of determination of known amounts of nitric oxide generated by sweeping nitrogen through a solution of ferrous sulfate and nitrous acid[54] gave 96 and 82% of the correct value. Control experiments using n-propylamine or cyclohexylamine instead of amine I produced a maximum of 1–2% of nitric oxide.

Reaction of 9-(Aminomethylene)fluorene (II) with Nitrosyl Chloride. To 2.5 g. (0.013 mole) of II in 110 ml. of methylene chloride at 25° was added rapidly a solution of 26 ml. (0.013 mole) of 0.5 M nitrosyl chloride in methylene chloride. Vigorous gas evolution occurred for several minutes. The solution turned red-brown, then yellow-orange, but remained clear. After 1 hr. the solvent was removed to give 2.8 g. of crude products. The dimeric aldehyde XV, isolated below, determined from an n.m.r. spectrum of this product in methylene chloride using the absorption of the aldehydic proton at τ 0.0 and 2,6-dimethoxybenzaldehyde (τ −0.6) as an internal standard as was done for the chloro aldehyde XIV in the previous section, accounted for 59 mole % of the fluorenyl groups of the starting amine II. Chromatography of 2.5 g. of the solid on acid-washed alumina gave three fractions. A yellow oil (0.08 g.) eluted with Skelly-

(53) L. H. Milligan, *J. Phys. Chem.*, 28, 544 (1924).
(54) A. A. Blanchard, *Inorg. Syn.*, 2, 126 (1946).

Table III

—Reaction conditions—, II (g.); NOCl/II; ml. of CH₂Cl₂; temp. (°C.); time (hr.); atmosphere	Dialdehyde XV, % fluorene units of II acctd. for (2 × mole % based on II)	Nitric oxide, mole %	9-Chloro-phenanthrene (XVI), mole %	9-Chloro-methylene fluorene (XVII), mole %
2.5; 1.0; 136; 25; 1; air	59 (31)[a]	..	5	0.2
1.0; 1.04; 106; 0; 0.25; N₂	50 (35)[a,b]	48		..
	47	48	(5)[c]	..
0.5; 0.92; 28; 0; 1; N₂	61	..	..	..
1.0; 1.02; 53[d]; 0; 1; N₂	35	50	..	..
2.0; 1.2; 60[e]; 0; 1.5+; N₂	35 (16)[f]	46	..	..
1.0; 1.4; 109; −78; 0.75[g]; N₂	47, 53 / 56, 51	62 / 62	..	..
1.0; 1.4; 109; 78; ..; N₂	64[h]	33,[i] 53[j] / 55,[k] 63[h]	..	..

[a] The value given first is that based on the n.m.r. analysis; that in parentheses is based on the weight of isolated product, m.p. 215–217°. [b] When a similar run was carried out with purified NOCl, the phenanthrene, separated by chromatography, amounted to 7%; aldehyde, not completely purified, amounted to 58%. [c] Thin layer chromatography on silica G with methylene chloride as eluent showed five spots; two corresponded to XV and XVI R_f values. Chromatography gave a fraction shown by ultraviolet at 349 mμ (ε 210) to be 76% pure. [d] Amine II in 30 ml. of CH₂Cl₂ was added over 1 hr. to 23.5 ml. of CH₂Cl₂ solution containing the NOCl. [e] Amine II in 60 ml. of CH₂Cl₂ was added over 1.5 hr. to 20 ml. of CH₂Cl₂ containing the NOCl. The solution was then allowed to warm to room temperature before the work-up. [f] Isolate XV, m.p. 213–215°. [g] The reaction was held at −78° for the time indicated, then allowed to warm to 25°. [h] After 3.5 hr. at −78° and then warming to room temperature. [i] After 0.33 hr. [j] After 1.7 hr. [k] After 3.5 hr.

solve B was submitted to gas phase chromatography on a 10-ft. column packed with 20% SF-96 on Chromosorb at 250° and showed two components with retention times of 23.4 (small shoulder) and 24.6 min. A benzene solution of a mixture of 9-(chloromethylene)-fluorene (XVI) and 9-chlorophenanthrene (XVII) had similar peaks with retention times of 23.4 (shoulder) and 24.6 min. The two fractions were collected (without separation) and the infrared spectrum was identical with that of XVI except for weak absorption at 775 and 765 cm.⁻¹. Authentic XVII had strong absorption at 772 and 762 cm.⁻¹. The ultraviolet spectrum in ethanol of the mixture was similar to that of XVI except for enhancement of the maximum at 312 mμ and was essentially identical with the spectrum of a mixture of XVI and XVII, 20:1. The second fraction obtained from the alumina chromatography by elution with 50:50 Skellysolve B–benzene gave 0.11 g. of an orange oil not identified. The third fraction obtained by elution with methylene chloride gave 1.1 g. of light tan aldehyde dimer XV. Recrystallization from benzene–ether gave 0.7 g. of XV as pale yellow crystals, m.p. 216–218° (lit.²⁹ m.p. 217–218°). A mixture with authentic XV showed no melting point depression. Identification was confirmed by comparison of infrared and n.m.r. spectra. In reactions where it was determined, the analysis for nitric oxide was carried out in the same way as in the reactions of amine I above. Results are summarized in Table III.

cis- and trans-α-Chlorostilbene.⁵⁵ cis- and trans-XIII were prepared from meso- and dl-stilbene dichloride, respectively, by dehydrohalogenation with 0.5 M ethanolic potassium hydroxide. The cis isomer, cis-XIII, was an oil, b.p. 107.5–108.5° (0.65 mm.), n^{19}D 1.6281; lit.⁵⁵ b.p. 97–99° (0.25 mm.), n^{20}D 1.6280. G.p.c. with an 8-ft. column packed with 20% Carbowax 20M on Chromosorb showed a single component with a retention time of 11.5 min. at 225°. The n.m.r.

(55) S. J. Cristol and R. S. Bly, J. Am. Chem. Soc., 82, 155 (1960).

(25% solution in deuteriochloroform) showed the vinyl proton resonance at τ 3.10. The ultraviolet spectrum (ethanol) had λmax 223 mμ (ε 20,000) and 271 mμ (ε 11,000). The trans isomer, trans-XIII, crystallized from ethanol had m.p. 51–53° (lit.⁵⁵ m.p. 52–54°). G.p.c. carried out by injecting a benzene solution and using an 8-ft. column packed with 20% Carbowax 20M on Chromosorb at 225° showed in addition to the solvent two peaks, one with the retention time of 12.4 min. characteristic of cis-XIII and an area less than 1% of the total absorption due to XIII, and the other due to trans-XIII with a retention time of 22.8 min. The n.m.r. spectrum (30% solution in deuteriochloroform) showed vinyl proton absorption at τ 3.02.⁵⁶ The ultraviolet spectrum in ethanol had λmax 220 mμ (ε 13,000) and 284 mμ (ε 22,000).

2-Chloro-2,2-diphenylacetaldehyde (XIV). Diphenylacetaldehyde (20.0 g., 0.10 mole) in 200 ml. of ether was heated under reflux for 4.5 hr. with 13.5 g. (0.10 mole) of sulfuryl chloride. After 10 hr. at 25° the mixture was distilled through a short Vigreux column. Aldehyde XIV (17.2 g., 75%) was a pale yellow oil, b.p. 128–130° (0.6 mm.), n^{18}D 1.5969. The infrared spectrum (10% solution in carbon tetrachloride) had strong absorption at 1737, medium at 2820, and weak at 2700 cm.⁻¹. The n.m.r. (30% carbon tetrachloride solution) had singlets at τ 0.35 and 2.70 (relative areas 1.1:9.9); the CHO absorption was at τ 0.2 in methylene chloride. The aldehyde XIV, stable indefinitely under nitrogen, decomposed rapidly on standing in air to form, among other products, benzophenone. For example, a sample which had stood 4 days had less than half of the absorbance at 1737 cm.⁻¹, and new strong absorption

(56) The observation that the vinyl proton of the cis isomer is at higher field is in agreement with results found with the parent stilbenes: D. Y. Curtin, H. Gruen, and B. A. Shoulders, Chem. Ind. (London), 1205 (1958); D. Y. Curtin, H. Gruen, and Y. G. Hendrickson, J. Am. Chem. Soc., 83, 4838 (1961); N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog," Vol. 1., Varian Associates, Palo Alto, Calif., 1962, Spectra No. 305 and 506.

had appeared at 1665, 1278, 940, and 920 cm.$^{-1}$. Chromatography of 1.5 g. of XIV on silica gel (elution with Skellysolve B–benzene, 50:50) gave a sample (1.0 g.) prepared for analysis by heating under reduced pressure to remove traces of solvent, after which it had n^{18}D 1.5962 and was stored under nitrogen. G.p.c. of a benzene solution of a sample of XIV (possibly contaminated with a small amount of benzophenone) at 225° on an 8-ft. column packed with 20% Carbowax on Chromosorb showed, in addition to solvent, peaks with retention times characteristic of XIV, 19.9 min.; benzophenone, 16.8 min.; and diphenylacetaldehyde, 25.3 min. (relative areas 81:15:4).

Anal. Calcd. for C$_{14}$H$_{11}$ClO: C, 72.9; H, 4.8; Cl, 15.4. Found: C, 72.8; H, 4.6; Cl, 15.4.

2,4-Dinitrophenylhydrazine derivatives of XIV were obtained from 1.0 g. (0.004 mole) of XIV and 1.0 g. (0.005 mole) of 2,4-dinitrophenylhydrazine in 20 ml. of diglyme following the procedure of Shine.[57] After addition of 3 ml. of acetic acid and standing for 2 hr. at 25° and 10 hr. in a refrigerator, water was added until the solution became turbid, and after 2 hr. more in the refrigerator 0.50 g. of dark red crystalline solid, m.p. 160–161°, separated. Recrystallization from ethanol–ethyl acetate gave dark red needles, m.p. 164–165°, with ultraviolet–visible absorption (ethanol) at 285 mμ (ϵ 6700) and 400 mμ (ϵ 26,000). It seems likely this compound is 2-[2',4'-dinitrobenzeneazo]-1,1-diphenylethylene although no other structural evidence is available.

Anal. Calcd. for C$_{20}$H$_{14}$N$_4$O$_4$: C, 64.2; H, 3.8; N, 15.0. Found: C, 63.9; H, 3.7; N, 15.1.

A second substance (0.40 g.), a light orange solid, m.p. 185° dec., was deposited from the filtrate above after a few hours standing, and more of the product was obtained when water was added. Recrystallized by the addition of water to a solution in hot ethanol–ethyl acetate, the total was 0.30 g., m.p. 186° dec. The ultraviolet spectrum (in ethyl acetate) with λ_{max} 348 mμ (ϵ 39,000) resembled that of a golden yellow product, m.p. 200° dec., λ_{max} 345 mμ (ϵ 38,000), obtained previously[58] from dinitrophenylhydrazine and α-hydroxydiphenylacetaldehyde and believed to be α-(2,4-dinitrophenylhydrazino)diphenylacetaldehyde 2,4-dinitrophenylhydrazone.

(57) H. J. Shine, *J. Org. Chem.*, **24**, 1790 (1959).
(58) D. Y. Curtin and Y. G. Hendrickson, *ibid.*, **21**, 1260, (1956).

Anal. Calcd. for C$_{26}$H$_{20}$N$_8$O$_8$: C, 54.6; H, 3.5; N, 19.6. Found: C, 54.3; H, 3.5; N, 19.4.

9,9'-Biformyl-9,9'-bifluorenyl (*XV*), m.p. 215–217 (lit.[29] m.p. 217–218°), was prepared from 9-hydroxymethylenefluorene (XVIII) and thionyl chloride in ether[29] and recrystallized from benzene. The infrared spectrum (10% in chloroform) had absorption at 1715, 2725, and 2830 cm.$^{-1}$. The n.m.r. (20% in methylene chloride) had a singlet at τ 0.2 and complex multiplet between τ 2.5 and 3.3 (relative areas 1.1:7.9).

Concentration of the ether solution remaining after crystallization of the aldehyde XV (29% yield) gave an oil with a weight 60% of the starting XVIII, with a sulfurous odor and carbonyl absorption in the infrared at 1720 and 1735 cm.$^{-1}$ as well as at 2700 and 2800 cm.$^{-1}$. The n.m.r. in carbon tetrachloride showed a major aldehyde absorption at τ 0.85 and a somewhat smaller one at τ 0.25. Reaction of 5 g. of XVIII with an equimolar amount of sulfuryl chloride in ether[59] gave after 4 hr. under reflux 5.5 g. of an oil of which the infrared spectrum showed carbonyl absorption at 1735 cm.$^{-1}$, and the n.m.r. showed a singlet only at τ 0.9.

9-Chlorophenanthrene (*XVI*), m.p. 46–50° (lit.[60] m.p. 53–53.5°), was obtained by the chlorination of phenanthrene[60] and purified by distillation (b.p. 130–133° at 0.2 mm.) and recrystallization from ethanol. The ultraviolet spectrum in ethanol agreed with that previously reported.[60]

Reaction of Diphenylacetaldehyde with Thionyl Chloride. 2,2-Diphenylacetaldehyde (10 g., contaminated by about 8% of benzophenone) in 100 ml. of ether was heated under reflux for 2 hr. with 17 g. of thionyl chloride. After 2 days a portion of the product was distilled through a 1-ft. Vigreux column to give the chloro aldehyde XIV, b.p. 98° at 0.1 mm., as the major product (about 60% yield). Identification was made by the infrared spectrum which showed the characteristic absorption at 1735, 2700, and 2820 cm.$^{-1}$ and by the n.m.r. which had the singlet at 0.35 due to the CHO. Chromatography of a portion of the product on silica gel (elution with 1:1 benzene–Skellysolve B) gave a 75% recovery of XIV which may not yet have been pure since a carbon analysis was 0.7 low.

(59) The use of sulfuryl chloride as a chlorinating agent for aldehydes was suggested by the work of C. L. Stevens, E. Farkas, and B. Gillis, *J. Am. Chem. Soc.*, **76**, 2695 (1954).
(60) P. B. D. de la Mare, N. V. Klassen, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961).