ArCH$_3$), 6.40–5.92 (m, 4 H, CH$_2$CO, OCH$_3$CH$_3$, the dd of CH$_2$CO is not distinguishable from the quartet of OCH$_2$CH$_3$), 2.78–2.10 (m, 8 H, ArH).

Anal. Calcd for $C_{19}H_{18}O_4$: C, 73.5; H, 5.8. Found: C, 73.9; H, 5.9.

On pyrolysis of 0.80 g of **7** at 200° for 2 hr there was obtained 0.6 g (97%) of n,ψ-anhydride, mp and mmp (with above anhydride) 168–169°.

1-Ethoxyvinyl 3,6-Dimethyl-2-benzoylbenzoate (8).—Treatment of 3,6-dimethyl-2-benzoylbenzoic acid[11] as described[4a] yielded **8**, mp 73–75° in almost quantitative yield. Recrystallization from ether–petroleum ether (bp 30–60°) gave with little loss colorless **8**: mp 74.5–75.5°; nmr 8.77 (t, 3 H, J = 7.5 Hz, OCH$_2$CH$_3$), 7.89, 7.49 (each s, 3 H, ArCH$_3$), 6.53 (dd, 2 H, J = 3.5 Hz, =CH$_2$), 6.30 (q, 2 H, J = 7.5 Hz, OCH$_2$CH$_3$), 2.88–2.10 (m, 7 H, ArH).

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.1; H, 6.2. Found: C, 73.9; H, 6.2.

3-Carboethoxymethyl-4,7-dimethyl-3-phenylphthalide (8_{LE}).—Pyrolysis of 4.68 g of **8** at 220–230° for 1 hr yielded a mixture which on trituration afforded 0.55 (8%) of solid, mp 255–260°. After two recrystallizations from benzene–petroleum ether a solid, mp 278–280°, was obtained with little loss. Because of limited solubility no nmr was run. We are uncertain of the structure of this anhydride.

Anal. Calcd for $C_{32}H_{26}O_5$: C, 78.3; H, 5.3. Found: C, 78.6; H, 5.7.

Bulb-to-bulb distillation of the remainder of the pyrolysis products (0.05 mm) yielded a liquid which was redistilled to yield 4.1 g (85%) of 8_{LE} as a pale yellow oil which distilled (two-bulb system) with the heating bath at 185–190° (0.0014 mm); nmr 9.05 (t, 3 H, J = 7.0 Hz, OCH$_2$CH$_3$), 7.88, 7.30 (each s, 3 H, ArCH$_3$), 6.38 (dd, 2 H, J = 14.8 Hz, CH$_2$CO), 6.11 (q, 2 H, J = 7.0 Hz, OCH$_2$CH$_3$), 2.70 (each s, 7 H, ArH).

Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.1; H, 6.2. Found: C, 73.9; H, 6.3.

3-Carboxymethyl-4,7-dimethyl-3-phenylphthalide.—On hydrolysis with barium hydroxide, 2.0 g of 8_{LE} yielded 1.4 g (89%) of colorless needles (from chloroform–benzene) of acid: mp 155.0–155.5°; nmr (acetone-d_6), 7.84, 7.31 (each s, 3 H each, ArCH$_3$), 6.24 (dd, J = 15.0 Hz, CH$_2$CO), 2.63 (s, 1 H, disappears on addition of D$_2$O, COOH), 2.58 (s, 7 H, ArH).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 73.0; H, 5.4. Found: C, 73.0; H, 5.5.

Pyrolysis Experiments, Table I.—The esters **5–8** were heated in flasks which had been steamed out for 30 min and dried. Disappearance of nmr bands in the τ 6.33–6.48 region (characteristic of the vinyl hydrogens) was taken as a measure of completion of reaction.

Registry No.—**5**, 6158-56-1; **5_{LE}**, 6158-57-2; **6**, 24766-40-3; **6** anhydride, 24766-41-4; **6_{LE}**, 24766-42-5; **7**, 24766-43-6; **7** anhydride, 24766-44-7; **8**, 24766-45-8; **8_{LE}**, 24766-46-9; 3-carboxymethyl-7-methyl-3-phenylphthalide, 24766-47-0; 3-carboxymethyl-4,7-dimethyl-3-phenylphthalide, 24766-48-1.

[11] M. S. Newman and B. T. Lord *J. Amer. Chem. Soc.* **66**, 733 (1944).

The Acid-Catalyzed Nitramine Rearrangement. VII. Intramolecularity[1-3]

WILLIAM N. WHITE AND J. TERENCE GOLDEN

Department of Chemistry, The Ohio State University, Columbus, Ohio 43219, and
Department of Chemistry, University of Vermont, Burlington, Vermont 05401

Received December 29, 1969

Concurrent rearrangement of N-nitro-N-methylaniline and *p*-fluoro-N-nitro(^{15}N)-N-methylaniline yielded *p*-nitro-N-methylaniline containing a considerable excess of ^{15}N. This indication of intermolecularity in the nitramine rearrangement was strengthened by the exclusion of other possible pathways for the formation of *p*-nitro(^{15}N)-N-methylaniline. It was found that the yields of nitroanilines were reduced and the nitro-group exchange was eliminated in the presence of reducing agents, suggesting that they intercept the species involved in the intermolecular process. These results are readily interpreted in terms of a previously proposed mechanism.

Most mechanisms for the nitramine rearrangement are based upon the need to account for the intramolecularity of the reaction. A varied series of studies support the assumption of intramolecularity. Rearrangement of N-nitroaniline in 85% sulfuric acid at 10° yielded only *o*- and *p*-nitroanilines while nitration of aniline under similar conditions gave chiefly the *meta* and *para* isomers.[4,5] If the nitramine dissociated into aniline and nitronium ion during the rearrangement, then the product should have been identical to that from direct nitration.

A number of investigators have shown that a nitro group is not transferred from rearranging nitramine to an easily nitratable substance added to the reaction medium. Thus, the acid-catalyzed rearrangement of 2,4,6-tribromo-N-nitroaniline in the presence of either acetanilide or 2,4-dichloroaniline failed to produce nitroacetanilide or 2,4-dichloro-6-nitroaniline.[6] Similarly, it was found that when N,4-dinitro-N-methylaniline was converted to 2,4-dinitro-N-methylaniline in the presence of xylene or phenol, no nitroxylenes or nitrophenols were formed and no *p*-nitro-N-methylaniline (from loss of a nitro group) could be detected. Thus, no substance that could nitrate acetanilide, 2,4-dichloroaniline, *p*-xylene, or phenol existed during these rearrangements. However, the behavior of N,2,4-trinitro-N-methylaniline[5] is somewhat paradoxical. In 80% sulfuric acid, this compound yielded the expected product, 2,4,6-trinitro-N-methylaniline, but in other acid media, such as dilute hydrochloric acid and acetic–sulfuric acid mixtures, the denitration product, 2,4-dinitro-N-methylaniline, was obtained. Furthermore, when the rearrangement was conducted in sulfuric acid in the presence of *p*-xylene, 2-nitro-1,4-xylene and 2,4-dinitro-N-methylaniline were isolated

---

[1] Previous papers in this series: (a) W. N. White, D. Lazdins, and H. S. White, *J. Amer. Chem. Soc.*, **86**, 1517 (1964); (b) W. N. White, C. Hathaway, and D. Huston, *J. Org. Chem.*, **35**, 737 (1970); (c) W. N. White and J. R. Klink, *ibid.*, **35**, 965 (1970); (d) W. N. White, J. T. Golden, and D. Lazdins, *ibid.*, **35**, 2048 (1970); (e) W. N. White and H. S. White, *ibid.*, **35**, 1803 (1970).

[2] Part of this work has been reported in a preliminary form: W. N. White, J. R. Klink, D. Lazdins, C. Hathaway, J. T. Golden, and H. S. White, *J. Amer. Chem. Soc.*, **83**, 2024 (1961).

[3] This work was supported by Grants G-7345 and GP-1970 from the National Science Foundation.

[4] A. F. Holleman, J. C. Hartogs, and T. van der Linden, *Ber.*, **44**, 704 (1911).

[5] E. D. Hughes and G. T. Jones, *J. Chem. Soc.*, 2678 (1950).

[6] K. J. P. Orton, *Chem. News*, **106**, 236 (1912).

along with the usual rearrangement product. This evidence might suggest that rearrangement was occurring by dissociation of the substrate into nitronium ion and 2,4-dinitro-N-methylaniline followed by reaction of these species to form the isomerization product. Other easily nitratable substances could also then react with the nitronium ion. Weak acids would be of insufficient strength to affect the renitration. However, this interpretation is apparently incorrect. It was found impossible to nitrate 2,4-dinitro-N-methylaniline in 80% sulfuric acid, while *p*-xylene was converted to 2,3-dinitro-1,4-xylene. In addition, although nitration of phenol in 80% sulfuric acid gave nitrophenol, the latter product was not obtained when the trinitro compound was rearranged in the same medium in the presence of phenol even though 2,4-dinitro-N-methylaniline, the denitration product, was formed from the nitramine.

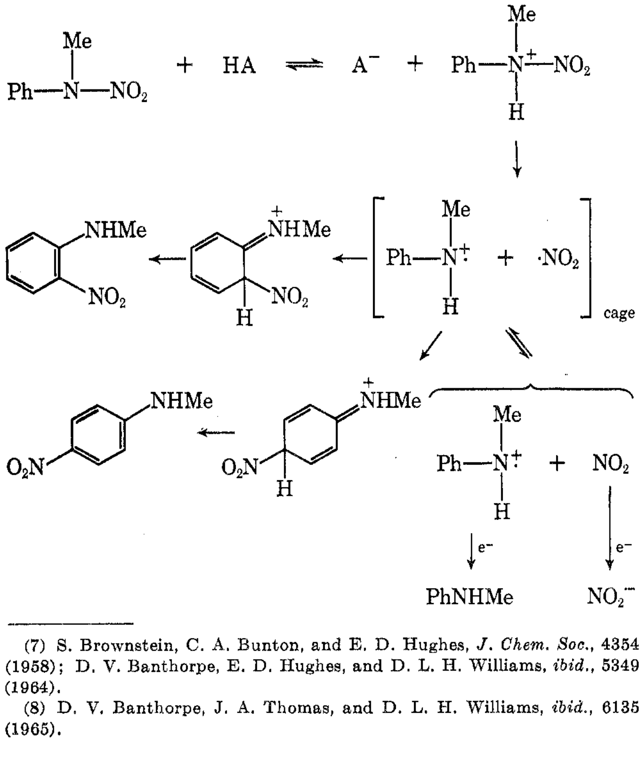
Additional evidence supporting an intramolecular course for the rearrangement was obtained by rearranging N-nitroaniline[7] and N-nitro-N-methyl-1-naphthylamine[8] in the presence of ^{15}N-labeled nitric acid and ^{15}N-labeled potasssium nitrite. In no case was an appreciable excess of ^{15}N detected in the nitrated products indicating that the nitramine nitro group did not become equilibrated with the pool of nitric or nitrous acid in the medium.

In spite of this overwhelming evidence for the intramolecularity of the nitramine rearrangement, there are some bothersome unexplained discrepancies such as the above-described reactions of N,2,4-trinitro-N-methylaniline. Recently reported studies of the effect of reducing agents on the rearrangement of N-nitro-N-methylaniline[1e] can be most reasonably interpreted on the basis of the following mechanism (Chart I) which involves an intermolecular pathway as a side reaction. All of the above quoted evidence for intramolecularity can be interpreted on the basis of this mechanism. Only *ortho*- and *para*-substituted products would be formed since significant odd-electron density in the anilinium radical occurs only at these positions. Nitration of easily nitratable foreign substances would not be expected unless the caged radicals dissociate and a reducing agent is present to reduce nitrogen dioxide to nitrous acid. The latter may then cause nitration through nitrosation or it may disproportionate to nitric acid. The perplexing results with N-2,4-trinitro-N-methylaniline become understandable in terms of this mechanism. The rearrangement of this compound may be largely intermolecular. In the absence of a reducing agent the dissociated radicals recombine to form a rearrangement product. However, in the presence of a reductant the normal reaction is diverted: denitration product and nitrous acid are formed from the nitramine. Phenol, if present, will be nitrosated and the resulting compound will be polymerized by the strong acid. Nitration of xylene may also occur through nitrosation. Product incorporation of ^{15}N from ^{15}N-labeled nitrous or nitric acid in the medium would not be expected since the oxidation state of the nitrogen in the rearrangement intermediate is different.

These considerations make it seem likely that the nitramine rearrangement may have an intermolecular component in those cases where dissociation of the caged radicals occurs at a rate similar to or faster than rebonding of the radicals in the cage to form the intermediates leading to nitrated products.

If the aromatic nitramine rearrangement is, in part, intermolecular, then crossover of a nitro group from one molecule to another should occur. An attempt to detect this exchange was made by concurrently rearranging N-nitro-N-methylaniline and *p*-fluoro-N-nitro(^{15}N)-N-methylaniline.

CHART I



Results and Discussion

Rearrangement of a mixture of *p*-fluoro-N-nitro-(^{15}N)-N-methylaniline and N-nitro-N-methylaniline did, in fact, result in an excess of ^{15}N in a product from the unlabeled nitramine (Table I). This indicates that the nitro groups from the two nitramines became mixed in solution and returned indiscriminately to the two different aniline moieties. Thus, the nitramine rearrangement is at least partially intermolecular.

TABLE I

^{15}N CONTENTS OF REARRANGEMENT[a] PRODUCTS OF MIXED NITRAMINES

10^4 *M* $PhNMeNO_2$	10^4 *M* *p*-FC_6H_4-$NMeN^{15}O_2$[b]	10^4 *M* *p*-HOC_6H_4-OH	% ^{15}N in *p*-$O_2NC_6H_4NHMe$ Found	Calcd
5.64	4.41	0.00	2.9	3.1
2.48	4.41	0.00	4.5	4.2
5.15	4.42	25.50	0.4[c]	0.4[c]

[a] $HClO_4$ = 0.511 *M*, $NaClO_4$ = 0.500 *M*, HSO_3NH_2 = 0.05 *M*, 40.0°. [b] 13.6% ^{15}N. [c] Natural abundance of ^{15}N is 0.4%.

The per cent of ^{15}N expected in the *p*-nitro-N-methylaniline may be calculated from the following pieces of information: (1) the molarity of each nitramine in the mixture, (2) the per cent of ^{15}N in each of these compounds, (3) the rearrangement rates of each

---

[7] S. Brownstein, C. A. Bunton, and E. D. Hughes, *J. Chem. Soc.*, 4354 (1958); D. V. Banthorpe, E. D. Hughes, and D. L. H. Williams, *ibid.*, 5349 (1964).

[8] D. V. Banthorpe, J. A. Thomas, and D. L. H. Williams, *ibid.*, 6135 (1965).

nitramine, (4) the degree of intermolecularity in the reaction of each nitramine, and (5) the percentage of each nitrated product formed. The first of these pieces of data was obtained during the preparation of the solution. The second was available from the direct determination of the ^{15}N contents of the nitramines. The rate of reaction of N-nitro-N-methylaniline under the conditions of the concurrent rearrangement was 1.5×10^{-3} sec^{-1} or almost identical with the rearrangement rate of *p*-fluoro-N-nitro-N-methylaniline (1.6×10^{-3} sec^{-1}) under similar circumstances (Table II). To simplify the calculations these rates were assumed to be identical.

TABLE II

NITRAMINE REARRANGEMENT[a] PRODUCTS AND RATES

Compound	10^4 *M* *p*-HOC$_6$H$_4$-OH	10^3 k_1 (sec^{-1})	Products % 2	Products % 4
PhNMeNO$_2$	0.00	1.5	49	31
	2.20	1.5	42	19
p-FC$_6$H$_4$NMeNO$_2$	0.00	1.6	78	
	2.20	1.6	47	

[a] HClO$_4$ = 0.511 *M*, NaClO$_4$ = 0.500 *M*, HSO$_3$NH$_2$ = 0.05 *M*, 40°.

It was shown in previous work[1e] that a fraction of the nitramine rearrangement could be diverted by reducing agents and that this portion of the reaction corresponds to an intermolecular component of the process: dissociated free radicals capable of reduction are formed. Thus, it should be possible to determine the extent of intermolecularity by finding the amount of rearrangement which can be diverted in the presence of a reducing agent. Rearrangement of N-nitro-N-methylaniline and *p*-fluoro-N-nitro-N-methylaniline were carried out in the presence and absence of hydroquinone (a reductant). The results are listed in Table II and show that 39% of the acid-catalyzed reaction of N-nitro-N-methylaniline is intermolecular and 53% of the reaction of *p*-fluoro-N-nitro-N-methylaniline is intermolecular. Furthermore, 39% of all of the *p*-nitro-N-methylaniline formed must arise from an intermolecular pathway.

The above information was used to obtain calculated values in Table I. There is excellent agreement between the experimental and calculated data. Since the assumptions involved in making the computations are derived from the mechanism in Chart I, the close correspondence of these results indicates the essential correctness of this reaction scheme. It is apparent from Table I that no crossover occurs in the presence of hydroquinone. This is in accord with the proposed mechanism since reducing agents destroy the dissociated radicals and eliminate the intermolecular portion of the rearrangement.

Other possible pathways for formation of labeled *p*-nitro-N-methylaniline were excluded by experimental investigation. Chromatography of the reaction product from *p*-fluoro-N-nitro-N-methylaniline and spectrophotometric analysis of the eluate showed that less than 0.16% *p*-nitro-N-methylaniline is formed from the fluoro compound. This amount would increase the ^{15}N content of all of the *p*-nitro-N-methylaniline formed by only 0.1%. It was found that nitrous and nitric acids (which might be formed from the labeled nitramine) did not convert N-methylaniline or N-nitro-N-methylaniline into *p*-nitro-N-methylaniline under rearrangement conditions. Direct transfer of a nitro group from *p*-fluoro-N-nitro-N-methylaniline to N-methylaniline or N-nitro-N-methylaniline is excluded by the finding that nitro-group exchange was eliminated in the concurrent rearrangements when a reducing agent was added. The latter should not affect a direct transfer process. Thus, the only course for crossover of nitro groups is that implied in the mechanism in Chart I.

The rearrangement of N-nitro-N-methylaniline and *p*-fluoro-N-nitro-N-methylaniline and probably other aromatic nitramines are, therefore, partially intermolecular and partially intramolecular. Direct collapse of the caged radicals (formed by N–N bond cleavage in the original nitramine) is the source of the intramolecular component of the reaction while dissociation and later recombination of these same radicals results in the intermolecular portion of the rearrangement.

Experimental Section

***p*-Fluoro-N-nitro(^{15}N)-N-methylaniline.**—A finely ground mixture of 1.584 g of potassium nitrate-^{15}N, 4.0 g of copper powder, and 4.0 g of sodium hydroxide was placed in a test tube and heated at 360° for 1 hr while the test tube was slowly rotated. After cooling, the contents of the tube were leached with about 10 ml of water. The solution was filtered through a sintered glass disk. The filtrate was held at 0° while 25% sulfuric acid solution (about 15 ml) was added to neutralize it. The neutral nitrite solution was poured over a frozen solution of 1.75 g of *p*-fluoroaniline in 12 ml of 15% sulfuric acid solution. The clear solution, which resulted when the mixture was warmed to 0°, was allowed to stand in an ice bath for 15 min. A solution of 32 g of potassium hydroxide and 96 g of potassium ferricyanide in 360 ml of water was added, and the mixture was stirred for 24 hr at room temperature. It was then filtered and the filtrate was washed with 100 ml of ether and subsequently neutralized with acetic acid. The neutral solution was extracted with four 100-ml portions of ether. The combined ether extracts were washed with 40 ml of water and then mixed with 20 ml of water and evaporated at 40°. The resulting oily suspension of nitramine in water was rendered homogeneous by addition of a solution of 40 g of potassium bicarbonate in 140 ml of water. Alkylation with methyl sulfate was carried out as described previously.[9] The product was crystallized from petroleum ether (bp 30–60°) yielding 0.59 g of white crystals, mp 68–69° (lit.[1c] mp 68.6–69.1°).

N-Nitro-N-methylaniline.—This compound, mp 36.8–37.5° (lit.[10] mp 38.5–39.5°), was available from previous investigations.[9]

***p*-Fluoro-N-nitro-N-methylaniline.**—This substance, mp 68.6–69.1°, was also available from earlier studies.[1c]

Concurrent Rearrangement of N-Nitro-N-methylaniline and *p*-Fluoro-N-nitro(^{15}N)-N-methylaniline.—A solution of the appropriate quantities of the two nitramines in 10.0 ml of dioxane was quantitatively transferred to a thermostated (40.0 ± 0.2°) solution of 500.0 ml of 1.022 *M* perchloric acid, 61.28 g (0.500 mol) of sodium perchlorate, 5.0 g of sulfamic acid, and about 450 ml of water contained in a 1-l. volumetric flask. Sufficient water at 40° was added to bring the total volume to 1 l. and the mixture was shaken and kept at 40.0 ± 0.2° for 90 min. The solution was allowed to cool and the pH was adjusted to about 8.5 with sodium hydroxide. The rearrangement product was then extracted with four 100-ml portions of ether, and the combined ether solutions were evaporated. The residue was taken up in 3 ml of carbon tetrachloride and chromatographed on a 26 × 170 mm column of activity grade II neutral alumina using 300 ml of 1:1 diethyl ether–petroleum ether (bp 30–60°) as developer. The *ortho* isomers moved down the column in a single band and were completely eluted by 200 ml of developer. The *para* isomer formed a band 85–125 mm from the top of the column. The column was extruded and the zone containing the *para*

---

(9) W. N. White, E. F. Wolfarth, J. R. Klink, J. Kindig, C. Hathaway, and D. Lazdins, *J. Org. Chem.*, **26**, 4124 (1961).

(10) E. Bamberger, *Ber.*, **27**, 379 (1894).

isomer was cut out and extracted with 120 ml of ether. The residue obtained by evaporation of the ether solution was recrystallized twice from petroleum ether (bp 30–60°) to give yellow crystals, mp 148–149° (lit.[10] mp 150–151°). The mixture melting point of this substance with an equal quantity of authentic *p*-nitro-N-methylaniline was 149–150°. The chromatographic behavior of the reaction product was also identical with that of *p*-nitro-N-methylaniline.

Determination of Nitrogen-15 Content.—Kjeldahl digestion of the sample converted it into ammonia which was oxidized to nitrogen by hypobromite. The nitrogen was analyzed by mass spectrometry.[11] In the Kjeldahl procedure, excess glucose was added to the potassium sulfate–sulfuric acid digestion mixture, and it was cooled to 0° before addition of the sample to avoid the loss of nitrogen oxides. Titration of an aliquot of the distillate indicated that conversion of organically bound nitrogen to ammonia was complete in each case. Methylamine was shown to be absent by gas chromatography.

The ammonium ion in the distillate was converted into nitrogen by oxidation with sodium hypobromite which contained 0.1% sodium iodide. The nitrogen was then analyzed by mass spectrometry.

Spectrophotometric Analysis of the Rearrangement Products of N-Nitro-N-methylaniline and *p*-Fluoro-N-nitro-N-methylaniline.—The previously described procedure[1a,c] was utilized. However, the reaction mixtures were made up somewhat differently: 25.0 ml of 1.022 *M* perchloric acid, 3.061 g (0.025 mol) of sodium perchlorate, 0.25 g of sulfamic acid, and about 20 ml of water was thermostated at 40.0 ± 0.2° before the addition of 2.0 ml of a dioxane solution of the sample and enough water to bring the volume to 50.0 ml. The presence of sulfamic acid in the reaction mixture obviated the necessity of heating aliquots of the latter with sulfamic acid solution before diluting with buffer.

Kinetic Measurements.—Rate constants for rearrangement of the two nitramines were determined spectrophotometrically.[1b,c] The reaction mixtures were made up as described in the previous paragraph.

Chromatographic Analysis of Rearrangement Product of *p*-Fluoro-N-nitro-methylaniline.—The concurrent rearrangement procedure described above was utilized with *p*-fluoro-N-nitro-N-methylaniline alone being added to the reaction mixture. The chromatographic eluate containing the *ortho* isomer was evaporated, and the residue was diluted with 95% ethanol to a concentration convenient to measure. The column was extruded and the central portion which should contain any *p*-nitro-N-methylaniline formed was cut out and extracted with ether. The residue from evaporation of the ether solution was also dissolved in a convenient amount of 95% ethanol. The absorbances of these two ethanol solutions at 370, 390, 410, and 430 mμ were determined. By comparing these with the absorbances of standard solutions of 2-nitro-4-fluoro-N-methylaniline and *p*-nitro-N-methylaniline in 95% ethanol, it was possible to compute the yields of these two compounds from the rearrangement: 77.2 ± 0.7% of the former and 0.16 ± 0.10% of the latter.

A synthetic mixture containing 1.31% *p*-nitro-N-methylaniline and 98.69% 2-nitro-4-fluoro-N-methylaniline was subjected to the same rearrangement conditions, separated chromatographically, and analyzed spectrophotometrically. The assay indicated that the mixture consisted of 1.37 ± 0.1% *p*-nitro-N-methylaniline and 94.3 ± 0.4% of 2-nitro-4-fluoro-N-methylaniline.

Reaction of N-Methylaniline with Nitrous Acid and Nitric Acid.—A 1.00-ml aliquot of 0.10 *M* sodium nitrite solution was added to a thermostated (40.0 ± 0.2°) solution of 25.0 ml of 1.022 *M* perchloric acid, 3.061 g (0.025 mol) of sodium perchlorated, 2.00 ml of 0.025 *M* N-methylaniline, and about 20 ml of water. Enough water at 40° was added to bring the volume to 50.0 ml, and the mixture was shaken and then kept at 40.0 ± 0.2° for 90 min. The solution was cooled and a 5.0-ml aliquot was heated with 5.0 ml of 5% ammonium sulfamate solution and then analyzed for *o*- and *p*-nitro-N-methylaniline as previously described.[1a] Not more than 0.21 ± 0.11% of the *ortho* isomer and 0.14 ± 0.09% of the *para* isomer were detected.

Substitution of 0.10 *M* sodium nitrate solution for the sodium nitrite resulted in not more than 0.16 ± 0.08% of the *ortho* isomer and 0.08 ± 0.10% of the *para* isomer.

Registry No.—*p*-Fluoro-N-nitro(^{15}N)-N-methylaniline, 24454-09-9; N-nitro-N-methylaniline, 7119-93-9; *p*-fluoro-N-nitro-N-methylaniline, 655-56-1; *p*-nitro-N-methylaniline, 100-15-2.

---

[11] D. Rittenberg in D. W. Wilson, A. O. C. Nier, and S. P. Riemann, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Mich., 1948, p 31.

Electron Acceptors Derived from Fluorenecarboxylic Acids and Their Charge-Transfer Complexes

THEODORE SULZBERG AND ROBERT J. COTTER

Union Carbide Corporation, Chemicals and Plastics, Bound Brook, New Jersey 08805

Received January 13, 1970

Fluorenone-2,7-dicarboxylic acid (XII) and fluorenone-2-carboxylic acid (XVI) and -4-carboxylic acid (XIX) have been nitrated to give 4,5-dinitrofluorenone-2,7-dicarboxylic acid (Va), 4,5,7-trinitrofluorenone-2-carboxylic acid (XVII), and 2,5,7-trinitrofluorenone-4-carboxylic acid (XX), respectively. Reaction of these acids, or the corresponding methyl esters, with malononitrile in the presence of piperidine gave the 9-dicyanomethylene derivatives. These compounds, which represent a new class of functionalized electron acceptors, readily formed charge-transfer complexes with aromatic hydrocarbons and aromatic monoamines. With N,N,N′,N′-tetramethyl-*p*-phenylenediamine, the radical anions and cations were formed exclusively. By use of simple molecular orbital theory, it was shown that these compounds have acceptor strengths similar to chloranil.

Charge-transfer complexes have been studied by many workers from various viewpoints. Their research has been described in several reviews.[1] Until recently, this work was limited to the interactions of monomeric electron donors and electron acceptors. Because of active interest in preparing practical organic semiconductors, these studies were extended to include donor polymer–acceptor monomer complexes.[2] Interactions between polymers containing donor substituents with polymers containing acceptor groups were recently reported for the first time.[3] The donor polymers were prepared from aryliminodiethanols and the acceptor polymers from nitrated isophthalic and terephthalic acids. We found, however, that, while the donors

---

[1] (a) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964. (b) E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965). (c) F. E. Gutmann and L. E. Lyons, "Organic Semiconductors" John Wiley & Sons, Inc., New York, N. Y., 1967.

[2] (a) W. Slough, *Trans. Faraday Soc.* **158**, 2360 (1962); British Patent 1,009,361 (Nov 10, 1965). (b) J. H. Lupinski and K. D. Kopple, *Science*, **146**, 1038 (1964); U. S. Patent 3,346,444 (Oct 10, 1967).

[3] (a) T. Sulzberg and R. J. Cotter, *Macromolecules*, **1**, 554 (1968). (b) *ibid.*, **2**, 146 (1969). (c) *Chem. Eng. News*, **46** (54), 28 (1968).