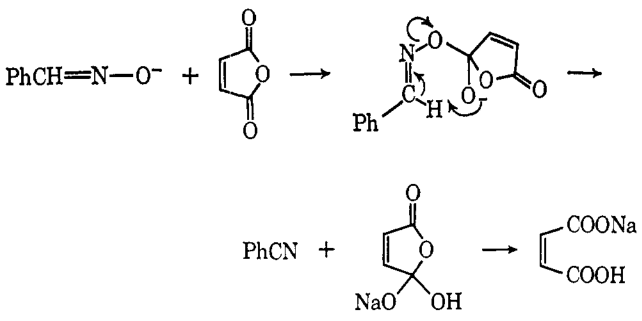
anion to the anhydride. A plausible reaction path involves initial addition to a carbonyl group (Scheme II).

SCHEME II



The contrast between these results and the smooth cycloaddition of C-phenyl-N-methyl nitrone to dienophiles[4] suggests that the positive charge on the central nitrogen atom is indeed essential for concerted cycloaddition. A possible explanation is as follows: in the 4 + 2 electrocyclic reaction between enes and allylic anions, the negative charge of the allylic system becomes localized on a single atom in the product (eq 1) and thus also in the transition state. In the absence of structural features which would stabilize this localized charge, the concerted electrocyclization will be energetically unfavorable compared to nonconcerted nucleophilic attack on the double bond.

Experimental Section

Reaction of Sodium Benzaldoximate with Dimethyl Acetylenedicarboxylate. A. Without Solvent.—Sodium *syn*-benzaldoximate, prepared according to Vogel,[7] was washed with saturated aqueous NaCl until free of hydroxide and was dried *in vacuo* over P_2O_5 at 110°. The dry sodium salt (3.87 g, 0.027 mol) was added in small portions to dimethyl acetylenedicarboxylate (3.87 g, 0.027 mol), the exothermic reaction being moderated by ice-bath cooling. The reaction mixture was dissolved in water, acidified (pH 1) with hydrochloric acid, and extracted with ether. The ethereal extract was treated with ethereal diazomethane. Chromatography on alumina yielded benzonitrile (eluted with hexane, 1.92 g, 70%, identified by ir spectra and vpc retention time), benzaldoxime-O-methyl ether (eluted with 6:1 hexane–ether, 0.48 g, 14%, identified by ir comparison with an authentic sample[8]), and **3b** (eluted with ether, 2.44 g, 65%): mp 89.5–90° (prisms from hexane–benzene); uv λ_{max} (95% ethanol) 258 mμ (ϵ 11,700); ir (Nujol mull), 5.60, 5.69, 5.73, 5.80 (ester and lactone C=O), 6.03 (C=C), 13.2 μ; nmr ($CDCl_3$), δ 4.28, 3.80, 3.77, 3.63 (all sharp s, 3 each, OCH_3), 3.28 (broad s, 2, CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 302 (0.6), 258 (21), 243 (44), 215 (12), 211 (100), 201 (49), 199 (18), 173 (16), 141 (13), 115 (13).

Anal. Calcd for $C_{12}H_{14}O_9$: C, 47.7; H, 4.64. Found: C, 47.5; H, 4.79.

Authentic **3b** was prepared by reaction of ethereal diazomethane with **3a** (made by the procedure of Michael and Smith[6]). The two samples had identical ir spectra and showed no mixture melting point depression.

B. In Methanol.—Benzaldehyde *syn*-oxime[7] (0.80 g, 0.0066 mol) was added to a solution of 0.15 g (0.0066 mol) of sodium in 25 ml of methanol, followed by 0.94 g (0.0066 mol) of dimethyl acetylenedicarboxylate in 25 ml of methanol. The mixture was refluxed for 24 hr, then was poured into water and extracted with ether. The ether-soluble material was separated by chromatography on alumina into benzonitrile (0.31 g, 46%, eluted with hexane), benzaldehyde *syn*-oxime (0.46 g, 57%, eluted with 30:1 hexane–ether), and dimethyl 2,2-dimethoxysuccinate[9] (0.86 g, 63%, eluted with 3:1 hexane–ether): ir (thin film), 5.80 μ; nmr (CCl_4), δ 3.73 (s, 3, CO_2CH_3), 3.62 (s, 3, CO_2CH_3), 3.23 (s, 6, OCH_3), 2.86 (s, 2, CH_2). A comparison sample was prepared by reaction of sodium methoxide in methanol with dimethyl acetylenedicarboxylate.[10]

Reaction of Sodium Benzaldoximate with Maleic Anhydride.—A mixture of the dry sodium salt of benzaldehyde *syn*-oxime (0.75 g, 0.0052 mol) and maleic anhydride (0.51 g, 0.0052 mol) was heated in an oil bath at 115° for 10 min. The reaction mixture was dissolved in hot ethanol–water; on cooling 0.38 g (53%) of sodium maleate was obtained. The mother liquor was evaporated and the residue was taken up in hexane. Passage through a column of alumina yielded benzonitrile (0.31 g, 58%).

Registry No.—**3b**, 17061-09-5.

Acknowledgments.—A portion of this work was supported by a grant from the Academic Research Committee, Stevens Institute of Technology. The author is grateful to Dr. P. T. Funke, for obtaining and interpreting the mass spectra, and to Mr. Roger Wise, for assistance with portions of the experimental work.

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[7] A. I. Vogel, "Practical Organic Chemistry," 3rd ed, John Wiley and Sons, New York, N. Y., 1956, p 719.

[8] O. L. Brady, F. P. Dunn, and R. F. Goldstein, *J. Chem. Soc.*, 2386 (1926).

[9] W. J. Croxall and H. J. Schneider, *J. Amer. Chem. Soc.*, **71**, 1257 (1949).

[10] The analogous reaction of diethyl acetylenedicarboxylate with sodium ethoxide in ethanol has been described: A. Michael and J. E. Bucher, *Chem. Ber.*, **29**, 1792 (1896).

Reactions of Peroxides. I. Preparation of Aryl and Alkyl Iodides by Decomposition of Aroyl and Acyl Peroxides in the Presence of Iodine

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The preparative value of decomposition of benzoyl peroxide in boiling carbon tetrachloride solutions of iodine was reported by Hammond and Soffer who obtained an 85% yield of iodobenzene in 36–48 hr.[3] Low yields (15–20%) were observed in benzene and chlorobenzene.[4] *o*-Iodotoluene was similarly obtained in about 49% yield from *o*-toluoyl peroxide in boiling carbon tetrachloride in 17 hr.[5] The reaction of peroxide with iodine may be more usefully applied by reducing the reaction times at higher temperatures. Accordingly, benzoyl and pelargonyl peroxide, representing aromatic and aliphatic classes, were each decomposed in iodine solutions of higher boiling aromatic and aliphatic solvents to determine the appropriate solvent, optimum conditions, and some of the accompanying side products of the reaction.

Benzoyl peroxide is converted into iodobenzene to the extent of 80–90% in 2–4 hr at 100–110° in several

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[3] G. S. Hammond and L. M. Soffer, *J. Amer. Chem. Soc.*, **72**, 4711 (1950).

[4] G. S. Hammond, *ibid.*, **72**, 3737 (1950).

[5] F. D. Greene, G. R. Van Norman, J. C. Cantrill, and R. D. Gilliom, *J. Org. Chem.*, **25**, 1790 (1960).

haloaliphatic solvents (Tables I and II), but aromatic solvents are unsuitable. However, conversions increase in aromatic solvents with electron-withdrawing and decrease in those with electron-donating groups.

TABLE I

REACTION OF BENZOYL PEROXIDE WITH IODINE IN VARIOUS SOLVENTS. CONVERSION INTO IODOBENZENE[a]

	Mol %	
Aromatic solvents	Iodobenzene[b]	Iodine consumed
Anisole[c]	~1	35
Toluene	13	18
Benzene[d]	18	19
Chlorobenzene[e]	37	64
1-Chloro-3-fluorobenzene	57	83
Nitrobenzene[f]	32	78
Aliphatic solvents	Iodobenzene[b]	Iodine consumed
Carbon tetrachloride[g]	87	90
Freon 112[h]	83	83
1,3-Dichloropropane[i,j]	83	88
1,3-Dibromopropane[k]	80	84
1,1,2,2-Tetrachloroethane	57	56
1-Iodobutane	14	*l*
N,N-Dimethylacetamide	9	80

[a] Reaction conditions: benzoyl peroxide (0.4 *M*); iodine (0.6 *M*), 110°, 2 hr (complete peroxide decomposition). [b] $2([C_6H_5I]/[\text{peroxide}]) \times 100$. [c] Methoxyphenyl benzoates (14%) and iodoanisoles (34%) were also formed. [d] After 48 hr at 80°, phenyl benzoate formed (72%). [e] Chlorophenyl benzoates (13%) and chloroiodobenzenes (31%) were also formed. [f] No nitrophenyl benzoate was formed. Iodonitrobenzenes were obtained (33%). [g] Run for 65 hr at 75°; 0.2 *M* benzoyl peroxide. [h] Run for 4 hr at 100°. [i] 1,2-Dichloroethane, 16 hr at 85°; C_6H_5I (77%). [j] 1-Chlorohexane; C_6H_5I (71%). [k] 1-Bromobutane, 4 hr at 100°; C_6H_5I 71%. [l] Iodine was liberated from solvent to the extent of about 0.4 mol per mole of peroxide.

TABLE II

EFFECTS OF CONCENTRATION AND MOLE RATIO ON IODOBENZENE YIELDS[a]

	% yield of iodobenzene[b]			
Benzoyl	Iodine/peroxide mole ratio			
peroxide, *M*	1:1	1.1:1	1.5:1	3:1
0.1	54	63	72	77
0.4	82	80	82	85
0.6	85	85	90	

[a] The solvent was 1,3-dichloropropane (2 hr at 110°). [b] Based on peroxide conversions.

Phenyl benzoate and iodobenzene together account for 90% of the peroxide decomposed in benzene solutions. In three other aromatic solvents, the following products were found: 2- and 4-methoxyphenyl benzoates (in equal amounts) and iodoanisole in anisole; 2- and 4-chlorophenyl benzoates (in equal amounts) and *o*- and *p*-chlorobenzene (the *para* isomer predominating) in chlorobenzene; and *o*- and *p*-iodonitrobenzene (the *ortho* isomer predominating) in nitrobenzene. In the last solvent nitrophenyl benzoates do not appear as products but phenyl benzoate, nitrobiphenyl, and phenylnitrocyclohexadiene are suggested by mass spectra on fractions isolated by column chromatography and glpc. Benzoic acid and polymeric compounds are formed in all aromatic solvents.

Polymeric compounds, from reactions in benzene and nitrobenzene solutions, contain iodine. These insoluble compounds are products of benzoyl hypoiodite addition to an olefinic bond of the "hydroaromatic" tetrahydroquaterphenyl class of compounds, the latter having been characterized previously for products isolated from aroyl peroxide decompositions in benzene and chlorobenzene.[6,7]

Pelargonyl peroxide decomposes completely within 2 hr at 100–110° in iodine solutions of most of the solvents to form 1-iodooctane in 55–75% based on conversions of peroxide (Tables III and IV). Solvents have little influence on pelargonyl peroxide conversions into its iodide.

TABLE III

REACTION OF PELARGONYL PEROXIDE WITH IODINE IN VARIOUS SOLVENTS. CONVERSION INTO IODOOCTANE[a]

	Mol %	
Solvents	Iodooctane[b]	Iodine consumed
Aromatic group[c]	60–66	63–66
Nitrobenzene	42	54
Aliphatic group[d]	60–66	62–70
1,1,2,2-Tetrachloroethane	56	59

[a] Reaction conditions: pelargonyl peroxide (0.3 *M*), iodine (0.45 *M*), 110°, 2 hr (complete peroxide decomposition). [b] $2([RI]/[\text{peroxide}]) \times 100$. [c] Anisole, toluene, benzene (10 hr at 80°), chlorobenzene, 1-chloro-3-fluorobenzene. [d] Carbon tetrachloride (16 hr at 75°), tetrachlorodifluoroethane (4 hr at 100°), 1,3-dichloropropane, 1,2-dichloroethane, 1-chlorohexane, 1-iodobutane (24 hr at 70°, 2 hr at 110°), 1-iodopropane.

Other products arising from the pelargonyl peroxide–iodine reaction are hexadecane, octyl pelargonate, and compounds tentatively designated as "iodooctane isomers" (Table IV). The latter have glpc retention times of 2- and 3-iodooctanes. Yields of the "isomers" seem to depend on solvent type and temperature; *e.g.*, none formed in carbon tetrachloride or 1-butyl iodide at 70°; 3% in 1-butyl iodide at 110° and up to 3% in chlorobenzene at 70–120° formed for complete peroxide decompositions.

Hexadecane and octyl pelargonate are formed in approximately equal amounts totaling 20–35 mol % in reactions conducted at varying concentrations and mole ratios of iodine and peroxide. Hydrocarbon and ester formation have been explained by a "cage" mechanism based on quantitative measurements of decomposition products from two peroxide systems: ethane and methyl acetate from acetyl peroxide, and butane and ethyl propionate from propionyl peroxide.[8,9] The "cage" products are stated to arise independently of scavenger concentrations, but the scavenger concentrations are relatively low in those experiments. The mass effect of scavenger on the cage reaction of peroxides has not been noted before but has been detailed for azobisisobutyronitrile in solution at high scavenger (halogen and α,α-diphenyl-β-picrylhydrazyl) concentrations.[10,11]

At high concentration (0.6 *M* peroxide, 1.8 *M* iodine) ester is completely eliminated as a product and there is a sharp reduction in alkane. Reduction in the "cage" products is accompanied by an increase in iodooctane yield, although not proportionally. Evidently, iodine can effectively compete with solvent in the "cage" process at higher concentrations and mole ratios owing to

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(6) D. F. DeTar and R. A. J. Long, *J. Amer. Chem. Soc.*, **80**, 4742 (1958).

(7) D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, 5604 (1963).

(8) A. Rembaum and M. Szwarc, *J. Amer. Chem. Soc.*, **77**, 3486 (1955).

(9) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961).

(10) H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1911 (1964).

(11) G. S. Hammond and J. R. Fox, *ibid.*, **86**, 1918 (1964).

TABLE IV

PELARGONYL PEROXIDE CONVERSIONS INTO IODOOCTANES, HEXADECANE, AND OCTYL PELARGONATE. EFFECT OF CONCENTRATIONS AND MOLE RATIOS[a]

Pelargonyl peroxide, M	I_2/peroxide, mole ratio	Mol %				
		1-Iodooctane[b]	"Isomers" [b,c]	Hexadecane[d]	Octyl pelargonate[d]	Total
0.1	1	52				
0.1	1.1	55	Trace	21	15	91
0.1	1.5	56				
0.3	1	57	0.7	8	14	80
0.3	1.1	55				
0.3	1.5	66	3.0	14	17	100
0.3	3	65				
0.6	1	55	1.0	12	11	79
0.6	1.1	64				
0.6	1.5	63				
0.6	3	75	1.5	8	0	85
0.01	10	56				
0.01	60	64	3.0	12	11	90

[a] The solvent was chlorobenzene (2 hr at 110°). [b] Calculated as 2[RI]100/[peroxide]. [c] Tentatively considered to be iodooctane isomers as determined by glpc analysis with 2- and 3-iodooctanes. [d] Calculated as [product]/[peroxide] × 100.

increased probability for interaction with peroxide, but complete elimination of alkane as the other "cage" product is not attained.

The reaction was extended to a few additional peroxides (see Experimental Section). From a comparison of these results with those from the Hunsdiecker reaction[12] and its modifications,[13] it is concluded that the Hunsdiecker modifications are superior to the peroxide method for aliphatic iodide preparations, but that the peroxide method is superior for aryl iodides containing nitro groups and possibly other electronegative functions. None of the procedures is satisfactory for aryl iodides containing methoxyl substitutions.

Experimental Section

All solvents were fractionally distilled. 1,1,2,2-Tetrachlorodifluoroethane (Freon 112) was kindly supplied by E. I. du Pont de Nemours and Co.[14] Pelargonic acid, used to prepare pelargonyl peroxide, was purified by the method of Port and Riser[15] and by a final fractional distillation of the methyl ester.

Benzoyl peroxide, Eastman White Label (99.2%) purity), was used as supplied. Pelargonyl peroxide,[16] myristoyl peroxide,[16] 3-nitrobenzoyl peroxide,[17] 4-nitrobenzoyl peroxide,[17] and *p*-methoxybenzoyl peroxide[17] were prepared as reported.

Precautionary Note.—We experienced no difficulties with the syntheses and handling of 3- and 4-nitrobenzoyl peroxides. However, others have reported[18] that manipulative care must be exercised as a 1-g sample of 4-nitrobenzoyl peroxide, after weighing and sealing in an ampoule, exploded when the sealed glass tube was lightly tapped with a file.

Iodobenzene Analytical Method.—A benzoyl peroxide reaction that is *typical for both aroyl and acyl peroxides* is described. Benzoyl peroxide (0.005 mol) and iodine (0.0075 mol) were weighed into a volumetric flask (50-ml capacity equipped with a ₸ 14/20 female joint) containing a Teflon-coated magnetic microbar for stirring. Solvent (1,3-dichloropropane, 11 ml) was added, the flask and its accompanying condenser were briefly flushed with nitrogen and a small positive nitrogen bleed-in was affixed to the top of the condenser. The reactants were magnetically stirred and heated at 110° for 2 hr. After the reaction mixture had cooled, the condenser and joints were carefully rinsed with benzene or chloroform so that rinsings drained into the flask; the flask was filled to mark with solvent, and samples were removed for glpc and iodometric analysis.

A complete material balance on products of benzoyl peroxide decompositions in 1,3-dichloropropane was obtained for reactions at 0.4 M peroxide: iodobenzene (82.5%), chlorobenzene (14.4%), benzoic acid (3.8%), phenyl benzoate (0.01%), benzene (~0.01%), and an unidentified trace component (~0.002% with a retention time slightly less than that for diphenyl).

Iodobenzene Preparative Method.—Tetrachlorodifluorethane is a useful solvent for the preparative scale because its lower boiling point permits easier separation from iodobenzene by distillation. Benzoyl peroxide (0.05 mol) and iodine (0.055 mol) were heated at 100° for 4 hr in the Freon solvent (110 ml). Free iodine was removed by conventional treatment with sodium thiosulfate solution and iodobenzene (65% yield) obtained by vacuum distillation of the Freon layer.

Other Peroxide Reactions. 4-Iodonitrobenzene.—4-Nitrobenzoyl peroxide (0.0075 mol) and iodine (0.0083 mol) were heated in 1,3-dichloropropane (16 ml) at 120° for 2 hr. Solvent and iodine were evaporated in a rotary evaporator by heating the mixture under reduced pressure by water aspiration. The solids were chromatographed on a column containing silica gel and eluted with petroleum ether (bp 35–50°) containing benzene whose concentration was progressively increased from 5 to 50%. The yield of 4-iodonitrobenzene was 70%, mp 173°.

3-Iodonitrobenzene.—3-Nitrobenzoyl peroxide was decomposed in analogous fashion to yield 3-iodonitrobenzene in 60% yield, mp 36°.

4-Iodomethoxybenzene.—4-Methoxybenzoyl peroxide yielded 4-iodomethoxybenzene in 11% conversion by glpc analysis.

1-Iodotridecane.—Myristoyl peroxide (0.02 mol) and iodine (0.03 mol) and iodine (0.03 mol) were heated in chlorobenzene (30 ml) for 2 hr at 120°. After cooling, ethyl ether was added and iodine was removed by sodium thiosulfate treatment. The solution was filtered, the ether was distilled off, and 1-iodotridecane (45% yield) was isolated by vacuum distillation.

Analyses. Gas Chromatography.—Glpc analyses were performed on an F & M Model 720 chromatograph. In the majority, an 8 ft, 0.25 in. steel column, packed with silanized 60/80 Chromosorb W (acid-washed) coated with gum rubber (SE 30, 10%), was used. The injection port temperature was maintained below 190° for analyses of alkyl iodides as assurance against decomposition. Quantitative analyses by means of external standards were obtained by injections of standard solutions of the compounds analyzed and quantitation determined with a Daystrom Attenumatic integrator.

Iodometry.—Samples (10 ml) were removed for differential analysis of unreacted iodine and peroxide. Free iodine was conventionally determined by addition of water (50 ml), chloroform (10 ml), and glacial acetic acid (15 ml), and titration with

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[12] (a) R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956); (b) C. V. Wilson, *Org. Reactions*, **9**, 332 (1957).

[13] (a) S. J. Cristol and W. C. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961); (b) J. A. Davis, *et al.*, *ibid.*, **30**, 415 (1965); (c) D. H. R. Barton and O. P. Serebryakov, *Proc. Chem. Soc.*, **1962**, 309; (d) D. H. R. Barton, H. P. Paro E. P. Serebryakov, and N. F. Woolsey, *J. Chem. Soc.*, 2438 (1965); (e) J. K Kochi, *J. Org. Chem.*, **30**, 3265 (1965).

[14] Mention of brand or firm names does not constitute an endorsement by the Department of Agriculture over others of a similar nature that are not mentioned.

[15] W. S. Port and G. Riser, U. S. Patent 2,890,230 (June 9, 1959).

[16] L. S. Silbert and D. Swern, *J. Amer. Chem. Soc.*, **81**, 2364 (1959).

[17] C. C. Price and E. Krebs, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 649.

[18] R. I. Milyutinskaya, Kh. S. Bagdusar'yan, and E. A. Izrailevich, *Zh. Fiz. Khim.*, **31**, 1019 (1957).

0.1 *N* sodium thiosulfate to a starch end point. Total iodine, equivalent to unreacted iodine plus the iodine liberated from unreacted peroxide whenever present, was determined by conducting the analysis as described for diacyl peroxides.[19] Unreacted iodine was calculated as the difference between the two iodine titrations.

Isolation and Identification of "Hydroaromatic" Products. Reaction of Benzoyl Peroxide and Iodine in Nitrobenzene.—The mixture from a reaction of benzoyl peroxide (0.05 mol) and iodine (0.075 mol) in nitrobenzene (110 ml) (2 hr at 110°) was evaporated *in vacuo*. The residue was stirred in hexane and a trace quantity of insoluble material was filtered and washed with hexane. The insoluble component (analyzed without further purification) contained iodine in approximate agreement with that calculated for benzoyl hypoiodite addition to one double bond of dinitrotetrahydroquaterphenyl ($C_{31}H_{26}O_6N_2I$).

Anal. Calcd: C, 57.4; H, 3.89; N, 4.32; I, 19.6. Found: C, 60.8; H, 4.03; N, 4.20; I, 17.8.

The hexane filtrate was chromatographed on silica gel and eluted with benzene–petroleum ether cosolvent. A portion of the chromatographed material was further resolved by preparative gas–liquid partition chromatography into a liquid and a solid isomer but isolation, purification, and analyses of all components were not attempted in this limited effort. Both isomers showed the presence of nitro bands (1350 and 1520 cm^{-1}) and aromatic bands and each contained a strong 199 mass peak in its fragmentation pattern[20] corresponding to nitrodiphenyl. Elemental analysis for the solid isomer supports this structure but is less satisfactory for the liquid isomer.

Anal. Calcd: C, 72.35; H, 4.55; N, 7.03; Found for the solid isomer: C, 72.4; H, 4.83; N, 6.82. Found for the liquid isomer: C, 72.6; H, 5.04; N, 6.41.

Reaction of Benzoyl Peroxide and Iodine in Benzene.—Several of the reaction mixtures were filtered to collect a small amount of a black, insoluble compound. This was washed with benzene and dried. The compound contained 22.7% iodine in agreement with the calculated value (22.7%) for the product expected from a benzoyl hypoiodite addition to the olefinic diphenyltetrahydroquaterphenyl.

Registry No.—Iodine, 7553-56-2; benzoyl peroxide, 94-36-0; pelargonyl peroxide, 762-13-0; myristoyl peroxide, 3530-28-7; 3-nitrobenzoyl peroxide, 904-58-5; 4-nitrobenzoyl peroxide, 1712-84-1; *p*-methoxybenzoyl peroxide, 849-83-2; 4-iodonitrobenzene, 636-98-6; 3-iodonitrobenzene, 645-00-1.

[19] L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958); L. S. Silbert and D. Swern, *J. Amer. Chem. Soc.*, **81**, 2364 (1959).

[20] Mass spectral analysis by Mr. C. Dooley.

The Nuclear Magnetic Resonance Spectra of N-Acylanilines.[1] The Effect of Substituents on the Chemical Shift of the *ortho* Proton

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The shielding parameters of various substituents on benzene have been shown by Martin and Dailey[3] to be additive and have been used to predict successfully the chemical shifts of the protons on the benzene nucleus. This additivity fails for *ortho* protons on *ortho*-disubstituted benzenes. These deviations are relatively small (less than 0.5 ppm) and can occur at either higher or lower field, but in a recent study in these laboratories, the proton magnetic resonances of a series of N-acylanilines was determined and extremely large deviations were observed. It was noted, in certain cases, that one aromatic proton consistently appeared much farther downfield than expected and only appeared if the acylaniline was *ortho* substituted. This deshielding cannot be explained by analogy with any known effect and its cause was therefore investigated.

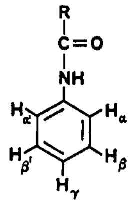

Figure 1.

Results and Discussion

The nmr spectra of a number of substituted N-acylanilines were determined and proton assignments were made where possible and when consistent with known chemical shifts. When several substituents were present, the characteristic splitting patterns were also utilized *via* first-order analysis in making assignments. The results are shown in Table I. Figure 1 details the designation of the ring protons. As can be seen from Table I, H$_\alpha$ consistently appears as the most deshielded proton in compounds VII–XVIII. This deshielding is minimal with unsubstituted acetanilide or when the substituents are other than *ortho*. The first six compounds in Table I contain no *ortho* substituent. The chemical shifts for aromatic protons of these compounds (I–VI) are quite close to their predicted values if either Martin and Dailey's[3] or Corio and Dailey's[4] shielding parameters are utilized. In addition it was necessary to assign a shielding parameter for the acylamino group. A calculated value of +0.16 ppm (δ scale) was determined by the analysis of several *para*-substituted acylanilines.

When a similar treatment was attempted with the *ortho*-substituted (H$_{\alpha'}$ = R) compounds (VII–XVIII), the proton *ortho* to the acylamino group (H$_\alpha$) appeared farther downfield than could be reasonably explained by electrostatic effects, and the deviation of the observed chemical shifts from those calculated using shielding parameters was unusually large. Initially it was thought that the magnitude of this deshielding effect would be relatively constant regardless of the nature of the *ortho* substituent. This, however, was not the case. Using Corio and Dailey's[4] values for shielding parameters, the effects of the *ortho* substituents were subtracted from the total chemical shift difference of the *ortho* proton. This gave some measure of the magnitude of the anisotropic deshielding of the carbonyl group in the various compounds. The results are summarized in Table II. Corio and Dailey's[4] values were chosen, not because they are the most accurate but because the list of substituents is the most exten-

[1] Presented at the Symposium on the Application of Spectral Techniques to Problems of Structure and Mechanism, 3rd Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., February 1, 1968.

[2] To whom all correspondence should be addressed.

[3] J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).

[4] P. L. Corio and B. P. Dailey, *J. Amer. Chem. Soc.*, **78**, 3043 (1956).