cedure as shown above, triethyl orthoformate (29.6 g, 0.20 mole) and chloropentafluoroacetone (110.0 g, 0.60 mole) gave 2,4-bis(trifluoromethyl)-2,4-bis(chlorodifluoromethyl)-5,5-diethoxy-1,3-dioxolane, 60.5 g (64.7%), bp 110° (23 mm), $n^{25}D$ 1.3728. The infrared spectrum contained no OH, C=O, or C=C bonds.

Anal. Calcd for $C_{11}H_{10}Cl_2F_{10}O_4$: C, 28.22; H, 2.37; Cl, 15.15. Found: C, 28.50; H, 2.09; Cl, 14.79.

D. 2,2-Bis(trifluoromethyl)-5-methyl-5-formyloxymethyl-1,3-dioxane (VII).—A mixture of 2-ethyl-2,6,7-trioxabicyclo-[2.2.2]octane (Kay-Fries Chemicals, Inc., 13.0 g, 0.1 mole), benzene (50.0 g), and hexafluoroacetone (50.0 g, 0.3 mole) was heated in a bomb at 150° for 6 hr. The bomb was cooled and vented to remove unreacted hexafluoroacetone. The liquid residue was fractionated on a spinning-band column to give 16.4 g (55.4%) of VIII, bp 60–62° (0.25 mm), $n^{25}D$ 1.3772. The infrared absorption spectrum contained no hydroxyl or C=C bands but did show an ester carbonyl band at 5.74 μ. The doublet at 8.77 and 8.95 μ is due to the C–O–C of the dioxane ring. The proton nmr spectrum showed singlets at 8.0 (area 1, –COOH proton), 4.20 [area 2, $-C(=O)-O-CH_2-C$ protons), 3.94 (area 4, ring $C-CH_2-O$ protons), and 0.98 ppm (area 3, $C-CH_3$ protons).

Anal. Calcd for $C_9H_{10}F_6O_4$: C, 36.50; H, 3.40; F, 38.49; mol wt, 296. Found: C, 36.41; H, 3.45; F, 38.00; sapon equiv, 285.

E. Methyl 1,1,3,3-Tetrakis(trifluoromethyl)-3,5-oxacaproate (VIII).—5,5-Dimethoxy-2,2,4,4-tetrakis(trifluoromethyl)-1,3-dioxolane (Ia, 20.0 g, 0.049 mole) was heated at reflux (160 ± 5°) for 75 hr. The residue in the flask was 90% Ia and 10% VIII, and the separation was made by preparative-scale gc on a 3 ft × 0.75 in. column packed with 25% tetra[fluoroalkyl (C_5 and C_7)]pyromellitate on Chromosorb P at 150° (flow, 860 cc of He/min). The first peak was Ia (6.6 min), and the only other peak was VIII (25.6 min), bp 156°, fp −6°, $n^{25}D$ 1.3678. The infrared spectrum of VIII contained no OH or C=C peaks but did show a C=O peak at 5.65 μ. The C=O band is not due to an aldehyde or ketone, since the compound did not react with 2,4-dinitrophenylhydrazine reagent. The proton nmr spectrum contains two singlets of equal area at 2.68 and 2.79 ppm. The mass spectrum of VIII contained *m/e* 375 (parent − OCH_3), 171 [$C(OCH_3)(CF_3)COOCH_3$)], and 59 ($-COOCH_3$).

Anal. Calcd for $C_9H_6F_{12}O_4$: C, 26.61; H, 1.49; F, 56.14. Found: C, 27.24; H, 1.85; F, 56.19.

F. Decomposition of 2,2,4,4-Tetrakis(trifluoromethyl)-7-chloromethyl-1,3,6,9-tetraoxaspiro[4.4]nonane (IXa).—Thirty grams (0.066 mole) of IXa was heated at 190–200° in a flask fitted with a water-cooled condenser leading to an ice trap followed by a Dry Ice trap. After 3 hr 2.5 g of IXa remained in the flask. The ice trap contained 0.7 g and the Dry Ice trap contained 29.2 g which was separated by trap-to-trap transfer into a fraction with boiling point less than −30° (13.4 g). Gc analysis showed this to be a mixture of CO_2 (28%) and hexafluoroacetone (69%). A fraction with boiling point greater than −30° was also obtained. Gc analysis showed this to be a mixture of hexafluoroacetone (10%) and allyl chloride (83%). The allyl chloride was further identified by fractional distillation of the high-boiling fraction, bp 45–46° (lit.[17] bp for allyl chloride 45–45.5°). The infrared and proton nmr spectra were identical with those of an authentic sample of allyl chloride.

Anal. Calcd for C_3H_5Cl: C, 47.09; H, 6.59. Found: C, 46.98; H, 6.44.

G. Decomposition of 2,2,4,4-Tetrakis(trifluoromethyl)-7-phenoxymethyl-1,3,6,9-tetraoxaspiro[4.4]nonane (IXb).—Using the same procedure as in the previous experiment, IXb (39.0 g, 0.076 mole) was decomposed by heating at 180° for 6 hr. Hexafluoroacetone and carbon dioxide were identified as the primary volatile products by mass spectral analysis. The residue was fractionated to give 6.2 g (77.5%) of allyl phenyl ether, bp 95° (31 mm), $n^{25}D$ 1.5191. The infrared and proton nmr spectra are in complete agreement with that expected for allyl phenyl ether.

Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.66; H, 7.68.

The residue from the distillation was undecomposed IXb (8.3 g).

(17) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p 308.

Nuclear Magnetic Resonance Study of Some N,N-Dimethylcarbamates

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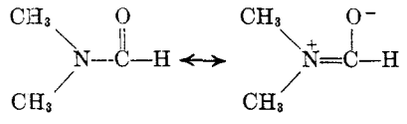
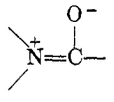
The nmr spectra of 26 N,N-dimethylcarbamates were obtained. The effect on the splitting and chemical shifts of the N,N-dimethylamino protons induced by varying the substituents on the carbonyl carbon atom is reported.

N,N-Dimethylformamide is the classic example of nuclear magnetic nonequivalence of two methyl groups attached to nitrogen.[1-3] At room temperature, rotation about the nitrogen–carbonyl carbon bond in this compound is so reduced, because of resonance interaction, that the methyl groups are magnetically non-



equivalent. This gives rise to a distinct peak for each methyl group in the nmr spectrum. By measuring C^{13}–H coupling constants of N,N-dimethylacetamide, Haake, *et al.*,[4] have verified Pauling's conclusion that the dipolar form of such amides contributes about 40% to the total structure.



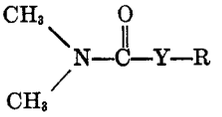
There have been several recent studies of the magnetic nonequivalence of protons of alkyl groups attached to nitrogen, *e.g.*, in N,N-disubstituted amides by LaPlanche and Rogers,[5] 3-(dimethylamino)acrolein by Martin and Martin,[6] N-methylcyclohexylacetamide,[7] N,N-dimethyl-*t*-hexylsulfinamide,[7] and N,N-diethylmethanesulfinamide[8] by Moriarty.

The present paper reports the effect on the splitting and chemical shifts of the methyl protons of some N,N-dimethylcarbamates when the substituent on the car-

(1) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 69–71.
(2) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).
(3) A. G. Whittaker and S. Siegel, *J. Chem. Phys.*, **42**, 3320 (1965).
(4) P. Haake, W. B. Miller, and D. A. Tyssee, *J. Am. Chem. Soc.*, **86**, 3577 (1964).
(5) L. A. LaPlanche and M. T. Rogers, *ibid.*, **85**, 3728 (1963).
(6) M. Martin and G. Martin, *Compt. Rend.*, **256**, 403 (1963).
(7) R. M. Moriarty, *J. Org. Chem.*, **28**, 1296 (1963).
(8) R. M. Moriarty, *ibid.*, **30**, 600 (1965).

TABLE I

NMR SPECTRAL DATA OF METHYL PROTONS OF N,N-DIMETHYLCARBAMATES[a]

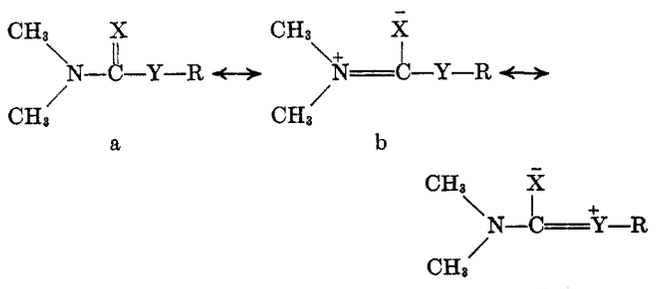


Compd	Y	R	Concn, wt %	TMS, $w_{1/2}$	NNDM, $w_{1/2}$	NNDM, δ
I	O	$CH_2CH_2CH_3$	*Ca.* 21	1	1	2.86
II	O	$CH_2CH_2CH_2CH_3$	*Ca.* 30	1	1	2.86
III	S	$CH_2CH_2CH_2CH_3$	*Ca.* 21	1	1	2.97
IV	O	C_6H_5	11	2	6.5	2.94
V	S	C_6H_5	*Ca.* 15	2	1	2.86
VI	O	$C_6H_4NO_2$-*o*	12	1	3	2.97, 3.10
VII	O	$C_6H_4NO_2$-*m*	11	1	2.5	2.97, 3.07
VIII	O	$C_6H_4NO_2$-*p*	*Ca.* 1	1	3	3.02, 3.12
IX	S	$C_6H_4NO_2$-*p*	*Ca.* 8[b]	1	1	3.08
X	O	C_6H_4Cl-*o*	14	1	11	2.94, 3.05
XI	O	C_6H_4Cl-*m*	20	1	6	2.90, 2.95
XII	O	C_6H_4Cl-*p*	11	1	7	2.93, 2.99
XIII	S	C_6H_4Cl-*p*	8	1	1	2.97
XIV	O	C_6H_4Br-*o*	13	1	4.5	2.95, 3.08
XV	O	C_6H_4Br-*m*	14	1	6	2.94, 2.99
XVI	O	C_6H_4Br-*p*	11	2	8	2.97, 3.00
XVII	S	C_6H_4Br-*p*	7	1	1	2.98
XVIII	O	$C_6H_4CH_3$-*o*	13	1	7	2.95
XIX	O	$C_6H_4CH_3$-*m*	14	1	5	2.95
XX	O	$C_6H_4CH_3$-*p*	13	1	6	2.95
XXI	S	$C_6H_4CH_3$-*o*	14	1	1.5	2.90
XXII	S	$C_6H_4CH_3$-*m*	15	1	1	2.90
XXIII	S	$C_6H_4CH_3$-*p*	15	2	2	2.90
XXIV	O	$C_6H_4OCH_3$-*m*	14	1	6	2.97
XXV	O	$C_6H_4OCH_3$-*p*	12	1.5	6	2.95

[a] Chemical shifts (δ) in parts per million = $10^6(H - H_{ref})/H_{ref}$ are relative to tetramethylsilane as internal standard at ν_0 = 60.0 Mc/sec. (See ref 1, p 21, and also, R. H. Bible, Jr., "Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1965, pp 13–17.) All spectra were obtained in carbon tetrachloride, unless otherwise noted, at the normal operating temperature of the Varian A-60 spectrometer probe (*ca.* 35°). TMS = tetramethylsilane, NNDM = N,N-dimethylamino, and $w_{1/2}$ = width at half-peak height (in cycles per second). [b] Spectrum obtained in deuteriochloroform solution.

bonyl carbon is varied. The compounds studied are listed in Table I with nmr spectral data obtained for them. Physical constants and elementary analyses of the compounds are given in Table II.

In the alkyl or unsubstituted phenyl esters of dimethylcarbamic acid, the protons of the methyl groups showed only one peak in the nmr spectrum (see Table I, compounds I, II, and IV). This implies that there is essentially free rotation of the dimethylamino group about the carbon–nitrogen bond in these compounds, and therefore, little resonance interaction between the free electron pair on nitrogen and the carbonyl group. This is in contrast to the situation in N,N-dimethylformamide. The inference is that the unshared electron pair of the ester oxygen is in resonance with the carbonyl group as depicted in resonance structures Ic and IVc.[2] However, the width of the N,N-dimethyl peak at half-peak height was observed to increase greatly in going from the alkyl esters (I and II) to the phenyl ester (IV). The methyl groups in the latter compound (IV) must be approaching nonequivalence. Resonance structure IVb probably contributes more to the hybrid structure in this compound than it does for compounds in which R = alkyl, but not as much as in the case of formamides. Presumably, the spectrum of the phenyl ester IV at a lower temperature would show split methyl peaks. Conversely, at a higher temperature the broadened methyl peak would sharpen considerably.[2]



a b c

I, X, Y = O; R = alkyl
IV, X, Y = O; R = phenyl
XI, X, Y = O; R = chloro- or bromophenyl
XIII, X = O; Y = S; R = alkyl, phenyl, or substituted phenyl
XXVI, X, Y = S; R = *t*-butylsulfenyl

If there were an electron-withdrawing group on the phenyl ring, then the unshared pair of electrons on the ester oxygen would be drawn away to some extent from the carbonyl group toward, or into conjugation with, the phenyl ring and its substituent. This should increase the double bond character of the >N—C(=O)— linkage and thus cause a splitting of the methyl protons. The spectra of the nitrophenyl compounds VI–VIII show this effect. Since the *m*-nitro substituent also caused a splitting of the methyl peaks, this indicates that the inductive effect of the electron-withdrawing group on the phenyl ring is sufficient to pull the unshared electron pair of the ester oxygen away from the carbonyl group. However, since the Hammett σ constants for *m*-nitro (+0.71) and *p*-

TABLE II

CHARACTERIZATION DATA ON N,N-DIMETHYLCARBAMATES[a]

Compd	Obsd[b] Bp, °C (mm)	Obsd[b] Mp, °C, or n^{25}D	Lit. Bp, °C (mm)	Lit. Mp, °C, or n^{25}D	Formula	Carbon, %[c] Calcd	Carbon, %[c] Found	Hydrogen, %[c] Calcd	Hydrogen, %[c] Found	Nitrogen, %[c] Calcd	Nitrogen, %[c] Found	Other, %[c]	Other, %[c] Found
I	51–65[d] (17)	1.4205			$C_6H_{13}NO_2$	54.94	54.38	9.99	9.90	10.68	10.70		
II	61–76[d] (16)	1.4240			$C_7H_{15}NO_2$	57.90	57.71	10.41	10.23	9.65	9.73		
III	115–116.5 (17)	1.4806	114–115 (18)	1.4846[e]									
IV		44–46		44–45.5[f]									
V		47.5–49		48[g]									
VI		55–57		56–57[h]									
VII		61.5–62.5		63[h]									
VIII		105.5–107.5		107–109[f]									
IX		120–122			$C_9H_{10}N_2O_3S$	47.77	48.01	4.46	4.75	12.38	12.11	S 14.17	14.08
X	79–83 (0.04)	1.5308			$C_9H_{10}ClNO_2$	54.14	53.97	5.05	5.09	7.02	7.08	Cl 17.76	17.93
XI	86–92 (0.04)	1.5315			$C_9H_{10}ClNO_2$	54.14	54.14	5.05	5.01	7.02	6.91	Cl 17.76	17.75
XII		33.5–34.5	143–145 (10)	31.2[i]	$C_9H_{10}ClNO_2$	54.14	54.21	5.05	5.14	7.02	7.03	Cl 17.76	17.68
XIII		76–81			$C_9H_{10}ClNOS$	50.11	50.30	4.67	4.69	6.49	6.43	Cl 16.44	16.60
												S 14.89	14.87
XIV	93–96 (0.09)	1.5509			$C_9H_{10}BrNO_2$	44.28	44.27	4.13	4.12	5.74	5.72	Br 32.74	32.94
XV	90–93 (0.02)	1.5534			$C_9H_{10}BrNO_2$	44.28	44.20	4.13	4.19	5.74	5.62	Br 32.74	32.63
XVI		37–39			$C_9H_{10}BrNO_2$	44.28	44.50	4.13	4.10	5.74	5.88	Br 32.74	32.77
XVII		85–88			$C_9H_{10}BrNOS$	41.55	42.07	3.87	3.99	5.38	5.10	Br 30.72	30.51
												S 12.33	12.51
XVIII	79–81 (0.10)	1.5233	115–117 (0.3)[j]		$C_{10}H_{13}NO_2$	67.02	67.28	7.31	7.24	7.82	7.71		
XIX	88–89 (0.14)	1.5157	88–90 (0.15)[j]										
XX		51.5–52.5		50–53[j]									
XXI	108.5–110 (0.10)	1.5765			$C_{10}H_{13}NOS$	61.50	61.34	6.71	6.81	7.17	7.05	S 16.42	16.42
XXII	113–114 (0.11)	1.5753			$C_{10}H_{13}NOS$	61.50	61.41	6.71	6.81	7.17	7.20	S 16.42	16.53
XXIII	116–116.5 (0.15)	1.5758			$C_{10}H_{13}NOS$	61.50	61.43	6.71	6.80	7.17	7.09	S 16.42	16.55
XXIV	103–104.5 (0.07)	1.5257			$C_{10}H_{13}NO_3$	61.52	61.49	6.71	6.90	7.18	6.99		
XXV		64–66			$C_{10}H_{13}NO_3$	61.52	61.48	6.71	6.74	7.18	7.04		

[a] The infrared and nmr spectra of all compounds were compatible with the assigned structures. [b] Melting points were taken on a Thomas–Hoover capillary melting point apparatus and are corrected; boiling points are uncorrected. [c] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. [d] Block temperature. [e] H. Tilles, *J. Am. Chem. Soc.*, **81**, 714 (1959). [f] L. W. Dittert and T. Higuchi, *J. Pharm. Sci.*, **52**, 852 (1963). [g] R. Riemschneider and O. Lorenz, *Monatsh.*, **84**, 518 (1953); *Chem. Abstr.*, **48**, 11347*c* (1954). [h] A. Deutsch and O. Ferno (to Aktiebolaget Leo), Swedish Patent 128,292 (May 30, 1950); *Chem. Abstr.*, **44**, P9477*d* (1950). [i] Societe des Usines Chimiques Rhone-Poulenc, British Patent 753,766 (Aug 1, 1956); *Chem. Abstr.*, **51**, P4640*d* (1957). [j] Union chimique belge S. A., Belgian Patent 532,057 (Jan 16, 1955); *Chem. Abstr.*, **54**, P5572*i* (1960).

nitro (+0.78) substituents are similar,[9] it is not surprising that this should be so.

Halogens on a phenyl ring are electron donating by resonance and electron withdrawing by induction.[10] The inductive effect of *m*-halogens is greater than the resonance effect of *p*-halogens, as shown by a greater positive σ constant for the *meta* isomers (Cl, σ_m = +0.37, σ_p = +0.23; Br, σ_m = +0.39, σ_p = +0.23);[9] however, the over-all total effect of *p*-halogen substitution is still electron attracting as evidenced by the positive values of σ. The spectra of the halogen-substituted phenyl compounds (X–XII and XIV–XVI) exhibit split methyl groups. This property is again indicative of the importance of resonance structures such as XIb. In these compounds the peaks are not as sharply split as for the nitro-substituted phenyl derivatives. Resonance structures such as XIc must contribute more to the hybrid in the halogen compounds than they do in the nitro-substituted analogs.

The spectra of compounds in which the phenyl is substituted by electron-donating groups (*e.g.*, XVIII–XXV) all show the N,N-dimethyl protons to be unsplit singlets. In these compounds the ester oxygen can resonate only with the carbonyl group since the adjacent phenyl carbon will be electron rich, owing to either the inductive or resonant effect of the substituents; thus, relatively free rotation of the dimethylamino group around the C–N bond would be possible.

It should be noted, however, that although the σ constants for *m*-methoxy (+0.12) and *p*-methoxy (−0.27) change sign,[9] indicating that *m*-methoxy is electron attracting by induction, the spectra of the N,N-dimethyl protons of these compounds (XXIV and XXV) remain essentially identical. Splitting of these protons did not occur until an electron-attracting group with a σ constant greater than about +0.2 (*e.g.*, chlorine or bromine) was substituted on the phenyl ring.

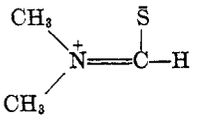
The spectra of the thiocarbamic acid derivatives (III, V, IX, XIII, XVII, and XXI–XXIII) all show a sharp singlet peak for the dimethylamino protons. Therefore, there must be little contribution from resonance structures such as XIIIb to the total structure of the ground-state molecule. The unshared electrons on the ester sulfur must compete with those on nitrogen for the carbonyl group resonance far more effectively than do the unshared electrons on the ester oxygen. Even such a powerful electron-attracting group as *p*-nitrophenyl (IX) could not disrupt the ester sulfur–carbonyl group resonance enough to be noticeable in the nmr spectrum.

Walter and Maerten[11] reported the nonequivalence of N,N-dimethyl groups in thioformamide. The following dipolar form

(9) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 221.

(10) Reference 9, pp 204, 213, 217–219.

(11) W. Walter and G. Maerten, *Ann.*, **669**, 66 (1963).



must contribute significantly to the hybrid structure in this compound also. We have obtained the nmr spectrum of *t*-butyl dimethyltrithioperoxycarbamate (XXVI) and found that it exhibited only two sharp singlets at 3.55 and 1.30 ppm. For this compound, resonance structure XXVIc must contribute an important amount to its over-all structure.

Experimental Section[12]

All compounds except XXVI were synthesized by adding N,N-dimethylcarbamoyl chloride to a benzene solution of pyridine and the appropriate alcohol, mercaptan, phenol, or thiophenol.[13] After the reaction mixtures were stirred at room temperature, usually overnight, they were processed by standard procedures.

Compound XXVI, *t*-butyl dimethyltrithioperoxycarbamate,[14] which was available from previous work, had mp 70–72.5°, lit.[15] mp 69–70°.

Anal. Calcd for $C_7H_{15}NS_3$: C, 40.15; H, 7.22; N, 6.69; S, 45.94. Found: C, 40.01; H, 7.08; N, 6.82; S, 45.75.

Acknowledgment.—Grateful acknowledgment is extended to Drs. M. Beroza, P. Sonnet, and N. Wakabayashi of this Division for helpful discussions. In addition, the author wishes to thank two other Division members: Mr. E. Gooden for obtaining the nmr spectra, and Mr. J. Ingangi for his helpful assistance.

(12) Mention of a proprietary product or company does not necessarily imply endorsement of the product or the company by the U. S. Department of Agriculture.

(13) The thiocresols were obtained as samples from Pitt-Consol Chemical Co.

(14) This compound was originally donated by Phillips Petroleum Co.

(15) C. M. Himel and L. O. Edmonds (to Phillips Petroleum Co.), U. S. Patent 2,792,394 (May 14, 1957); *Chem. Abstr.*, **52**, P1282*h* (1958).

Benzoyl Hypoiodite and the Radical-Chain Decomposition of Phenyliodine Dibenzoate[1]

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The decomposition of phenyliodine dibenzoate in chlorobenzene gives phenyl benzoate in which the phenyl moiety of the ester comes exclusively from the phenyliodine moiety of the dibenzoate. Benzoic anhydride suppresses a water-induced reaction and causes a fast reaction after a prolonged induction period. The nature of the products during the induction period, the effects of changes in concentration, and the effects of added styrene on the kinetics suggest an initial reaction: $*C_6H_5I(OCOC_6H_5)_2 \rightarrow *C_6H_5OCOC_6H_5 + C_6H_5COOI$, followed by reaction of the benzoyl hypoiodite with benzoic anhydride to form a chain-transfer agent. In the presence of benzaldehyde there is no induction period and the rate law at 126.8° is $-d[\text{dibenzoate}]/dt = 1.2 \times 10^{-5}[\text{dibenzoate}] + 66 \times 10^{-5}[\text{aldehyde}][\text{dibenzoate}]^{1/2}$. The rate constant 1.2×10^{-5} is the same as that for the disappearance of the dibenzoate during the induction period process in the absence of benzaldehyde. It is suggested that benzoyl radicals are chain carriers in both the reaction with aldehyde and the postinduction period reaction in the absence of aldehyde. The induction period is also eliminated by decomposition products of benzoyl peroxide.

The decomposition of phenyliodine dibenzoate in monosubstituted aromatic solvents gives iodobenzene, biaryls, phenyl benzoate, benzoic acid, and carbon dioxide as the major products.[2-4] The biaryls are unsymmetrical, one moiety originating from the benzoyloxy groups of the phenyliodine dibenzoate and the other from the solvent. *ortho* phenylation predominates, the percentages of the *ortho* isomer being 57.0 ± 0.5 for chlorobenzene[3] and 57.5 for nitrobenzene.[2,4] The corresponding figures for the decomposition of benzoyl peroxide in the same solvents are 62.2[5] and 56%.[4] Despite the similarity of these directive effects, we find on closer study that the decomposition of phenyliodine dibenzoate, although in part a radical reaction, is by no means a simple analog of the decomposition of benzoyl peroxide. The yield of phenyl benzoate is greater and the phenyl moiety comes exclusively from the iodosobenzene moiety of the phenyliodine dibenzoate and not at all from the decarboxylation of benzoyloxy groups.

The Effect of Water.—The presence of small amounts of water in nominally dry chlorobenzene[6] catalyzes a rapid decomposition of phenyliodine dibenzoate, as shown in Figure 1. Both the rate and the amount decomposed in the fast initial reaction vary from run to run, depending on how much the solvent has been exposed to atmospheric moisture. Runs that have slowed after expending their adventitious water can be made to resume their high rate by new injections of water.[7] The effect of water on the products can be judged by comparing the yields (Table I, reaction conditions IV and V) from experiments with high initial dibenzoate concentrations with those from experiments with low initial dibenzoate concentrations and hence higher water/dibenzoate ratios. The yields of biphenyls and ester are decreased.

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(2) B. M. Lynch and K. H. Pausacker, *Australian J. Chem.*, **10**, 329 (1957).

(3) See Table I.

(4) D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1475 (1956).

(5) (a) D. R. Augood, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 44 (1953); (b) D. R. Augood, J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *ibid.*, 3412 (1953); (c) D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953).

(6) (a) Distilled from P_2O_5. (b) Water has a solubility of about 0.03 *M* in chlorobenzene at room temperature and is monomeric: E. Högfeldt and B. Bolander, *Arkiv Kemi*, **21**, 161 (1963).

(7) The water-catalyzed reaction was investigated only briefly. It appears to be approximately second order with respect to total oxidizing titer. At 100°, 0.01 *M* benzoic acid reduces the rate by an order of magnitude, but at 127° the initial reduction in rate is followed by a pronounced acceleration, probably related to the effect of benzoic anhydride to be described later.