dissolved in 10 ml of purified cumene[18] and the solution was degassed, while cooled with liquid nitrogen. The reaction mixture was then allowed to warm up to room temperature and gradually heated to 132° under a nitrogen atmosphere and maintained at this temperature for 5 hr. The gases evolved were caught and analyzed in an Orsat apparatus.

When the reaction was finished, the mixture was allowed to cool to room temperature and kept overnight in the refrigerator. Colorless needles separated out and were identified as phthalic anhydride, mp 132°; a mixture melting point with an authentic sample gave no depression, yield 0.543 g (72%). From the filtrate (8.656 g) a vapor phase chromatogram was run showing the presence of acetone and *t*-butyl alcohol (column, polypropylene glycol UC oil LB-550-X; column temperature, 73°). The quantitative amounts of both products were determined from their peak areas of the chromatogram. In addition to the gas chromatographic identification, the formation of acetone and *t*-butyl alcohol was proved by preparing derivatives. The reaction solution was therefore fractionated in order to separate the mixture of acetone and *t*-butyl alcohol from most of the cumene. The distillate was divided into two portions which were treated with 2,4-dinitrophenylhydrazine and 3,5-dinitrobenzoylchloride,[19] respectively. The melting points of the corresponding acetone 2,4-dinitrophenylhydrazone and *t*-butyl-3,5-dinitrophenylbenzoate agreed with the literature values. The remaining cumene solution was subjected to a vacuum (2 mm) distillation to remove the cumene; more crystalline product separated. Petroleum ether was added, causing a partial solution of the solid material. This was separated by filtration and identified as additional phthalic anhydride (0.08 g), increasing the total yield of phthalic anhydride to 0.623 g (83%). From the filtrate, the petroleum ether was removed under vacuum and a yellow crystalline compound was obtained which was purified by recrystallization from ethanol and identified as dicumyl, mp 118°, and by a mixture melting point with an authentic sample[20] and comparison of the infrared spectra; yield 0.367 g.

Analysis of the gaseous products showed that no oxygen or carbon dioxide had been formed. An infrared spectrum run in a gas cell exhibited the following bands: 3050–2900 (triplet), 1730, 1440, 1340, 1300, 1260–1200, and 890 cm^{-1}. Furthermore, a mass spectrum was run showing absorptions at m/e 27 and 29. Both spectra indicate strongly the presence of ethane and ethylene.

Reaction of Unsymmetrical Phthalyl Chloride with *t*-Butyl Hydroperoxide in the Presence of Pyridine.—Unsymmetrical phthalyl chloride (2.03 g, 0.01 mole), dissolved in 10 ml of anhydrous ether, and *t*-butyl hydroperoxide (3.60 g, 0.04 mole), likewise dissolved in 10 ml of anhydrous ether, were dropped simultaneously in the course of 0.5 hr to a solution of dry pyridine (1.58 g, 0.02 mole) in 20 ml of anhydrous ether at 0° with stirring. Pyridine hydrochloride precipitated during the addition. The reaction mixture was then allowed to warm up to room temperature and stirring was continued overnight. After separation of the pyridine hydrochloride by filtration, the ether was removed under reduced pressure leaving a colorless liquid which was subjected to a vacuum of 2 mm to remove the excess *t*-butyl hydroperoxide. An infrared spectrum taken of the final product revealed that di-*t*-butyl diperoxyphthalate was the only peroxidic product present. For further purification, the product was redissolved in ether, and the ether solution was extracted with ice-cold 10% sodium hydroxide, the ether layer was washed with water, dried over magnesium sulfate, filtered, and the ether was removed under reduced pressure, leaving a viscous liquid which crystallized on standing. The crystals were washed with petroleum ether, dried (mp 48°), and identified as di-*t*-butyl diperoxyphthalate by mixture melting point and infrared spectrum; yield 2.28 g (73.6%).

Effect of *t*-Butyl Hydroperoxide on 3,3-Di-*t*-butyl Diperoxyphthalide.—Since the unsymmetric 3,3-di-*t*-butyl diperoxyphthalid contains a γ-lactone ring it was thought advisable to try the effect of *t*-butyl hydroperoxide on this ring. Consequently 0.2 g of 3,3-di-*t*-butyl diperoxyphthalid was heated with stirring at 60–70° with excess *t*-butyl hydroperoxide for 2.5 hr. The excess *t*-butyl hydroperoxide was then removed at 2 mm, whereby a slightly yellow viscous liquid was separated which crystallized on standing. When the crystals were washed with petroleum ether and dried, they melted at 86° and were shown by mixture melting point to be identical with the starting material and the recovery was nearly quantitative.

Acid Hydrolysis of 3,3-Di-*t*-butyl Diperoxyphthalide.—Sulfuric acid (1 ml, 50% concentrated) was added to a stirred solution of 3,3-di-*t*-butyl diperoxyphthalid (0.20 g) in 10 ml of ether at 0°. The reaction was allowed to continue for 2 hr, while the mixture was warmed to room temperature. Water was then added and the sulfuric acid was neutralized with magnesium carbonate, the ether layer was separated, dried over magnesium sulfate, filtered, and the ether was removed under reduced pressure. White crystals were separated (mp 84–85°) and identified by mixture melting point as the starting material and the recovery was nearly quantitative. This experiment shows that the acid failed to open the γ-lactone ring.

Basic Hydrolysis of 3,3-Di-*t*-butyl Diperoxyphthalide.—3,3-Di-*t*-butyl diperoxyphthalid (0.10 g, 3.22×10^{-4} mole) was dissolved in 6 ml of ethylene glycol monomethyl ether and to the solution was added 0.8 ml of 10% aqueous sodium hydroxide. The reaction mixture was stirred for 2 hr at 40°, then added to it successively 15 ml of acetic acid, 3 ml of saturated potassium iodide solution, and a piece of Dry Ice. After standing for 0.5 hr at 60°, the iodine liberated was titrated with standard sodium thiosulfate. On the basis of formula III, 86.5% of the expected 2 mole equiv of *t*-butyl hydroperoxide was found. In a separate experiment one of the hydrolysis products (phthalic acid) was isolated by extracting the acidified reaction mixture with ether and evaporating the solvent. A white solid was obtained mp 186–187° and identified as phthalic acid by mixture melting point.

Registry No.—I, 15042-77-0; II, 2155-71-7; III, 15044-23-2.

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Reactions of Hydrazines with Esters and Carboxylic Acids

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As part of a continuing study of the thermolytic and photolytic decomposition of amine imides,[3] we required large quantities of 1,1-dimethyl-2-acylhydrazines (I) for subsequent conversion to trimethylamine imides. Hinman[4] has reported that 1,1-dimethylhydrazine reacts with benzoyl chloride to give mixtures of 1,1-dibenzoyl-2,2-dimethylhydrazine and 1-benzoyl-2,2-dimethylhydrazine with the former predominating under

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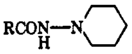
[4] R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956).

TABLE I

N-SUBSTITUTED HYDRAZIDES $RCONHN(CH_3)_2$

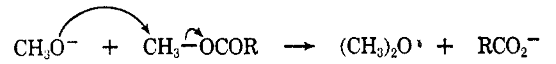
R[i]	Recrystn solvent	Mp, °C	Yield, %[a] From methyl ester	Yield, %[a] From acid	C, % Calcd	C, % Found	H, % Calcd	H, % Found	N, % Calcd	N, % Found
1. C_6H_5—	$EtOH-H_2O$	105–107[b]	56	67						
2. p-$CH_3C_6H_4$—	C_6H_6	111–112	32	68	67.38	67.79	7.92	7.93	15.72	15.75
3. p-$CH_3OC_6H_4$—	C_6H_6-PE[c]	116–118	14	68	61.83	61.66	7.26	7.38	14.43	14.22
4. m-$CH_3OC_6H_4$—	C_6H_6-PE	93–94		55	61.83	61.74	7.26	7.22	14.43	14.42
5. o-$CH_3OC_6H_4$—		Oil[d]	80	64						
6. p-$NO_2C_6H_4$—	C_6H_6	151–153		61	51.69	51.44	5.26	5.26	20.09	20.37
7. o-FC_6H_4—	C_6H_6-PE	116–117		46	59.33	59.07	6.08	6.09	15.38	15.29
8. p-BrC_6H_4—	$EtOH-H_2O$	150–152	51		44.46	44.17	4.56	4.55	11.52	11.60
9. 3,4-$CH_3OC_6H_3$—	C_6H_6-PE	145–147		41	58.91	58.97	7.19	7.33	12.49	12.36
10. $C_6H_5CH{=}CH$—	C_6H_6	111–112[e]	24	72					14.73	14.89
11. $C_6H_5C{\equiv}C$—	$CHCl_3$-PE	192–194 dec		68	70.17	69.80	6.43	6.34	14.88	14.73
12. $(C_6H_5)_2C(OH)$—	EtOH	185–187[f]	48		71.12	71.34	6.66	6.77	10.37	10.28
13. $(C_6H_5)_2CH$—	C_6H_6	165–167[g]		63	75.56	75.95	7.13	7.13	11.02	11.15
										
14. C_6H_5—	$MeOH-H_2O$	196–198[h]	74	60						
15. p-$NO_2C_6H_4$—	EtOH	218–219		23	57.82	57.95	6.06	6.02	16.86	16.73
			$RCON(CH_3)NH_2$							
16. p-$CH_3OC_6H_4$—	C_6H_6-PE	72–73.5		50	59.98	59.84	6.71	6.73	15.54	15.70
17. p-$NO_2C_6H_4$—	C_6H_6-PE	132–134		32	49.22	49.29	4.64	4.64	21.52	21.53

[a] Yields are based on unrecrystallized products. [b] Reference 4 reports mp 106–107°. [c] Petroleum ether, bp 38–52°. [d] Isolated as the methiodide, see Experimental Section. [e] Reference 5 reports mp 111–112°. [f] Reference 5 reports mp 192–193°. [g] Reference 5 reports mp 172–173°. [h] P. A. S. Smith and H. G. Pars, *J. Org. Chem.*, **24**, 1325 (1959). [i] Registry no.: 2, 14908-39-5; 3, 14908-40-8; 4, 14908-41-9; 6, 14908-42-0; 7, 14908-43-1; 8, 14908-44-2; 9, 14908-45-3; 11, 14908-46-4; 15, 2612-89-7; 16, 14908-48-6; 17, 14908-49-7.

the conditions employed.[5] These earlier results were confirmed in our laboratories and the dibenzoyl compound was also found as the major product when the acylation was conducted under Schotten–Baumann conditions (aqueous sodium hydroxide or pyridine).

Since acylation with acid chlorides did not appear to be a promising route to the desired compounds, we turned our attention to the use of esters as acylating agents for 1,1-dimethylhydrazine. Hinman and Fulton[6] reported that the reaction of ethyl formate with 1,1-dimethylhydrazine readily gave 1-formyl-2,2-dimethylhydrazine, but methyl acetate, ethyl acetate, and methyl benzoate did not react with 1,1-dimethylhydrazine when the reactions were conducted at reflux temperature. We have verified that no acylation occurs when methyl benzoate and 1,1-dimethylhydrazine are heated under reflux but under these conditions, some nucleophilic substitution does occur and we have isolated a low yield of 1,1,1-trimethylhydrazinium benzoate (II, R = C_6H_5)[7] from the reaction mixture. When the reaction was conducted at 130° in a sealed tube, the yield of II was increased to 42% and again no acylated products could be detected. The reactions of 1,1-dimethylhydrazine with methyl p-anisate and methyl p-nitrobenzoate, respectively, also resulted in the formation of the corresponding 1,1,1-trimethylhydrazinium salts in low yield. A small amount of the reductive coupling product, 4,4′-dicarbomethoxyazobenzene (III), was also formed from the latter reaction. To our knowledge, this is the first example of the reduction of a nitro group by an N,N-disubstituted hydrazine.[8]

Bunnett and Davis[9a] have observed that in the absence of added methoxide ion, the reaction between n-butylamine and methyl benzoate is too slow to be detected. However, in the presence of methoxide ion, the aminolysis reaction proceeded at reasonable rates and a first-order kinetic dependence on methoxide ion was established. Further encouraged by reports of general base catalysis in the aminolysis[9] and hydrazinolysis[10] of esters, we next undertook a study of methoxide ion catalysis in the reaction of methyl esters with 1,1-dimethylhydrazine. In contrast to the results described above, we have found that in the presence of methoxide ion, the reaction proceeds to give mixtures of hydrazides (I) and the sodium salts of the carboxylic acids. The sodium salts are undoubtedly formed by a nucleophilic displacement by the methoxide ion on the ester (eq 1). The yields of hydrazides obtained by



$$CH_3O^- + CH_3{-}OCOR \longrightarrow (CH_3)_2O + RCO_2^- \qquad (1)$$

this method (Table I) varied from 14 to 80%, but the products were easily obtained in a pure form. It was also found that in the presence of methoxide ion, 1-benzamidopiperidine is formed in 74% yield from the reaction of methyl benzoate and 1-aminopiperidine. The reaction of 1-methyl-1-phenylhydrazine with methyl benzoate in the presence of methoxide ion failed to yield a crystalline product.

We have also found that a variety of carboxylic acids can be used to acylate 1,1-dimethylhydrazine by means

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[5] More recently, and since the inception of our work, R. F. Meyer and B. C. Cummings [*J. Heterocyclic Chem.*, **1**, 186 (1964)] have reported that good yields of 1,1-dialkyl-2-acylhydrazines may be obtained by slow addition of acid chlorides to an excess of the hydrazine in ether or tetrahydrofuran.

[6] R. L. Hinman and D. Fulton, *J. Am. Chem. Soc.*, **80**, 1895 (1958).

[7] For a discussion of the alkylation of 1,1-disubstituted hydrazine derivatives, see H. H. Sisler, G. M. Omietanski, and B. Rudner, *Chem. Rev.*, **57**, 1027 (1957).

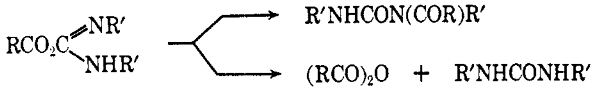
[8] A. Furst, R. C. Berlo, and S. Hooton, *ibid.*, **65**, 59 (1965).

[9] (a) J. F. Bunnett and G. F. Davis, *J. Am. Chem. Soc.*, **82**, 665 (1960); (b) W. P. Jencks and J. Carriuolo, *ibid.*, **82**, 675 (1960).

[10] T. C. Bruice and R. G. Willis, *ibid.*, **87**, 531 (1965).

of N,N′-dicyclohexylcarbodiimide. Although diimides have found extensive use in the synthesis of peptides and amides,[11] to our knowledge they have not previously been utilized for the synthesis of hydrazides. The hydrazides were easily obtained in a pure state by acid extraction of the filtrate obtained after removal of the insoluble N,N′-dicyclohexylurea. The yields and properties of the hydrazides obtained by this method are also recorded in Table I.

We have also found that 1-aminopiperidine can be acylated by benzoic acid and *p*-nitrobenzoic acid in yields of 60 and 23%, respectively. The latter represents the lowest yield obtained by the diimide method. We were able to isolate a small quantity of 1,3-dicyclohexyl(4-nitrobenzoyl)urea from the acid insoluble products formed in the latter reaction. The formation of the acylated urea is an expected side reaction since the O-acylisoureas initially formed from the reaction of carboxylic acids with diimides can, in addition to functioning as acylating agents, react further to give N-acylureas or a urea and the anhydride of the acid[12] (eq 2). Apparently, the diimide method cannot be used for the synthesis of N,N-diacylated hydrazines. Reaction of 1-aminopiperidine, benzoic acid and N,N′-dicyclohexylcarbodiimide in a 1:2:2 molar ratio afforded 60% of 1-benzamidopiperidine and 23% of 1,3-dicyclohexyl-1-benzoylurea.



$$RCO_2C(=NR')NHR' \longrightarrow R'NHCON(COR)R' \quad \text{or} \quad (RCO)_2O + R'NHCONHR' \qquad (2)$$

Benzoylhydrazine was converted to 1,2-dibenzoylhydrazine in 38% yield by the diimide method.

It was also of interest to ascertain the site of acylation of a monosubstituted hydrazine by the diimide method. Hinman and Fulton[6] have reported that methylhydrazine reacts with esters to give mainly the 1-acyl-2-methylhydrazine, but when anhydrides are employed as the acylating agent, the major product is the 1-acyl-1-methylhydrazine. Analogous results have recently been reported for the acylation of methylhydrazine with phenylacetic anhydride and ethyl phenylacetate.[13] We have found that benzoic, acetic, propionic, and phenylacetic acids react with methylhydrazine in the presence of N,N′-dicyclohexylcarbodiimide to give oily products which have been identified as 1-acyl-1-methylhydrazines. In the case of the acetyl, propionyl, and benzoyl derivatives, identity was established by conversion to the known[6] 1-acyl-1-methyl-4-phenyl-3-thiosemicarbazides (V). The crude 1-methyl-1-phenylacetylhydrazine was identified by conversion to the known 4-nitrobenzalhydrazine.[13] The yields and melting points[14] of these semicarbazides are reported in Table II. *p*-Anisic acid and *p*-nitrobenzoic acid were converted to crystalline acylmethylhydrazines by the diimide method. These compounds were assigned 1-acyl structures by analogy with the results described above. The reaction of *p*-nitrobenzoic acid with methylhydrazine resulted in the formation of a rather complex mixture of products which included 32% of the hydrazide, 5% of 1,3-dicyclohexyl-1-(4-nitrobenzoyl)urea, and an unidentified compound of high molecular weight.

TABLE II

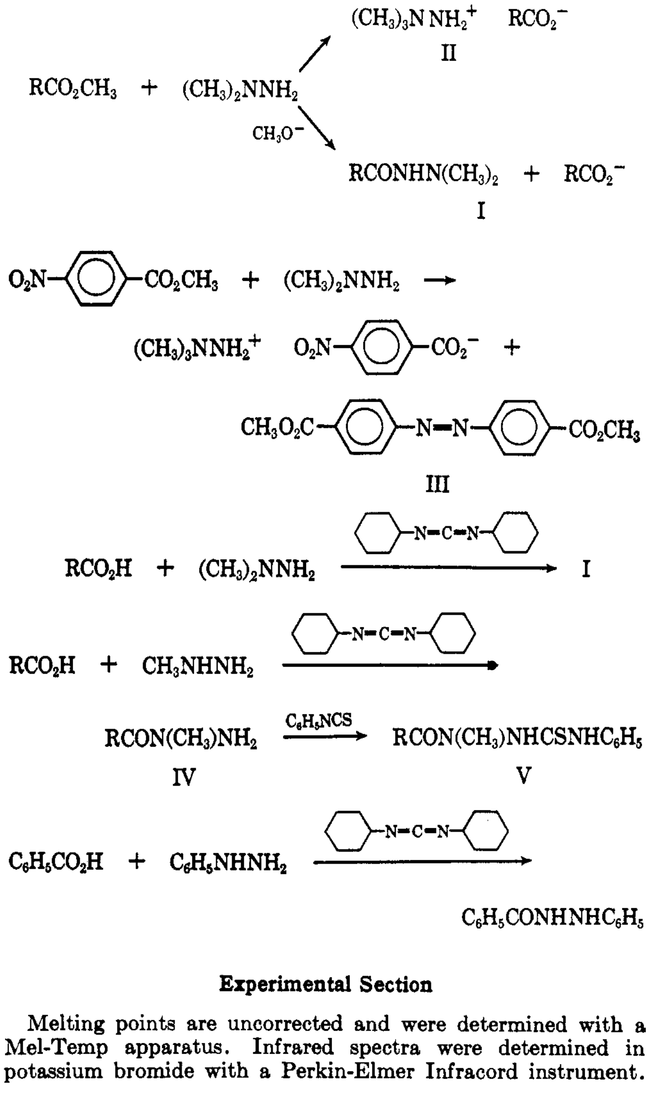
$RCON(CH_3)NHCSNHC_6H_5$ FROM $RCON(CH_3)NH_2$

R	Mp, °C Found[b]	Mp, °C Reported	Yield, %[a]
C_6H_5–	156–157	153–155	50
CH_3–	164–167	163–164	78
C_2H_5–	171–173	170–172	42
$C_6H_5CH_2$–[c,d]	154–156		58

[a] Yields are calculated for recrystallized products and are based on the quantity of acid employed in the acylation. [b] All melted with decomposition. See ref 14. [c] White crystals (from ethanol). *Anal.* Calcd for $C_{16}H_{17}N_3OS$: C, 64.18; H, 5.72; N, 14.04. Found: C, 64.20; H, 5.72; N, 14.12. [d] Registry no., 14908-50-0.

Reaction of phenylhydrazine with benzoic acid by the diimide method afforded negligible acid-soluble material. The neutral fraction contained a mixture from which it was possible to isolate 26% of 1-benzoyl-2-phenylhydrazine (Chart I).

CHART I



Experimental Section

Melting points are uncorrected and were determined with a Mel-Temp apparatus. Infrared spectra were determined in potassium bromide with a Perkin-Elmer Infracord instrument.

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[11] For leading references, see F. Kurzer and K. Douroghi-Zadeh, *Chem. Rev.*, **67**, 128 (1967).

[12] Reference 11, p 123.

[13] W. J. Theuer and J. A. Moore, *J. Org. Chem.*, **29**, 3734 (1964).

[14] Hinman and Fulton[6] noted that compounds of type V melt with gas evolution and resolidify to give higher melting substances. We have established that thermolysis of these compounds results in loss of water and the formation of mesoionic 1-methyl-3-thio-4-phenyl-5-*R*-1,2,4-triazolium hydroxide inner salts. The results of this study will be published at a later date. For leading references on other methods of synthesis of mesoionic 1,2,4-triazoles, see G. F. Duffin, J. D. Kendall, and H. R. Waddington, *J. Chem. Soc.*, 3799 (1959).

Analyses are by Galbraith Laboratories and by Mr. Kenneth Fleischer of the Sterling-Winthrop Research Institute.

1,1,1-Trimethylhydrazinium Benzoate.—A sealed tube containing 6.8 g (0.05 mole) of methyl benzoate and 3.0 g (0.05 mole) of 1,1-dimethylhydrazine was heated for 18 hr at 130°. On cooling, the contents solidified. On dilution with ether, an oil was obtained which crystallized on cooling to give 4.1 g (42%) of extremely hygroscopic crystals, mp 75–77°. When the reaction was conducted at reflux temperature for 14 hr, the yield was 9%. The analytical sample was prepared by several recrystallizations from ethanol–ether, mp 84–85°. Immediately prior to analysis, the compound was dried *in vacuo* at 60° (3.90% loss in weight).

Anal. Calcd for $C_{10}H_{18}N_2O_3$ (monohydrate): C, 56.05; H, 8.47; N, 13.08. Found: C, 56.11; H, 8.05; N, 13.12.

Addition of the pure salt to a saturated solution of potassium iodide gave 1,1,1-trimethylhydrazinium iodide, mp 254–256° dec, lit.[15] mp 258°. The infrared spectrum of the iodide was identical with that of an authentic sample. Acidification of an aqueous solution of the salt gave benzoic acid, mp and mmp 121–122°.

Reaction of 1,1-Dimethylhydrazine with Methyl *p*-Nitrobenzoate.—A solution of 9.1 g (0.05 mole) of methyl *p*-nitrobenzoate, 3.0 g (0.05 mole) of 1,1-dimethylhydrazine, and 15 ml methanol was heated under reflux for 7 days. Crude 4,4′-dicarbomethoxyazobenzene (0.54 g, 7.2%) was removed by filtration and washed with methanol, mp 225–234°. Recrystallization from acetic acid gave orange crystals, mp 240–241° (lit.[16] mp 242°). Its infrared spectrum (KBr) showed a carbonyl band at 1725 cm^{-1}.

Anal. Calcd for $C_{16}H_{14}N_2O_4$: N, 9.39. Found: N, 9.37.

The filtrate from the isolation of the azo compound was diluted with a large volume of ether to precipitate 1.98 g (8.2%) of crude 1,1,1-trimethylhydrazinium *p*-nitrobenzoate, mp 190–230°. A small amount of the ethanol-insoluble azo compound was isolated when the salt was dissolved in ethanol. Acidification of an aqueous solution of the salt gave *p*-nitrobenzoic acid, mp 234–238°. The salt was recrystallized from ethanol as white crystals, mp 213–215°.

Anal. Calcd for $C_{10}H_{15}N_3O_4$: C, 49.78; H, 6.27. Found: C, 49.99; H, 6.04.

1,1,1-Trimethylhydrazinium *p*-Anisate.—A solution containing 3.0 g (0.05 mole) of 1,1-dimethylhydrazine and 8.3 g (0.05 mole) of methyl *p*-anisate was heated under reflux for 3 days. Dilution with ether gave 3.2 g (29%) of product, mp 161–166°. The analytical sample was recrystallized from ethanol–ether, mp 168–169°.

Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.38; H, 8.02; N, 12.38. Found: C, 58.16; H, 7.76; N, 12.17.

General Procedure for the Reaction of 1,1-Dimethylhydrazine with Methyl Esters.—The ester (0.05 mole) and 12.0 g (0.20 mole) of 1,1-dimethylhydrazine were added to a solution containing 0.10 mole of sodium methoxide in 50 ml of anhydrous methanol. The reaction mixture was heated under reflux with magnetic stirring for 24 hr. Separation of the sodium salt of the acid was frequently observed within the first hour of the reaction period. The reaction mixture was poured into 200 ml of water, and the aqueous solution (or suspension) was extracted with three 50-ml portions of chloroform. Acidification of the aqueous fraction afforded the free acid. The combined chloroform extracts were extracted with three 50-ml portions of 3 *N* hydrochloric acid. The combined acid extracts were made basic with sodium carbonate and extracted with three 50-ml portions of chloroform. Evaporation of the dried chloroform extracts gave products which usually melted within a few degrees of the analytical sample.

General Method for Reaction of Carboxylic Acids with Hydrazines.—A solution consisting of 4.1 g (0.02 mole) of N,N′-dicyclohexylcarbodiimide and 0.02 mole of the hydrazine in 80 ml of methylene chloride was treated with 0.02 mole of the carboxylic acid. Occasionally it was necessary to moderate the exothermic reactions by external cooling. After 2 hr at room temperature, the precipitated N,N′-dicyclohexylurea was removed by filtration and the filtrate extracted with three 25-ml portions of 3 *N* hydrochloric acid. The combined acid extracts were made basic with sodium carbonate and extracted with three 50-ml portions of chloroform. The products were obtained by evaporation of the dried chloroform extracts.

1,1,1-Trimethyl-2-(2-methoxybenzoyl)hydrazinium Iodide.—Acylation of 1,1-dimethylhydrazine with 3.88 g (0.02 mole) of *o*-methoxybenzoic acid afforded an oil which resisted crystallization. The crude product was treated with 10 ml of methyl iodide. After 78 hr, the solid product was suspended in petroleum ether and filtered to give 3.7 g (64%) of crude product, mp 162–165° dec. Similar treatment of the oily product from acylation with methyl *o*-methoxybenzoate afforded the crude methiodide, mp 163–166° dec, in 80% yield. The analytical sample was recrystallized from ethanol as white crystals, mp 164–165° dec.

Anal. Calcd for $C_{11}H_{17}N_2O_2I$: C, 39.30; H, 5.10; N, 8.33. Found: C, 39.30; H, 5.06; N, 8.23.

Reaction of 1-Aminopiperidine with 4-Nitrobenzoic Acid.—*p*-Nitrobenzoic acid (3.34 g, 0.02 mole) was added to a solution containing 2.00 g (0.02 mole) of 1-aminopiperidine and 4.12 g (0.02 mole) of N,N′-dicyclohexylcarbodiimide in 100 ml of methylene chloride. After 2 hr, the N,N′-dicyclohexylurea was removed by filtration and the filtrate extracted with two 25-ml portions of 3 *N* hydrochloric acid. The insoluble material which was formed during the extraction was removed by filtration and was identified as 1,3-dicyclohexyl-1-(4-nitrobenzoyl)-urea, 0.75 g, mp 192–194°.

The combined acid extracts were made basic with sodium carbonate and the resulting suspension was extracted with chloroform. Evaporation of the dried extracts gave 1.12 g (23%) of 1-(4-nitrobenzamido)piperidine, mp 218–219°.

The methylene chloride solution was dried and evaporated. The residue was suspended in petroleum ether and filtered to give 2.54 g of crude material. After several recrystallizations from benzene and ethanol, crude 1,3-dicyclohexyl-1-(4-nitrobenzoyl)-urea, mp 195–196°, was obtained and identified by infrared.

Reaction of Benzoylhydrazine with Benzoic Acid.—To a solution containing 4.12 g (0.02 mole) of N,N′-dicyclohexylcarbodiimide and 2.72 g (0.02 mole) of benzoylhydrazine in 100 ml of methylene chloride was added 2.44 g (0.02 mole) of benzoic acid. The product, 1,2-dibenzoylhydrazine, precipitated with the N,N′-dicyclohexylurea and was separated by stirring the solid mixture with 200 ml of cold ethanol for 6 hr. Filtration gave 1.84 g (38%) of product, mp and mmp 238–240° (lit.[17] mp 237–239°).

Reaction of 4-Nitrobenzoic Acid with Methylhydrazine.—To a solution consisting of 1.84 g (0.04 mole) of methylhydrazine and 8.25 g (0.04 mole) of N,N′-dicyclohexylcarbodiimide in 100 ml of methylene chloride was added 6.68 g (0.04 mole) of 4-nitrobenzoic acid. The reaction mixture was warmed gently and stirred during the first hour to effect the solution of the 4-nitrobenzoic acid. After 4 hr, precipitation of insoluble material was noted. After 24 hr at room temperature, the reaction mixture was filtered. The filtrate was extracted with three 50-ml portions of 3 *N* hydrochloric acid. During the third extraction, 1.6 g of insoluble material separated from the methylene chloride. Recrystallization of this material from aqueous ethanol gave 0.65 g of 1,3-dicyclohexyl-1-(4-nitrobenzoyl)urea, mp 201–202° dec.

Anal. Calcd for $C_{20}H_{27}N_3O_4$: C, 64.32; H, 7.28; N, 11.25. Found: C, 64.15; H, 7.37; N, 11.10.

The combined acid extracts were made basic with sodium carbonate and the resulting suspension was extracted with three 50-ml portions of chloroform. Evaporation of the dried chloroform extracts gave 4.3 g of yellow solid, mp 110–124°. This crude material was suspended in 85 ml of boiling benzene. Filtration afforded 0.9 g of unidentified material, mp 185–189°. Recrystallization from chloroform gave the analytical sample as white crystals, mp 191–192°.

Anal. Found: C, 57.78; H, 10.32; N, 20.72; mol wt (osmometric in chloroform), 484. The infrared spectrum (KBr) exhibited strong intensity bands at 3.45, 6.20, and 6.41 μ and medium intensity bands at 3.08, 3.19, 3.29, 3.52, 6.93, 8.27, and 13.9 μ.

Addition of petroleum ether to the benzene filtrate obtained above gave 2.5 g (32%) of crude 1-methyl-1-(4-nitrobenzoyl)-hydrazine, mp 121–125°. Further details on the purification and properties of this compound are found in Table I.

1-Benzoyl-2-phenylhydrazine.—The reaction of benzoic acid with phenylhydrazine was carried out by the general procedure on a 0.02-mole scale. The usual work-up of the acid extracts

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(15) P. A. S. Smith and E. E. Most, Jr., *J. Org. Chem.*, **22**, 358 (1957).

(16) F. Meyer and K. Dahlem, *Ann.*, **326**, 331 (1903).

(17) H. H. Hatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N.Y., 1966, p 208.

afforded a minute quantity of an oil with the characteristic odor of phenylhydrazine. Evaporation of the dried methylene chloride solution afforded a crude solid which on one recrystallization from ethanol gave 1.1 g (26%) of 1-benzoyl-2-phenylhydrazine, mp and mmp 168–169° (lit.[18] mp 168°).

Registry No.—1,1,1-Trimethylhydrazinium benzoate, 15038-93-4; 1,1,1-trimethylhydrazinium *p*-nitrobenzoate, 14908-51-1; 1,1,1-trimethylhydrazinium *p*-anisate, 15038-94-5; 1,1,1-trimethyl-2-(2-methoxybenzoyl)hydrazinium iodide, 14908-52-2; 1,3-dicyclohexyl-1-(4-nitrobenzoyl)urea, 14908-53-3.

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(18) E. Fischer, *Ann.*, **190**, 126 (1878).

2-Azoxybenzoic Acids as Benzyne Percursors

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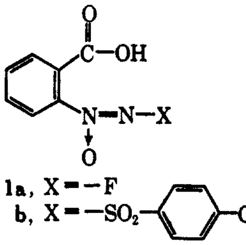
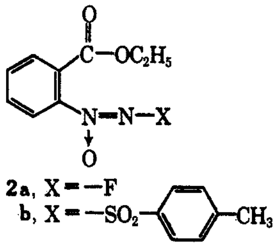
Various *ortho*-substituted benzoic acids have served as benzyne precursors.[1–3] As part of our study of fluoroazoxy[4] and related azoxy compounds,[5] it was of interest to see if the 2-substituted benzoic acids **1a** and **1b**, or their salts, would also generate benzyne when heated.

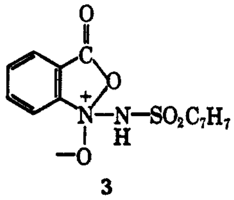


1a, X = —F
b, X = —SO_2—



2a, X = —F
b, X = —SO_2—

To prepare **1a** and **1b**, ethyl 2-nitrosobenzoate was converted to esters **2a** and **2b** by interaction with tetrafluorohydrazine[4] and chloramine-T,[6] respectively. The esters were converted into the acids by alkaline saponification. Only the infrared spectrum of **1b** requires additional comment. Although the infrared spectrum of **1a** (see Experimental Section) was that expected for a carboxylic acid dimer, that of **1b**, run in a Nujol mull, showed a bonded —OH at 3.13 μ and a sharp carbonyl band at 5.82 μ. Since **1b** is esterified by diazomethane or alcohols (acid catalyzed) to give **2b** and related esters, it appears that intramolecular hydrogen bonding, rather than a cyclic structure such as **3** or **4**, accounts for the unexpected infrared properties.[7]



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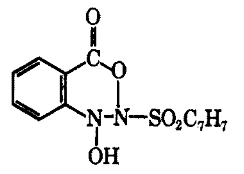
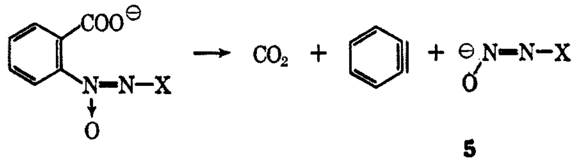


4

Only a small amount of N_2O was produced when **1a**, **1b**, or their salts were pyrolyzed in *o*-dichlorobenzene or in the dimethyl ether of triethyleneglycol (triglyme). Nitrogen and CO_2 were the major gaseous products. And, evidence for the intermediacy of benzyne was found in the thermal decomposition of salts of **1a** and of acid **1b**.[8]

Triptycene (2%) was isolated when a mixture of anthracene and the sodium salt of **1a** was refluxed in *o*-dichlorobenzene. However, triptycene (25%) was obtained from acid **1b** and anthracene in triglyme after 3 hr at 190°. Another effective trap for the benzyne produced from **1b** was 2,3,4,5-tetraphenylcyclopentadienone;[3] 1,2,3,4-tetraphenylnaphthalene (24%) was isolated in this experiment.

The nature of the decomposition process giving rise to nitrogen and benzyne remains obscure. Azoxy toluenesulfonates, structures similar to **1**, undergo thermal decomposition by an apparent radical mechanism and give nitrogen and aryl radicals.[9] An ionic pathway that produces CO_2, benzyne, and a nitrogen precursor such as diimide **5** is also conceivable.



5

Experimental Section

Preparation of N-(2-Carboethoxyphenyl)-N′-fluorodiimide N-Oxide (2a).—Ethyl 2-nitrosobenzoate (3 g) in 30 ml of chlorobenzene was exposed to an atmosphere of tetrafluorohydrazine[10] at 0–20°. When the uptake of tetrafluorohydrazine was complete, the solution was degassed thoroughly. The solution was chromatographed on silica gel in the usual manner.[4] The ester **2a** was isolated as a yellow oil. The F^{19} nmr spectrum had a single peak at φ −51.1.

Anal. Calcd for $C_9H_9N_2O_3F$: C, 50.93; H, 4.27; N, 13.21; F, 8.96. Found: C, 50.88; H, 4.35; N, 12.63; F, 8.41.

Preparation of N-(2-Carboxyphenyl)-N′-fluorodiimide N-Oxide (1a).—Compound **2a** (5 g), 100 ml of methanol, 10 ml of water, and 33 ml of 1.4 *N* sodium methoxide in methanol was refluxed for 1 hr. The mixture was poured into water, acidified, and extracted with methylene chloride. Evaporation of the methylene chloride left a solid residue, which was recrystallized from chloroform. Thus **1a** (3.2 g), mp 144–145°, was obtained. The F^{19} nmr spectrum had a single peak at φ −53.9.

Anal. Calcd for $C_7H_5N_2O_3F$: C, 45.66; H, 2.74; N, 15.22; F, 10.32. Found: C, 45.46; H, 2.90; N, 14.72; F, 10.66.

The infrared spectrum (Nujol mull) of **1a** indicated that it existed in the usual dimeric form. The bonded O–H stretch was 3.7–4.0 μ, and the carbonyl absorption was 5.95 μ.

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(1) Reviewed by G. Wittig, *Angew. Chem. Intern., Ed. Engl.*, **4**, 731 (1965).

(2) E. McNelis, *J. Org. Chem.*, **28**, 3188 (1963).

(3) F. M. Beringer and S. J. Huang, *ibid.*, **29**, 445 (1964).

(4) T. E. Stevens and J. P. Freeman, *ibid.*, **29**, 2279 (1964).

(5) T. E. Stevens, *ibid.*, **29**, 311 (1964).

(6) W. V. Farrar and J. M. Gulland, *J. Chem. Soc.*, 368 (1944).

(7) The infrared spectrum of deuterated **1b** was examined in an attempt to determine the functional group (azoxy or sulfonyl) involved in hydrogen bonding. No noticeable change in the azoxy absorption at 6.7–6.9 μ (masked by Nujol) or in the symmetric S=O stretch at 8.65 μ was observed, but the asymmetric S=O stretch at 7.45 μ in **1b** was a doublet, 7.45 and 7.55 μ, in the deuterated sample.

(8) The cesium salt of **1b** decomposed readily at about 180° and the acid **1b** required a temperature of about 200°. Since decomposition of the acid appeared clean, the benzyne trapping experiments were conducted with it.

(9) E. A. Dorko and T. E. Stevens, *Chem. Commun.*, 871 (1966).

(10) Currently available from K & K Laboratories, Inc.