Formation of Phenyldiimide and Phenyl Radical by Heterolysis of N-Phenyl-N′-benzoyldiimide[1]

SAUL G. COHEN AND JESSE NICHOLSON

The Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154

Received December 1, 1964

N-Phenyl-N′-benzoyldiimide, $C_6H_5CO{-}N{=}N{-}C_6H_5$ (I), is a stable compound which undergoes rapid acid- or base-catalyzed methanolysis, leading to free phenyl radical, presumably *via* phenyldiimide, $C_6H_5{-}N{=}N{-}H$ (III). At low initial concentration of I high yields of nitrogen, methyl benzoate, and benzene are formed. At high concentrations, yields of these products fall as III reacts with I, leading to $(C_6H_5)_2NNHCOC_6H_5$ (IV) and $C_6H_5NHN(C_6H_5)COC_6H_5$ (V). Similar results are obtained in 2-propanol, and acetone is formed as a major product. Methanolysis of I (a) in the presence of fumaric acid leads to phenylsuccinic acid; (b) in benzene, to biphenyl; (c) in carbon tetrachloride, to chlorobenzene and chloroform; (d) in nitrobenzene, to 2-, 4-, and less 3-nitrobiphenyl; (e) in the presence of naphthalene, to 1- and 2-phenylnaphthalenes; and (f) in acrylonitrile, to polyacrylonitrile. The mechanisms of formation of these products and of phenyl radical from III are discussed.

Aromatic azo compounds, Ar—N=N—Ar′, unlike their aliphatic counterparts, are not convenient sources of free radicals. Aryl radicals may be produced from related thermally unstable compounds, diazohydroxides,[2] diazoacetates,[2] and nitrosoacylarylamines,[3] from N-aryl-N′-alkyl azo compounds, arylazotriphenylmethanes[4] and arylazodiphenylmethanes,[5] and from diacyl peroxides.[6,7]

Of the acyl azo compounds, diethyl azodicarboxylate, $C_2H_5O_2C{-}N{=}N{-}CO_2C_2H_5$, is relatively stable thermally, decomposing at about 200°, while its acid- or base-catalyzed hydrolysis proceeds at room temperature with concomitant reduction of part of the azo compound to diethyl hydrazodicarboxylate.[8] It has been proposed that the reducing agent diimide, H—N=N—H, is formed in the hydrolysis.[9,10] Dibenzoyldiimide, $C_6H_5CO{-}N{=}N{-}COC_6H_5$, is less stable and decomposes in benzene at 75–100° with formation of free radicals in a complex reaction.[11] This decomposition was greatly accelerated in ethanol, but it was proposed that this represented largely an acceleration of the homolytic reaction rather than a change to a faster heterolysis. The decomposition and hydrolysis of dibenzoyldiimide led to some dibenzoylhydrazine,[12] and this may also be formed from diimide, which has been suggested as a product of reaction of dibenzoyldiimide with nucleophiles.[13] Although free radicals have not been shown to be formed in heterolyses of these diacyl azo compounds, it seemed of interest to study this and heterolysis of related monoacyl aryl azo compounds, N-phenyl-N′-benzoyldiimide,[14] $C_6H_5{-}N{=}N{-}COC_6H_5$ (I), and N-phenyl-N′-carbethoxydiimide,[15] $C_6H_5{-}N{=}N{-}CO_2C_2H_5$ (II). These are thermally stable compounds which, on hydrolysis, may form phenyldiimide,[15] $C_6H_5{-}N{=}N{-}H$ (III), which in turn might lead conveniently, *in situ*, to free phenyl radicals. In preliminary experiments compounds I and II were treated with dilute acid or base in methanol–benzene and led to biphenyl. Compound I appeared to lead to this free-radical arylation product in higher yield than did compound II, and subsequent study was carried out with it.

Results

As had been reported for ethanol solutions,[11] N,N′-dibenzoyldiimide decomposed rapidly in methanol at room temperature, 2×10^{-3} and 1×10^{-2} M solutions leading to 80 and 60% yields of nitrogen, respectively, the absorption band at 470 mμ disappearing in 2 hr.

N-Phenyl-N′-benzoyldiimide (I), which may be crystallized from alcohol,[14] appeared to lead to very little nitrogen and its visible spectrum was virtually unchanged during long standing in methanol. However, 0.01 N hydrogen chloride led to rapid decomposition of 6.6×10^{-3} M I in methanol, 45% yield of nitrogen in 10 min., 87% after 2.5 hr. at room temperature. Under these conditions a comparably high yield of methyl benzoate and a fair yield (>55%) of benzene were formed. Similarly, 0.01 N sodium hydroxide led to rapid evolution of nitrogen, 43% in 4 min., 67% after 3 hr. With increasing initial concentration of I, yields of these three products decreased. At 0.6 M I, yields of methyl benzoate and benzene were 51 and 25%, respectively, and at 1.56 M I the yields were 43 and 12%. Other products were being formed, including biphenyl, azobenzene, N,N-diphenyl-N′-benzoylhydrazine, $(C_6H_5)_2N{-}NHCOC_6H_5$ (IV), and N,N′-diphenyl-N-benzoylhydrazine, $(C_6H_5)NHN(C_6H_5)COC_6H_5$ (V), the latter two apparently arising from reactions of phenyldiimide III and/or phenyl radical with unreacted I. These reactions are favored at higher initial contration of I. Acid and base catalysis led to similar products.

Analogous results were obtained when compound I was decomposed in 2-propanol containing hydrochloric acid. Yields of nitrogen fell from 77% at 0.005 M I to 35% at 0.20 M I; yields of 2-propyl benzoate

---

[1] We are pleased to acknowledge generous support of this work by the National Science Foundation, Grants G14049 and GP1833, and a fellowship under Title IV of the National Defense Education Act. For a preliminary report, see S. G. Cohen and J. Nicholson, *J. Am. Chem. Soc.*, **86**, 3892 (1964).

[2] M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **46**, 2339 (1924).

[3] W. S. M. Grieve and D. H. Hey, *J. Chem. Soc.*, 1797 (1934).

[4] D. H. Hey, *ibid.*, 1966 (1934).

[5] S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 3628 (1955).

[6] H. Gelissen and P. H. Hermans, *Ber.*, **58**, 285 (1925).

[7] For a review of the chemistry of aryl radicals, see G. H. Williams, "Homolytic Aromatic Substitution," Pergamon Press, London, 1960.

[8] T. Curtius and K. Heidenreich, *Ber.*, **27**, 773 (1894).

[9] S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961).

[10] E. J. Corey, D. J. Pasto, and W. L. Mock, *ibid.*, **83**, 2957 (1961).

[11] J. E. Leffler and W. B. Bond, *ibid.*, **78**, 335 (1956).

[12] R. Stolle and A. Benrath, *J. prakt. Chem.*, **70**, 263 (1904).

[13] J. F. Neumer and J. T. Gerig, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.

[14] G. Ponzio and G. Charrier, *Gazz. chim. ital.*, **39** (1), 598 (1909).

[15] O. Widman, *Ber.*, **28**, 1927 (1895).

TABLE I

PRODUCTS OF CATALYZED ALCOHOLYSIS OF $C_6H_5CO—N=N—C_6H_5$ (I)

Expt. no.	I, *M*	N_2, %	$C_6H_5CO_2R$, %	C_6H_6, %	Other products, %[a]
M-2	0.0066	87	...	...	...
M-4	0.0054	93	85[b]	>55	...
M-5	0.019	74	79[b]	48	IV, 11; V, 13
M-7	0.22	...	60[b]	32	IV, 17; V, 12
M-8	0.20	...	64[b]	34	IV, 13; V, 12 Biphenyl, 4; azobenzene, 2
M-9	0.60	...	51[b]	25	IV, 9; V, 6
M-10	1.56	...	43[b]	12	IV, 42; V, 11
P-1	0.0050	77	52[c]	61	Acetone, 45
P-2	0.022	60	44[c]	43	IV, 16; V, 9 Acetone, 31
P-3	0.20	35	33[c]	27	
P-4	0.24	...	39[c]	22	IV, 19; V, 15 Acetone, 23
P-5	1.04	...	34[c]	23	IV, 25; V, 2 Acetone, 21
MF[d]	0.20	...	75[b]	4	Phenylsuccinic acid, 52
MB-1[e]	0.20	...	67[b]	39	IV, 8; V, 8 Biphenyl, 4; azobenzene, 1

[a] IV, $(C_6H_5)_2NNHCOC_6H_5$; V, $C_6H_5NHN(C_6H_5)COC_6H_5$; yields based on 2 moles of I/mole of IV, V, biphenyl, or azobenzene. [b] Methyl benzoate, reaction in methanol. [c] 2-Propyl benzoate, reaction in 2-propanol. [d] Reaction in methanol contaning 2 *M* fumaric acid. [e] Reaction in methanol containing 0.05 *M* sodium methoxide; all other reactions were acid catalyzed.

TABLE II

METHANOLYSIS OF $C_6H_5CO—N=N—C_6H_5$ (I) IN THE PRESENCE OF BENZENE

Expt. no.	I, *M*	C_6H_6, *M*	Catalyst	$C_6H_5C_6H_5$, %	$C_6H_5CO_2CH_3$, %
B-1	0.044	7	0.25 *M* HCl	24	..
B-2	0.23	7	0.40 *M* HCl	..	36
B-3	0.17	11	0.25 *M* HCl	38	41
B-4	0.16	11	0.03 *M* $NaOCH_3$	29	26

fell from 52% at 0.005 *M* I to 34% at 1.0 *M* I; and benzene fell from 61% at 0.005 *M* I to 23% at 1.0 *M* I. Substantial amounts of compounds IV and V were also obtained. In addition acetone, apparently formed in a free-radical process, was found, 45% yield at 0.005 *M* I, falling to about 20% at 1.0 *M* I.

Results of experiments in methanol and 2-propanol are summarized in Table I.

Experiments were also carried out which showed that products of the heterolysis, phenyldiimide (III) or phenyl radical, may add to other unsaturated compounds, if present. Reaction of 0.2 *M* I in methanol containing 2 *M* fumaric acid, with and without added hydrochloric acid, led to 75% yield of methyl benzoate, 52% of phenylsuccinic acid, and 4% of benzene (expt. MF, Table I).

Evidence that free phenyl radicals may be formed after heterolysis is seen in a series of reactions carried out in methanol in the presence of (1) carbon tetrachloride, (2) benzene, (3) nitrobenzene, (4) naphthalene, and (5) acrylonitrile.

(1) Reaction of 0.17 *M* I in 3:1 carbon tetrachloride–methanol, 0.3 *M* in hydrochloric acid, led to 58% yield of methyl benzoate, 40% chlorobenzene, 19% chloroform, and 9% combined yield of compounds IV and V. The yield of benzene was lowered to about 9% by the presence of carbon tetrachloride.

(2) Methanolysis of I in the presence of benzene, catalyzed by acid or base, led to fair yields of methyl benzoate and to comparable yields of biphenyl. Results are summarized in Table II.

(3) Methanolysis reactions of compound I in the presence of high concentrations of nitrobenzene led to a complex mixture of products including benzene, the three nitrobiphenyls, methyl benzoate, and small quantities of biphenyl and azobenzene. An acid-catalyzed methanolysis of 0.18 *M* I in 3:1 nitrobenzene–methanol led to high yield (57%) of methyl benzoate, low yield (10%) of benzene, and to 33% combined yield of nitrobiphenyls, 10, 2.5, and 20% of the 2-, 3-, and 4-isomers, respectively. A base-catalyzed reaction led to 20% combined yield of the nitrobiphenyls with similar isomer ratio.

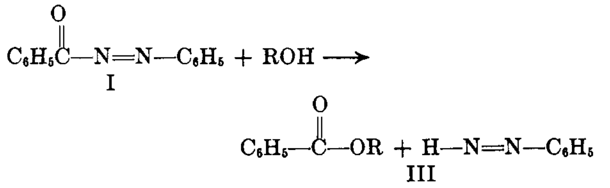
(4) Methanolysis of 0.2 *M* I in the presence of naphthalene and acid or base also led to a mixture of products including 1- and 2-phenylnaphthalenes. In the presence of acid, there were formed 4.4% of 1-phenylnaphthalene, 0.8% of 2-phenylnaphthalene, 53% of methyl benzoate, 24% of benzene, 12% combined yield of compounds IV and V, and some biphenyl and azobenzene. In the presence of sodium methoxide, there were formed 7.4% of 1-phenylnaphthalene, 0.7% of 2-phenylnaphthalene, 57% of methyl benzoate, 26% of benzene, 10% combined yield of compounds IV and V, and small quantities of azobenzene, biphenyl, and anisole.

(5) Finally, treatment of 5 ml. of 0.075 *M* I in acrylonitrile with 1 ml. of methanol and 0.5 ml. of

concentrated hydrochloric acid led to exothermic polymerization and 65% yield of polyacrylonitrile.

Discussion

N,N'-Dibenzoyldiimide decomposed rapidly in methanol, while N-phenyl-N'-benzoyldiimide (I) was quite stable in methanol alone, reacting rapidly only in the presence of acid or base. It seems highly likely that the latter reaction is heterolytic, and the former may well be also, the two compounds being related to each other as an anhydride is to an ester, the azo linkage corresponding to the ether oxygen. Omitting details of the catalysis, the first stage of the reaction of I may be the heterolysis below. Formation of III, as a discrete

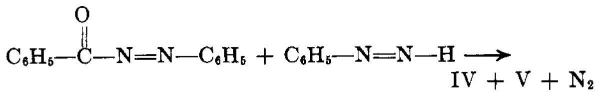


$$\underset{\mathrm{I}}{C_6H_5C(=O)-N=N-C_6H_5} + ROH \longrightarrow C_6H_5-C(=O)-OR + \underset{\mathrm{III}}{H-N=N-C_6H_5} \quad (1)$$

entity, or its anion in the alkali-catalyzed reaction, is probable and is consistent with the formation from azodicarboxylates[9,10] of diimide, which is likely to be less stable than III.

The data of Table I indicate that in dilute solution ($<10^{-2}$ M) the heterolysis proceeds effectively, leading to very high yields of nitrogen, to comparable yields of methyl benzoate, and to moderate yields of benzene. The benzene derives from compound III by reactions which do not consume much I at low initial concentrations of the latter. Most simply, in dilute solution phenyldiimide may to a large extent collapse synchronously or decompose in a solvent cage to form benzene and nitrogen. A sequence of bimolecular reactions with compound I involving several transfers of hydrogen atoms would require regeneration of I to account for the high yields of nitrogen and methyl benzoate, and seems less likely.

However, compound I appears to be very reactive toward phenyldiimide and/or the free radicals that may be produced in this system. These secondary bimolecular reactions become important with increase in the initial concentration of I and with change of solvent from methanol to 2-propanol in which the heterolysis is slower. Part of compound I is thus diverted from the reaction of eq. 1, yields of ester and of nitrogen decrease to 35–45%, and the yield of benzene decreases even more. The products of addition of phenyl and hydrogen to I are isolated, $(C_6H_5)_2NNHCOC_6H_5$ (IV) and $C_6H_5NHN(C_6H_5)COC_6H_5$ (V). In expt. M-10, with highest (1.56 M) initial concentration of I, a minor proportion of III leads to benzene, a major part leads to IV and V, and these products account for half of the total initial I. Phenyldiimide (III) in effect adds to I with loss of nitrogen.



$$C_6H_5-C(=O)-N=N-C_6H_5 + C_6H_5-N=N-H \longrightarrow IV + V + N_2 \quad (2)$$

Addition of III to I to form IV and V may be a synchronous cyclic process, analogous to stereospecific *cis* reduction by diimide,[10] or, perhaps preferably, it may proceed by transfer of a hydrogen atom from III to the carbonyl oxygen or to the terminal azonitrogen of I, followed quickly by loss of nitrogen from phenyldiimide radical and addition of phenyl radical from the same molecule of III, forming IV and V, respectively. Transfer of the hydrogen atom to oxygen may be preferred, leading to somewhat higher yield of IV than V. The course of these additions is similar in acid and base, indicating that the radical or synchronous mechanisms may be preferred to polar mechanisms for the additions. After transfer of the hydrogen atom, if the phenyl radical fails to complete the addition and diffuses away, it abstracts hydrogen from methanol leading to benzene and a solvent-derived radical. Such hydrogen transfer processes may be the major course of formation of the low yield of benzene in concentrated solutions of I, while collapse or cage decomposition of phenyl diimide to benzene dominates in dilute solutions of I. The data of expt. M-10 may be interpreted: 43% of I leads to methyl benzoate and phenyldiimide; a portion of the latter corresponding to 26% of I transfers hydrogen and/or adds to I to form IV and V, while 12% transfers hydrogen to I and forms benzene and hydroxymethyl radical; the latter may add to I consuming an additional 12%, these processes accounting for a minimum of 93% of I. The correspondence in molar yield of methyl benzoate with the combined yields of benzene and compounds IV and V is good. The portion of I to which hydrogen atoms or hydroxymethyl radicals may add are lost as colored products which are formed in these reactions.

The reactions in 2-propanol are somewhat more informative; acetone is formed in lower yield than benzene at low concentration of I and is formed in yield corresponding to that of benzene at high initial concentration of I when hydrogen transfer reactions may dominate. The data of expt. P-5, Table I, may be interpreted: 35% of I leads to 2-propyl benzoate and phenyldiimide (III); a portion of the latter corresponding to 14% of I adds to I, forming IV and V (eq. 2); a portion of III corresponding to 21% of I transfers a hydrogen atom to I, loses nitrogen, and abstracts a hydrogen atom from 2-propanol forming benzene and 2-hydroxy-2-propyl radical, $(CH_3)_2\dot{C}-OH$. The latter in turn transfers hydrogen to 21% of I and is converted to acetone, a reaction related to the rapid transfer of hydrogen from this radical to benzophenone in the photochemical reduction of benzophenone in 2-propanol.[16] These processes may account for 90% or more of compound I. In expt. P-5 very little of the benzene arises directly from diimide, and the radical reactions lead to correspondence in yields of benzene and acetone. At lower initial concentrations of I, more 2-propyl benzoate and III are formed, a lesser part of the III adds to I or transfers hydrogen to I, and a larger proportion decomposes synchronously or in a cage to benzene.

When another appropriate unsaturated compound, 2 M fumaric acid, is present during methanolysis it competes effectively for the phenyldiimide and/or phenyl radical. In this experiment, MF, Table I, with 0.2 M initial concentration of I, the yield of methyl benzoate rose to 75%, which is characteristic of more dilute solutions. Furthermore, the yield of benzene

---

[16] J. N. Pitts, Jr., R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Recktenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959).

fell to a very low value (4%). The fumaric acid reacted well with phenyldiimide and/or phenyl radical, greatly decreasing the proportion of these intermediates which either added to I or were converted to benzene, and led to 52% phenylsuccinic acid. The combined yield of phenylsuccinic acid and benzene corresponds well to the molar yield of benzene and compounds IV and V in expt. M-5.

$$HO_2CCH{=}CHCO_2H + C_6H_5N{=}N{-}H \longrightarrow HO_2CCH_2CH(C_6H_5)CO_2H \quad (3)$$

Formation of substantial yields of acetone in the heterolysis in 2-propanol implies the occurrence of free-radical processes, and this was confirmed by study of a number of systems which may be diagnostic for and are best interpreted in terms of free-radical abstraction, substitution, and addition reactions. Methanolysis of 0.2 *M* I in the presence of carbon tetrachloride, leading to 58% yield of methyl benzoate, 40% chlorobenzene, 9% benzene, 19% chloroform, and a trace of hexachloroethane, indicates that 58% yield of phenyldiimide was probably formed; of this the equivalent of 40% led to phenyl radical which abstracted chlorine from carbon tetrachloride, while 9% led to benzene, 3% led to V, and 2% to IV. The chloroform may arise by abstraction of hydrogen by trichloromethyl radical from either methanol or phenyldiimide. A substantial part of the phenyldiimide probably transferred hydrogen to I, leading to colored products.

In the presence of benzene, methanolysis of I led to 29–38% of biphenyl and comparable yields of methyl benzoate (Table II). Since phenyldiimide (III) may be formed only when methyl benzoate is (eq. 1), substantially all of III appeared to lead to phenyl radical and substitution into benzene when the latter was present. The remainder of I may be consumed by abstraction of hydrogen from III to lead to the phenyl radical, and by abstraction of hydrogen from the phenyl cyclohexadienyl radical intermediate, leading to the biphenyl.

The presence of nitrobenzene during methanolysis led similarly to 33% yield of the nitrobiphenyls, reducing the yield of benzene to 10%. Small quantities of biphenyl and azobenzene were also formed; these added to the combined yields of nitrobiphenyls and benzene still probably do not equal the yield of methyl benzoate (57%), a part of the phenyldiimide remaining unaccounted for. The isomer ratio, 4:1:8, for the 2-, 3-, and 4-nitrobiphenyls shows the predominant *ortho–para* orientation of free-radical arylations, but the low *ortho–para* ratio is somewhat unexpected.[17] It may be that, in the presence of methanol, solvation of the nitro group introduces a steric factor favoring *para* substitution.

Acid- or base-catalyzed methanolysis in the presence of naphthalene led to a substantial yield of methyl benzoate (~55%), to somewhat diminished yields of benzene (~25%), and to compounds IV and V. A part of the phenyl radical was diverted to reaction with the naphthalene leading to 5–8% yields of 1- and 2-phenylnaphthalenes, in proportion consistent with the predominant formation of the 1-isomer in the phenylation of naphthalene by benzoyl peroxide.[18] The low yields of arylation products in this case may simply reflect the high methanol–naphthalene ratio compared with the methanol–benzene and methanol–nitrobenzene ratios in the preceding experiments.

Low yields of biphenyl and azobenzene were found in most of the experiments carried out in methanol, in the presence and absence of scavengers. These products may result from bimolecular reactions involving phenyldiimide, phenyldiimide radical, and phenyl radical.

Radicals produced in the acid-catalyzed methanolysis of I proved moderately effective as initiators of the polymerization of acrylonitrile. The infrared spectrum of the polymer showed bands characteristic of a monosubstituted phenyl group indicating that phenyl radical may have added in the initiation step. Evidence for the possible presence of O–H, C–O, C=O, and phenyl–azo linkages indicates that other radicals produced in this system may also be incorporated into the polymer, in initiation or in termination steps.

Conclusion.—Compound I is thermally stable and not particularly reactive to hydroxylic solvents, but is readily attacked by acid or base. Heterolysis leads to phenyldiimide and may then lead to free phenyl radical at room temperature in homogeneous medium in yields comparable with those from previously reported sources of aryl radicals.[2-5] However, phenyldiimide, $C_6H_5N{=}NH$, may not decompose spontaneously to phenyl radical, nitrogen, and a hydrogen atom. Left to itself, it may to a considerable extent decompose to form nitrogen and benzene. The mode of formation of benzene is now being examined by the use of deuterated solvents. Formation of free radicals may depend to a large extent on oxidation of phenyldiimide, by compound I itself in the absence of other oxidizing agents. This may lead to consumption of I, lower yield of phenyl radical, and formation of stabilized radicals from I which are undesirable. Study of heterolysis of I in the presence of oxidizing agents may prove informative and is in progress.

Experimental

N-Phenyl-N′-benzoyldiimide (I).—Benzoyl chloride, 19.0 g. (0.14 mole), was added slowly with stirring to an ice-cold solution of 15 g. (0.14 mole) of freshly distilled phenylhydrazine in 60 ml. of dry pyridine. The mixture was stirred overnight and treated with excess dilute sulfuric acid, leading to **N-phenyl-N′-benzoylhydrazine**, 21 g. (0.1 mole), 70% yield, m.p. 168–169°, from ethanol, lit.[19] m.p. 168°.

A.—A mixture of this compound (10 g., 0.047 mole) and lead tetraacetate (22 g., 0.05 mole, Arapahoe Chemical Co., Inc.) was boiled under reflux for 2 hr. in 500 ml. of dry 20–40° petroleum ether. The red solution was filtered, and the solids were boiled in fresh petroleum ether. The filtrates were washed with water, sodium bicarbonate, and water, dried, and cooled in Dry Ice, leading to yellow crystals of I, 7.5 g. (0.035 mole), 75% yield, m.p. 28° from ether–petroleum ether, lit. m.p. 30°[14] from ethanol, 32°[20] from ether. The N–H absorption in the infrared was absent; the visibile spectrum showed λ_{max} 441 mμ (ε 130). In a melting point capillary it decomposed over a range starting at 150°.

B.—A mixture of 19.3 g. (0.091 mole) of N-phenyl-N′-benzoylhydrazine, 20.0 g. (0.092 mole, Fisher Certified reagent) of yellow mercuric oxide, and 20 g. (0.14 mole) of anhydrous sodium sulfate was stirred at room temperature for 3 hr. in 600 ml. of 40–60° petroleum ether. The mixture was filtered and the

---

[17] G. H. Williams, ref. 7, p. 68.

[18] D. I. Davis, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1878 (1958).

[19] F. Just, *Ber.*, **19**, 1203 (1884).

[20] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 3340 (1954).

filtrate was cooled in Dry Ice, leading to 15.5 g. (0.074 mole) of I, 81% yield, m.p. 28–29°. The infrared spectrum was identical with that of the compound prepared with lead tetraacetate.

N,N'-Dibenzoyldiimide.—N,N'-Dibenzoylhydrazine was prepared according to directions in the literature.[21] Reaction of 65 g. (0.5 mole) of hydrazine sulfate, 145 g. (1.0 mole) of benzoyl chloride, and 93 g. (1.3 moles) of sodium hydroxide led to 90 g. (0.37 mole, 75% yield) of N,N'-dibenzoylhydrazine, m.p. 237–239°, lit.[11] m.p. 238°. This compound (10 g., 0.042 mole) was suspended in 250 ml. of 40–60° petroleum ether, 20 g. (0.044 mole) of lead tetraacetate was added, and the mixture was refluxed and worked up as described above for compound I. N,N'-Dibenzoyldiimide was obtained and crystallized from ether, 7.5 g. (0.032 mole), 75% yield, m.p. 119–120°, lit.[22] m.p. 119–121.5°.

N,N-Diphenyl-N'-benzoylhydrazine.—A solution of 3.6 g. (0.016 mole) of N,N-diphenylhydrazine hydrochloride (Eastman Organic Chemicals) in 15 ml. of dried pyridine was treated slowly with 1.37 ml. (0.016 mole) of benzoyl chloride, stirred overnight at room temperature, and then diluted at 0° with 50 ml. of 10% sulfuric acid. The product was obtained, 4.0 g. (0.014 mole), 87% yield, m.p. 189–191° from acetone–water, lit.[23] m.p. 192°. This compound does not form a hydrochloride when its solution in CH_3OH–HCl is concentrated.

N,N'-Diphenyl-N-benzoylhydrazine.—A solution of 3.0 g. (0.016 mole) of N,N'-diphenylhydrazine (Eastman Organic Chemicals) in 20 ml. of dried pyridine was treated gradually with 1.37 ml. (0.016 mole) of benzoyl chloride as described above, leading to 3.5 g. (0.012 mole), 76% yield, of product, m.p. 136–138° from acetone–water, lit.[24] m.p. 138–139°. Hydrochloric acid was added to a solution of this compound in methanol, the solvent was evaporated, and the hydrochloride was isolated, melting at 300–320° dec. The infrared spectrum (KBr) showed absorption bands: 3.0 (m), 3.5 (s), 3.9 (s), 5.0 (w), 6.0 (s), 6.25 (m), 6.65 (s), 7.0 (m), 7.1 (m), 7.45 (m), 7.55 (m), 7.65 (m), 7.8 (w), 7.9 (w), 8.1 (w), 8.3 (w), 8.7–9.0 (w), 9.25 (w), 9.65 (w), 9.9 (w), 10.7 (w), 11.0 (w), 12.2 (s), 14.05 (m), and 14.45 μ (m).

Anal. Calcd. for $C_{19}H_{17}ClN_2O$: C, 70.2; H, 5.28; Cl, 10.92; N, 8.63. Found: C, 69.1; H, 5.79; Cl, 10.71; N, 8.65.

N-Phenyl-N'-carbethoxydiimide.—Ethyl chloroformate (Eastman Organic Chemicals), 5.0 g. (0.046 mole), was added slowly, at 30° with stirring, to a solution of 10 g. (0.092 mole) of freshly distilled phenyl hydrazine (Fisher reagent) in 150 ml. of dry ether, leading to **ethyl phenylhydrazocarboxylate,**[15] 4.6 g. (0.026 mole), 56% yield, m.p. 81.5–82°, from 1:1 petroleum ether–benzene, lit.[15] m.p. 82–83°. This compound, 11.6 g. (0.062 mole), was dissolved in 180 ml. of glacial acetic acid, cooled and treated with 0.2 *M* potassium permanganate until a brown color remained. A little 30% hydrogen peroxide was added. The solution was extracted with chloroform; the extract was washed with sodium bicarbonate and water, dried, and concentrated, leading to a red oil, **N-phenyl-N'-carbethoxydiimide,**[15] 9.1 g. (0.051 mole), 83% yield, b.p. 108° (0.5 mm.).

Vapor Phase Chromatography.—Analyses were carried out on an Aerograph A-90-P instrument, generally with an 8-ft. column containing 20% SE-30 on 60–80 acid-washed Chromosorb-W. In analyses for acetone a 6-ft. column was used, containing 20% adipate resin (R. C. Polymeric B. G. A., Rubber Corp. of America), on 80–100-mesh Celite. Retention times of reaction products were compared with those of authentic samples. When these were found to be identical, the samples were added to a portion of the reaction mixture and the chromatogram was examined for symmetry of the increased peak. The chromatograms were complex and quantities of products were not determined by use of internal standards. Instead peak areas from known volumes of reaction mixtures were compared with corresponding peak areas of known volumes of synthesized solutions of authentic samples. When possible products were isolated by vapor phase chromatography and characterized by melting point and infrared spectrum.

Methanolysis of Dibenzoyldiimide. A.—A solution of 0.050 g. (0.21 mmole, 0.0021 *M*) of N,N'-dibenzoyldiimide in 100 ml. of methanol, at 24°, led in 2 hr. to 4.1 ml., 80% yield of nitrogen. The color of the solution was discharged, and the absorption band at 470 mμ disappeared.

B.—Evolution of nitrogen from a solution of 0.247 g. (1.01 mmoles, 0.01 *M*) of N,N'-dibenzoyldiimide in 100 ml. of methanol at 24.0° was followed as a function of time. The final volume of nitrogen after 130 min. was 14.95 ml., 31°, 60% yield. The reaction was rapid for the first 25 min., 12.7 ml. of nitrogen being evolved with approximate first-order kinetics. The remainder was evolved quite slowly.

Methanolysis of N-Phenyl-N'-benzoyldiimide (I). **M-1.**—A solution of 0.050 g. (0.24 mmole, 0.0024 *M*) of I in 100 ml. of methanol was kept at 24° for 8 hr. Little, if any, gas was evolved, and the visible spectrum of the solution was essentially unchanged. Concentrated hydrochloric acid, 1 ml., was added, leading to rapid change in color and 4.2 ml., 71% yield, of nitrogen after 1 hr.

M-2.—Evolution of nitrogen from a solution of 0.070 g. (0.33 mmole, 0.0066 *M*) of I in 50 ml. of 0.01 *N* hydrogen chloride in methanol at 25° was followed. The final volume, after 135 min., was 7.30 ml. at 31°, 87% yield, half of which was evolved in the first 10 min.

M-3.—Evolution of nitrogen from a solution of 0.070 g. (0.33 mmole, 0.0066 *M*) of I in 50 ml. of 0.01 *N* sodium methoxide was followed. The final volume, after 3 hr., was 5.50 ml. at 30°, 67% yield, the first 3.5 ml. appearing in 4 min.

M-4.—A solution of 0.0564 g. (0.268 mmole, 0.0054 *M*) of I in 50 ml. of 0.10 *M* hydrogen chloride in methanol led to 6.20 ml. (93% yield) of nitrogen (at 30°), 0.031 g. (0.23 mmole, 85% yield) of methyl benzoate, and to 0.01 g. (0.15 mmole, 55% yield) of benzene. Analyses for the ester and hydrocarbon were carried out by vapor phase chromatography; the error in the yield of benzene was high in this experiment because of the dilution, and the indicated value is a minimum.

M-5.—A solution of 0.202 g. (0.96 mmole, 0.019 *M*) in 50 ml. of 0.10 *M* hydrogen chloride in methanol led to 17.8 ml. (74% yield) of nitrogen (at 30°), and by vapor phase chromatography to 0.103 g. (0.75 mmole, 79% yield) of methyl benzoate, and 0.036 g. (0.46 mmole, 48% yield) of benzene.

The reaction solution was concentrated and the residue was extracted with acetone. The acetone-insoluble material was dissolved in hot methanol and precipitated by a little acetone; N,N'-diphenyl-N-benzoylhydrazine hydrochloride was isolated, 0.020 g. (0.062 mole, 13% yield), dec. pt. 300–320°, not depressed by mixture with an authentic sample, spectrum identical with that of an authentic sample.

Anal. Found: C, 69.0; H, 5.35; Cl, 10.83; N, 8.53.

Treatment of this salt with dilute alkali led to N,N'-diphenyl-N-benzoylhydrazine, m.p. 136–138°, m.m.p. 136–137°, identical with an authentic sample. The acetone extract was concentrated and the residue was extracted with petroleum ether. This extract was placed on Fischer neutral alumina and eluted with petroleum ether leading to a trace of biphenyl, and eluted with 1:4 ether–petroleum ether, leading to methyl benzoate, the infrared spectrum of which was identical with that of an authentic sample. The petroleum ether insoluble material was redissolved in acetone, decolorized with Norit A, treated with a little water, and concentrated, leading to **N,N-diphenyl-N'-benzoylhydrazine,** 0.015 g. (0.052 mmole), 11% yield, m.p. 190–192°, m.m.p. 193–194° with the authentic sample; its infrared spectrum was identical with that of the authentic sample.

M-7.—A solution of 0.120 g. (0.573 mmole, 0.22 *M*) of I in 2.5 ml. of methanol and 0.05 ml. of concentrated hydrochloric acid led after 2 hr. to 0.046 g. (0.34 mmole, 60% yield) of methyl benzoate, 0.014 g. (0.18 mmole, 30% yield) of benzene, 0.011 g. (0.034 mmole, 12% yield) of N,N'-diphenyl-N-benzoylhydrazine hydrochloride, and 0.014 g. (0.048 mmole, 17% yield) of N,N-diphenyl-N'-benzoylhydrazine.

M-8.—A solution of 0.280 g. (1.33 mmoles, 0.20 *M*) of I in 6.5 ml. of methanol was stirred and treated with 0.05 ml. of concentrated hydrochloric acid. Nitrogen evolved and a deep red color developed. Vapor phase analyses, carried out after 2 hr., indicated 0.115 g. (0.85 mmole, 64% yield) of methyl benzoate and 0.035 g. (0.045 mmole, 34% yield) of benzene. The solution was concentrated and the residue was extracted with petroleum ether. This extract was placed on neutral alumina and eluted with petroleum ether, leading to biphenyl, 0.0038 g. (0.025 mmole, 3.7% yield) and to azobenzene, 0.0025 g. (0.014 mmole, 2% yield). Elution with 15% ether–petroleum ether led to methyl benzoate, 0.093 g. (0.69 mmole, 51% yield). The residue was treated with a small excess of hydrochloric acid and methanol, and concentrated to dryness. This residue was extracted with 4:1 ether–acetone, leaving a residue of the hydrochloride of N,N'-

---

[21] M. T. Folpmers, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 208.

[22] L. Horner and W. Neumann, *Ann.*, **587**, 81 (1954).

[23] E. Fischer, *ibid.*, **190**, 178 (1878).

[24] J. Biehringer and A. Busch, *Ber.*, **36**, 139 (1902).

diphenyl-N-benzoylhydrazine (V), 0.027 g. (0.083 mmole), 12% yield. The ether–acetone extract was concentrated and the residue was crystallized from acetone–water, leading to N,N-diphenyl-N'-benzoylhydrazine (IV), 0.025 g. (0.088 mmole), 13% yield.

M-9.—A solution of 0.243 g. (1.15 mmoles, 0.60 *M*) of I in 1.90 ml. of methanol and 0.05 ml. of concentrated hydrochloric acid was allowed to react for 2 hr. Vapor phase chromatography indicated presence of 0.080 g. (0.59 mmole, 51% yield) of methyl benzoate and 0.022 g. (0.28 mmole, 25% yield) of benzene. The solution was worked up as described in M-5, leading to 0.012 g. (0.036 mmole, 6.3% yield) of N,N'-diphenyl-N-benzoylhydrazine hydrochloride and 0.015 g. (0.052 mmole, 9% yield) of N,N-diphenyl-N'-benzoylhydrazine.

M-10.—A solution of 0.308 g. (1.47 mmoles, 1.56 *M*) of I in 0.90 ml. of methanol was flushed with nitrogen, treated with 0.05 ml. of concentrated hydrochloric acid and stirred for 2 hr. Vapor phase chromatography indicated 0.0142 g. (0.18 mmole), 12% yield, of benzene. The solution was worked up as described in M-5, leading to 0.086 g. (0.63 mmole, 43% yield) of methyl benzoate, 0.025 g. (0.078 mmole, 11% yield) of N,N'-diphenyl-N-benzoylhydrazine hydrochloride, and 0.090 g. (0.31 mmole, 42% yield) of N,N-diphenyl-N'-benzoylhydrazine.

M-11.—A solution of 0.52 g. (2.4 mmoles, 0.24 *M*) of I in 10 ml. of methanol was degassed three times at 10^{-5} mm. by the freeze–melt method, 0.5 ml. of hydrochloric acid was added, and the solution was allowed to stand for 2 hr. The solution was frozen in liquid nitrogen, the gas was transferred to a sample holder by a Toepler pump, and then passed through Molecular Sieve 13X at room temperature with helium carrier; analysis indicated the presence of nitrogen only and the absence of hydrogen and carbon monoxide. A similar reaction of 0.24 g. (1.1 mmoles) of I in 8 ml. of methanol, treated with 0.05 g. of sodium methoxide in 2 ml. of methanol, led to nitrogen as the only gaseous product.

MB-1.—A solution of 0.331 g. (1.58 mmoles, 0.20 *M*) of I in 4 ml. of methanol was treated with 4 ml. of 0.10 *M* $NaOCH_3$ in methanol. Nitrogen was evolved and the orange solution became yellow. Vapor phase chromatography carried out after 2 hr. indicated 0.144 g. (1.06 mmoles, 67% yield) of methyl benzoate and 0.047 g. (0.60 mmole, 38% yield) of benzene. The solution was concentrated and the residue was extracted with petroleum ether. The extract was concentrated and placed on alumina, leading to biphenyl, 0.0042 g. (0.027 mmole, 3.5% yield), to azobenzene, 0.0020 g. (0.017 mmole, 1.4% yield), and to methyl benzoate, 0.137 g. (1.00 mmole, 63% yield). The residue was dissolved in ether, washed with water, dried, concentrated, treated with hydrochloric acid and methanol, and again concentrated. The residue was extracted with ether–acetone, leaving the hydrochloride of N,N'-diphenyl-N-benzoylhydrazine (V), 0.0214 g. (0.066 mmole), 8.4% yield. The ether–acetone extract was concentrated and the residue was crystallized from acetone–water, leading to N,N-diphenyl-N'-benzoylhydrazine, 0.0185 g. (0.065 mmole), 8.2% yield. These products were identical with authentic samples.

MB-2.—A similar reaction starting with 0.169 g. (0.80 mmole, 0.10 *M*) of I led to methyl benzoate, 0.073 g. by vapor phase chromatography and 0.062 g. by elution (67 and 57% yield, respectively), to benzene, 0.025 g. (0.33 mmole, 41% yield), to biphenyl, 0.0020 g. (0.013 mmole, 3.2% yield), to azobenzene, 0.0015 g. (0.0083 mmole, 2% yield), to the hydrochloride of V, 0.0076 g. (0.023 mmole, 5.8% yield), and to IV, 0.0071 g. (0.025 mmole, 6.2% yield).

Reactions in 2-Propanol. P-1.—A solution of 0.053 g. (0.252 mmole, 0.0050 *M*) of I in 50 ml. of 0.10 *N* HCl in 2-propanol (Spectrograde, acetone free) was allowed to react at 18° in a nitrometer, leading to 4.80 ml. of nitrogen (at 30°), 77% yield. Vapor phase chromatography indicated the presence of 0.021 g. (0.13 mmole, 52% yield) of 2-propyl benzoate, 0.012 g. (0.15 mmole, 61% yield) of benzene, and 0.0065 g. (0.11 mmole, 45% yield) of acetone.

P-2.—A similar experiment was carried out starting with 0.229 g. (1.09 mmoles, 0.0218 *M*) of I, and leading to 15.7 ml. (60% yield) of nitrogen (30°), 0.0775 g. (0.47 mmole, 44% yield) of 2-propyl benzoate, 0.0365 g. (0.47 mmole, 43% yield) of benzene, 0.0198 g. (0.34 mmole, 31% yield) of acetone, 0.0165 g. (0.051 mmole, 9.3% yield) of the hydrochloride of V, and 0.025 g. (0.087 mmole, 16% yield) of IV.

P-3.—A solution of 0.211 g. (1.00 mmole, 0.201 *M*) of I in 5 ml. of 2-propanol was prepared. A portion, 0.50 ml., was treated with 0.2 ml. of concentrated hydrochloric acid and analyzed after 2 hr. at room temperature, leading to 5.85 ml. (35% yield) of nitrogen at 112 mm., 25°, 0.00535 g. (0.033 mmole, 33% yield) of 2-propyl benzoate, and 0.0021 g. (0.027 mmole, 27% yield) of benzene.

P-4.—A solution of 0.132 g. (0.63 mmole, 0.242 *M*) of I in 2.5 ml. of 2-propanol was treated with 0.05 ml. of concentrated hydrochloric acid and stirred for 2 hr. Vapor phase chromatography indicated 0.0108 g. (0.138 mmole, 22% yield) of benzene and 0.0085 g. (0.147 mmole, 23% yield) of acetone. Subsequent work-up, analogous to that of expt. M-5, led to 0.040 g. (0.24 mmole, 39% yield) of 2-propyl benzoate, 0.015 g. (0.046 mmole, 15% yield) of the hydrochloride of V, and 0.017 g. (0.059 mmole, 19% yield) of IV.

P-5.—A solution of 0.338 g. (1.61 mmoles, 1.04 *M*) of I in 1.5 ml. of 2-propanol was flushed with nitrogen, treated with 0.05 ml. of concentrated hydrochloric acid, and stirred for 2 hr. Vapor phase chromatography indicated formation of 0.020 g. (0.34 mmole, 21% yield) of acetone and 0.029 g. (0.37 mmole, 23% yield) of benzene. Subsequent work-up led to 0.090 g. (0.55 mmole, 34% yield) of 2-propyl benzoate, 0.005 g. (0.16 mmole, 2% yield) of the hydrochloride of V, and 0.061 g. (0.21 mmole, 25% yield) of IV. The acetone was characterized as its 2,4-dinitrophenylhydrazine, m.p. 122–124°, m.m.p. 122–125°.

Methanolysis of I in the Presence of Fumaric Acid. MF.—Compound I (0.500 g., 2.38 mmoles, 0.24 *M*) and 2.41 g. (0.0208 mole, 2 *M*) of fumaric acid, 10 ml. of methanol, and 0.5 ml. of hydrochloric acid were stirred under nitrogen at room temperature for 2 hr. Vapor phase chromatography indicated the presence of 0.240 g. (1.24 mmoles, 52% yield) of phenylsuccinic acid, 0.242 g. (1.78 mmoles, 75% yield) of methyl benzoate, and a trace of biphenyl. Succinic acid was not detected. A sample of the phenylsuccinic acid was isolated by vapor phase chromatography, m.p. 165–167°, m.m.p. 164–167° with an authentic sample, lit.[25] m.p. 167°. The infrared spectrum was identical with that of the authentic sample. Repetition of this experiment in the absence of hydrochloric acid led to similar results, 46% phenylsuccinic acid, 75% methyl benzoate, and 4% benzene.

Methanolysis of I in the Presence of Carbon Tetrachloride. C-1.—A mixture of 1.03 g. (4.9 mmoles, 0.26 *M*) of I in 15 ml. of carbon tetrachloride, 3 ml. of methanol, and 1 ml. of hydrochloric acid was stirred under nitrogen for 1 day at room temperature. Vapor phase chromatography indicated the presence of 0.036 g. (0.46 mmole, 9.4% yield) of benzene and 0.075 g. (0.67 mmole, 14% yield) of chlorobenzene. The latter was isolated by chromatography on alumina, 0.070 g., 13% yield. Its boiling point, 130–132°, and its infrared spectrum were identical with those of an authentic sample.

C-2.—A solution of 0.143 g. (0.682 mmole, 0.17 *M*) of I in 3 ml. of carbon tetrachloride and 1 ml. of methanol was treated with 0.05 ml. of hydrochloric acid and allowed to react for 2 hr. Vapor phase chromatography indicated the presence of 0.0535 g. (0.39 mmole, 58% yield) of methyl benzoate, 0.031 g. (0.28 mmole, 40% yield) of chlorobenzene, 0.015 g. (0.13 mmole, 19% yield) of chloroform, and a trace of hexachloroethane. Work-up led to 0.0055 g. (0.017 mmole, 5% yield) of the hydrochloride of V and 0.0044 g. (0.015 mmole, 4.4% yield) of IV.

Methanolysis of I in the Presence of Benzene. B-1.—A solution of 0.206 g. (0.98 mmole, 0.044 *M*) of I in 15 ml. of benzene was treated with 0.5 ml. of concentrated hydrochloric acid, no reaction occurring. Methanol, 7 ml., was added, leading to a homogeneous solution, immediate evolution of nitrogen and development of a deep red color. Vapor phase chromatography indicated the presence of 0.037 g. (0.24 mmole, 24% yield) of biphenyl. The solution was poured into water and ether and extracted with sodium bicarbonate; benzoic acid was not found. The ether solution was dried and concentrated and the residue was placed on Fischer neutral alumina. Biphenyl was obtained by elution with petroleum ether, 0.023 g. (0.15 mmole), 15% yield, m.p. and m.m.p. 70°, infrared spectrum (KBr) identical with that of an authentic sample.

B-2.—A similar reaction consisting of 0.74 g. (3.5 mmoles, 0.23 *M*) of I in 9 ml. of benzene, 6 ml. of methanol, and 0.5 ml. of hydrochloric acid stood under nitrogen for 2 days. Vapor phase chromatography indicated the presence of 0.173 g. (1.27 mmoles, 36% yield) of methyl benzoate.

B-3.—A mixture of I, 0.036 g. (0.17 mmole), in 1 ml. of benzene and 0.02 ml. of 1 *M* hydrogen chloride in methanol was

---

[25] P. A. S. Smith and J. P. Horwitz, *J. Am. Chem. Soc.*, **71**, 3418 (1949).

shaken for 1 hr. at room temperature. Vapor phase chromatography indicated the presence of 0.0095 g. (0.070 mmole, 41% yield) of methyl benzoate and 0.0097 g. (0.063 mmole, 38% yield) of biphenyl.

B-4.—A mixture of 0.034 g. (0.16 mmole) of I in 1 ml. of benzene and 0.03 ml. of 1.0 *M* sodium methoxide in methanol was shaken for 1 hr. Vapor phase chromatography indicated the presence of 0.0058 g. (0.043 mmole, 26% yield) of methyl benzoate and 0.0072 g. (0.046 mmole, 29% yield) of biphenyl.

Methanolysis of I in the Presence of Nitrobenzene. N-1.—A solution of 0.158 g. (0.75 mmole, 0.177 *M*) of I in 3 ml. of nitrobenzene, 1 ml. of methanol, and 0.1 ml. of hydrochloric acid was stirred for 2 hr. Vapor phase chromatography indicated the presence of 0.0060 g. (0.077 mmole, 10% yield) of benzene, 0.0154 g. (0.077 mmole, 10% yield) of 2-nitrobiphenyl, 0.0038 g. (0.019 mmole, 2.5% yield) of 3-nitrobiphenyl, 0.030 g. (0.15 mmole, 20% yield) of 4-nitrobiphenyl; by elution chromatography 0.059 g. (0.43 mmole, 57% yield) of methyl benzoate was obtained.

N-2.—A solution of 0.290 g. (1.38 mmoles, 0.28 *M*) of I in 3 ml. of nitrobenzene, 1.5 ml. of methanol, and 0.5 ml. of hydrochloric acid was stirred for 5 hr. Vapor phase chromatography indicated the presence of 0.0038 g. (0.025 mmole, 3.6% yield) of biphenyl, 0.031 g. (0.15 mmole, 11% yield) of 2-nitrophenyl, 0.0070 g. (0.036 mmole, 2.6% yield) of 3-nitrobiphenyl, and 0.044 g. (0.22 mmole, 16% yield) of 4-nitrobiphenyl. Samples of the nitrobiphenyls were isolated by vapor phase chromatography and found to have infrared spectra identical with those of authentic samples. Melting points of the 2- and 4-nitrobiphenyls were unchanged when mixed with authentic samples, 35–37° and 110–113°, respectively.

N-3.—A solution of 0.924 g. (4.4 mmoles, 0.18 *M*) of I in 16 ml. of nitrobenzene and 9 ml. of 0.10 *M* sodium methoxide in methanol stood for 2 days, the methanol was distilled, and the residue was filtered. Vapor phase chromatography of the filtrate indicated the presence of azobenzene, biphenyl, and 0.042 g. (0.21 mmole, 4.8% yield) of 2-nitrobiphenyl, 0.015 g. (0.076 mmole, 1.7% yield) of 3-nitrobiphenyl, and 0.117 g. (0.59 mmole, 13.4% yield) of 4-nitrobiphenyl.

Methanolysis of I in the Presence of Naphthalene. A.—A mixture of 0.181 g. (0.86 mmole, 0.19 *M*) of I and 1.17 g. (9.2 mmoles) of naphthalene in 4.3 ml. of methanol was stirred and treated with 0.05 ml. of concentrated hydrochloric acid. Nitrogen was evolved and a red color developed. After 2 hr., analysis by vapor phase chromatography indicated formation of 0.062 g. (0.46 mmole, 53% yield) of methyl benzoate, 0.016 g. (0.21 mmole, 24% yield) of benzene, 0.0076 g. (0.087 mmole, 4.4% yield) of 1-phenylnaphthalene, 0.0013 g. (0.0065 mmole, 0.8% yield) of 2-phenylnaphthalene, and small yields of biphenyl and azobenzene. The mixture was concentrated and washed with 40–60° petroleum ether. The residue was dissolved in methanol, treated with hydrochloric acid, concentrated, and extracted with 4:1 ether–acetone. The residue was the hydrochloride of N,N′-diphenyl-N-benzoylhydrazine (V), 0.016 g. (0.050 mmole), 5.8% yield. The extract was treated with water and acetone and concentrated, leading to IV, N,N-diphenyl-N′-benzoylhydrazine, 0.016 g. (0.056 mmole), 6.5% yield.

B.—A mixture of 0.179 g. (0.85 mmole, 0.20 *M*) of I and 1.61 g. (12.5 mmoles) of naphthalene treated with 4.2 ml. of 0.1 *M* sodium methoxide in methanol led to evolution of nitrogen and formation of a yellow color. After 2 hr. vapor phase chromatography indicated the presence of 0.066 g. (0.49 mmole, 57% yield) of methyl benzoate, 0.017 g. (0.22 mmole, 26% yield) of benzene, 0.013 g. (0.063 mmole, 7.4% yield) of 1-phenylnaphthalene, 0.0012 g. (0.006 mmole, 0.7% yield) of 2-phenylnaphthalene, and traces of biphenyl and azobenzene. The reaction mixture was worked up as described above in A, leading to the hydrochloride of V, 0.013 g. (0.039 mmole), 4.6% yield, and to IV, 0.012 g. (0.042 mmole), 4.9% yield.

Polymerization of Acrylonitrile by I.—Acrylonitrile (Eastman Kodak Co.) was distilled, b.p. 78–79°, at atmospheric pressure. A stock solution of 1.57 g. of I in 100 ml. of acrylonitrile (0.075 *M*) was prepared. Separate 5-ml. aliquots of this solution were flushed with argon and treated (a) with 0.1 ml. of methanol and 0.01 ml. of concentrated hydrochloric acid, (b) with 1.0 ml. of methanol and 0.5 ml. of hydrochloric acid, and (c) with 0.1 ml. of methanol. Blank solutions were 5-ml. portions of acrylonitrile containing (d) 0.1 ml. of methanol and 0.01 ml. of hydrochloric acid, and (e) 1.0 ml. of methanol and 0.5 ml. of hydrochloric acid.

Solution a turned red, and a precipitate soon formed. After 2 hr., 0.27 g., 6.8% yield, of polyacrylonitrile was collected, by precipitation into methanol. Solution b became red, cloudy, and warm. After 4 hr. the polymer was precipitated, 2.6 g., 65% yield. Solution c appeared unchanged after 2 hr.; after 48 hr., 0.14 g., 3.5% yield, of polyacrylonitrile was obtained. Solutions d and e remained unchanged; no precipitate formed.

Authentic polyacrylonitrile[26] was prepared by stirring 5 ml. of acrylonitrile, 6.5 ml. of water, 3.5 ml. of 0.065 *M* aqueous ferrous sulfate, and 2 ml. of 30% hydrogen peroxide for 3 hr. The polymer was washed with water, methanol, and petroleum ether and dried *in vacuo* at 60°. Conversion was quantitative. Infrared spectra were obtained for the samples of polyacrylonitrile. That prepared with hydrogen peroxide as initiator showed an O—H band at 2.85 μ, a C—O band at 9.3 μ, and a strong C≡N band at 4.45 μ. That prepared with compound I as initiator showed a very weak OH absorption at 2.8–3.0 μ, a medium C—O band at 9.2 μ, a very weak C═O band at 6.0 μ, characteristic monosubstituted phenyl bands at 13.2 and 14.2 μ, and the strong C≡N band at 4.45 μ. This sample of polymer had been extracted with petroleum ether for 48 hr. to remove occluded methanol. The ultraviolet spectrum of this sample of polymer showed a shoulder at 235 mμ and a broad shoulder at 330–360 mμ, perhaps indicative of phenyl and phenylazo groups. These absorptions were absent in the polymer prepared with hydrogen peroxide initiator.

---

(26) W. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 159, 165, 168.