The rate of exchange of 4-methyl protons was determined in 1.47×10^{-4} M base by integration of the singlet at δ 3.68 using the N-methyl signal as standard.

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Registry No.—**1**, 2301-80-6; **2**, 100-10-7; **3**, 959-81-9.

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Notes

N-Monochlorination and N-Monobromination of Carbamates and Carboxamides by Sodium Hypochlorite and Hypobromite[1a]

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Our studies on the chromous chloride promoted addition of N-chlorocarbamates to olefins[2] led us to devise a convenient method for the preparation of N-monochlorocarbamates in high yield, free from the N,N-dichloro derivatives. This method was also applied to the preparation of N-monochlorocarboxamides and of N-monobromocarbamates and -carboxamides needed for the chromous chloride promoted addition studies[2c] and some photochemical work.[3] The recent publication of Swern and coworkers[4] on the preparation of ethyl and methyl N-chlorocarbamates prompted us to report our results.

The method consists of the formation of the sodium salt of the monohalo derivative followed by careful neutralization. The salt is prepared by treating a slight excess (0.5–2%) of the amide with sodium hypochlorite or hypobromite[5] (5–6% solution) at *ca.* 0° (eq 1). After the addition of

$$ZCONH_2 + NaOX \longrightarrow ZCONXNa + H_2O \quad (1)$$

$$ZCONXNa + H_3O^+ \longrightarrow ZCONHX + H_2O + Na^+ \quad (2)$$

methylene chloride, dilute (1–2 N) sulfuric acid is added slowly until the sodium salt (eq 2) and the excess sodium hydroxyde are neutralized (an excess of acid must be avoided). The solvent is removed at reduced pressure at 20–25°. The results are recorded in Table I.

N-Chlorocarbamates. The yields of the N-monochlorocarbamates **1–6**[7] are excellent (86–98%) with the purity of the crude reaction products being satisfactory for use in reactions without further purification. The method is thus very efficient.

N-Chlorocarboxamides. The N-monochlorocarboxamides **8–16** were obtained in good yield, the purity of the crude reaction products being satisfactory for use in reactions. The method was not successful with the sterically hindered 2,2-dimethylpropionamide nor was it convenient for the preparation of the water-soluble N-chloroformamide (**7**). Beckwith and Goodrich[8] have prepared N-monochlorocarboxamides in good yield by the bromine-catalyzed reaction of primary carboxamides with *tert*-butyl hypochlorite.

N-Bromocarbamates. We have studied the bromination of ethyl, 2,2,2-trichloroethyl, and benzyl carbamates (**17**, **18**, and **19**) and, to our knowledge, this is the first reported preparation of N-bromocarbamates. It appears that the disproportionation of the N-bromocarbamates **17** and **18** (eq 3) does occur to a significant extent ($K^{eq.} \simeq 0.08$ and

$$2ROCONHBr \rightleftharpoons ROCONH_2 + ROCONBr_2 \quad (3)$$

0.1, respectively, at *ca.* 37°). Indeed, although both the iodometric and neutralization analyses of the crude N-bromocarbamates **17** and **18** indicated a purity of 100%, their ir and nmr spectra showed the presence of nonbrominated carbamate. A careful examination of the integration for the various protons of the nmr spectra indicated clearly the presence of a third product, most probably the N,N-dibromocarbamate, the aliphatic protons of which had the same chemical shift as those of the N-monobromocarbamate, the molar ratio being approximately equal to that of the nonbrominated carbamate (see Experimental Section for details).

The crude benzyl N-bromocarbamate (**19**) was found to decompose rapidly under reduced pressure, as evidenced by continuous evolution of gas within the oily product, the loss of active bromine, and reduction in weight of material (the yield and active bromine content reported in Table I refer to a crude product kept under reduced pressure for 10 min after evaporation to dryness). The crude N-bromocarbamates **17**, **18**, and **19** could be stored in the refrigerator for several days without any loss of active bromine.

N-Bromocarboxamides. Kergomard[6] has prepared N-bromoacetamide by adding a sodium hypobromite solution[5] to a solution of acetamide in acetic acid. N-Bromobenzamides have been prepared by using bromine in aqueous alkaline solution with subsequent rapid acidification

Table I
Preparation of *N*-Haloamides

N-Halo amide	(No.)	Yield,[a] %	Purity, % of theory: Iodometric	Purity, % of theory: Neutralization	% starting amide[b]	Mp, °C: Crude	Mp, °C: Purified[c]	Mp, °C: Lit.	Registry no.
$CH_3CH_2OCONHCl$	(1)	98	99	100		17–19		9[d]	51-79-6
$CH_3CH_2CH_2OCONHCl$	(2)	86	98			Oil			
$CH_3OCH_2CH_2OCONHCl$	(3)	93	96			Oil			
$ClCH_2CH_2OCONHCl$	(4)	91	96	98		53–55	56.5–57.5	42[e]	
$Cl_3CCH_2OCONHCl$	(5)	92	98	99		61–63	63–63.5		
$C_6H_5CH_2OCONHCl$	(6)	98	98	99		27–29			621-84-1
$HCONHCl$	(7)	50	86			Oil			75-12-7
$CH_3CONHCl$	(8)	70[f]	100				109–110	110[g]	60-35-5
$CH_3CH_2CONHCl$	(9)	78	94	95		Oil			79-05-0
$ClCH_2CH_2CONHCl$	(10)	88	96			69–74	74–74.5		5875-24-1
$BrCH_2CONHCl$	(11)	80	101			67–68	68.5–69		683-57-8
$ClCH_2CONHCl$	(12)	83	98	100		66–68	68–69.5		79-07-2
$FCH_2CONHCl$	(13)	79	101			98.5–100	100.5–101		640-19-7
$Cl_2CHCONHCl$	(14)	81	101			70–71	70–71		683-72-7
$Cl_3CCONHCl$	(15)	85	99			120–122	122–123		594-65-0
$F_3CCONHCl$	(16)	63	99			Oil[h]			354-38-1
$CH_3CH_2OCONHBr$	(17)	85	100	101	~10	Oil			
$Cl_3CCH_2OCONHBr$	(18)	92	100	101	~13	Oil			
$C_6H_5CH_2OCONHBr$	(19)	79	83		~15	Oil			
$CH_3CH_2CONHBr$	(20)	87	100	100		74–75	76–77		
$CH_3CH_2CH_2CH_2CONHBr$	(21)	80	94	96		Oil			626-97-1
$ClCH_2CH_2CONHBr$	(22)	89	97			87–88	89–90		
$BrCH_2CONHBr$	(23)	78	99	100		103–104.5			
$ClCH_2CONHBr$	(24)	79	98	98	~4	74–76	77–78	75[i]	
$FCH_2CONHBr$	(25)	65	99		~6	82–83	83.5–84		
$Cl_2CHCONHBr$	(26)	57	83		~18	73–77	94.5–95.5	96[i]	
$Cl_3CCONHBr$	(27)	45	77			95–97[j]		125[i]	
$F_3CCONHBr$	(28)	19	52					62[i]	

[a] Of active halogen compound before purification, based on the amide. [b] Starting amide present in the crude product as determined by nmr. [c] By recrystallization from methylene chloride or methylene chloride–hexane mixtures (iodometric purity >99%). [d] D. Saika and D. Swern, *J. Org. Chem.*, **33**, 4548 (1968). [e] P. Chabrier, *C. R. Acad. Sci.*, **214**, 353 (1942). [f] Of recrystallized product. [g] K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 986 (1927). [h] Crystalline in the refrigerator. [i] Reference 10. [j] The active bromine content was not significantly increased by recrystallization: 82%, mp 96–98°.

using acetic acid.[9] Our procedure gave better yields for the preparation of *N*-bromopropionamide (**20**) and *N*-bromopentanamide (**21**) and we have used it successfully also to prepare the *N*-bromocarboxamides **22–25.** The method is not convenient for the N-bromination of the dichloro-, trichloro-, and trifluoroacetamides (**26, 27,** and **28**), the yield and the purity of the crude product decreasing in the order **26 > 27 > 28.** Park, *et al.*,[10] has used bromine and silver oxide in anhydrous trifluoroacetic acid to prepare *N*-bromo-α-haloacetamides in good yield and Beebe and Wolfe[11] have obtained *N*-bromotrifluoroacetamide (**26**) in high yield using acetyl hypobromite.

In comparison to the *N*-bromocarbamates, the *N*-bromocarboxamides have much less tendency to undergo disproportionation into the carboxamide and the *N,N*-dibromo derivative. In the ir and nmr spectra of the pure (>99%) samples of the *N*-bromo-α-haloacetamides **23–26,** there is a small but detectable amount (2–4%) of nonbrominated carboxamide.[12]

Experimental Section[14]

Melting points were determined on a Büchi apparatus and are uncorrected. Ir spectra were recorded on a Perkin-Elmer spectrophotometer, Model 257. Nmr spectra were determined on a Varian A-60 spectrometer using TMS as internal standard. The sodium hypochlorite solution was obtained from Anachemia Chemicals Ltd.[15] and contained between 5.0 and 5.7% active chlorine (0.67–0.77 mmol/ml) and excess sodium hydroxide (~0.15 mmol/ml). The carbamates and carboxamides, unless specified otherwise, were obtained from Aldrich Chemical Co.

Iodometric Analyses. The samples (about 1 mmol accurately weighed) were dissolved in 50 ml of a 50:50 mixture of methanol and water. An excess of potassium iodide dissolved in water (5 ml) was added followed by sulfuric acid (1 ml of a 4 *N* solution). The solution was then titrated with 0.1 *N* sodium thiosulfate.

Neutralization Analyses. The samples (about 1 mmol accurately weighed) were dissolved in a 10:40 mixture of methanol and water. The solution was cooled in an ice bath and titrated with 0.1 *N* NaOH using a pH meter.

Preparation of *n*-Propyl, 2-Methoxyethyl, 2-Chloroethyl, and 2,2,2-Trichloroethyl Carbamate (29, 30, 31, and 32). These compounds were prepared from the corresponding alcohols according to the procedure described by Loev and Kormendy:[16] **29,** 65% yield (crude), mp 49–52° (lit.[17] mp 52.5°); **30,** 55% yield (crude), mp 44–46° (lit.[18] mp 46.8°); **31,** 33% yield (crude), mp 71–73° (lit.[19] mp 77°); **32,** 40% yield (recrystallized), mp 63–64°, ir ($CHCl_3$) 3540, 3430, 2940, 1750, 1585, 1385, 1325, 1115, and 1050 cm^{-1}, nmr ($CDCl_3$) δ 4.70 (s, 2 H), 5.62 (broad s, 2 H).

Anal. Calcd for $C_3H_4Cl_3NO_2$: Cl, 55.25. Found: Cl, 54.88.

2,2,2-Trichloroacetamide (31) was prepared by treating the acid chloride with concentrated NH_4OH: 76% yield; mp 141–142.5° (lit.[20] mp 137°).

Typical Procedure for the Monochlorination of Carbamates and Carboxamides. Preparation of Ethyl *N*-Chlorocarbamate (1). To 35.6 g (400 mmol) of ethyl carbamate in a 2-l. conical flask cooled in an ice bath was added 545 ml of yellow NaOCl solution (0.73 mmol/ml, 398 mmol). The mixture was stirred until it became colorless (15 min). Methylene chloride (300 ml) was added. Then 241 ml (482 mequiv) of 2 *N* H_2SO_4 was added dropwise with vigorous stirring. The addition took 2 hr. The organic phase was decanted and the aqueous layer was extracted with methylene chloride (4 × 100 ml). The combined extracts were dried (Na_2SO_4) and the solvent was removed on the rotatory evaporator at *ca.* 25° to yield 49.0 g of 1 as a pale yellow oil which crystallized upon cooling (see Table I): ir (CCl_4) 3400, 3300 (broad), 1770, 1730, 1700, 1380, 1330, 1310, 1200, and 1060 cm^{-1}; nmr

($CDCl_3$) δ 1.30 (t, J = 7 Hz, 3 H), 4.28 (q, J = 7 Hz, 2 H), and 6.63 (broad s, 1 H).

The other *N*-chloroamides listed in Table I were prepared in the same way but on a smaller scale (from 10 to 100 mmol), the excess of amide varying from 1 to 2%. With amides very insoluble in water, a larger reaction time was needed (up to 30 min) with a few milliliters of methylene chloride being added to speed up the reaction. When working on a 10–40-mmol scale, acidifications were carried out with 1 *N* H_2SO_4. Because of the higher solubility of *N*-chlorocarboxamides in water, four to ten extractions with methylene chloride were performed. The ir spectra (CCl_4) of the *N*-chlorocarbamates **2–6** are quite similar to that of ethyl *N*-chlorocarbamate (**1**) and they all show a band in the following regions: 3400 (free NH), 3200–3180 (broad, associated NH), 1770 (C=O), 1740–1730 (C=O), 1710–1700 (C=O), 1410–1380, 1350–1330, 1200 (ester), and 1080–1000 cm^{-1} (ester).

Typical Procedure for the Monobromination of Carbamates and Carboxamides. Preparation of Ethyl *N*-Bromocarbamate (17). To 4.43 g (43 mmol) of NaBr was added 53.4 ml of NaOCl solution (0.75 mmol/ml, 40 mmol). The mixture was stirred for 15 min at room temperature. The deep yellow hypobromite solution was cooled in an ice bath and 3.60 g (40.4 mmol) of ethyl carbamate was added. The reaction mixture was stirred until it became pale yellow (almost colorless). Methylene chloride (50 ml) was added followed by the dropwise addition of 41 ml (47 mequiv) of 1.15 *N* H_2SO_4 with vigorous stirring. The addition took 1.5 hr. The reddish organic phase was decanted and the aqueous layer was extracted with methylene chloride (3 × 15 ml). The combined extracts were dried (Na_2SO_4) and the solvent was removed on the rotatory evaporator to yield 5.71 g of **17** as a yellow oil (see Table I): ir (CCl_4) 3400, 3200 (broad), 1720 (broad, strong), 1415, 1375, 1330, 1220, 1190 (shoulder), and 1065 cm^{-1}, and weak bands at 3500 and 1590 cm^{-1} due to the presence of ethyl carbamate; nmr (CCl_4) δ 1.28 (t, J = 7 Hz, carbamate CH_3) and 1.33 (t, J = 7 Hz, *N*-bromo- and *N,N*-dibromocarbamate CH_3), 4.17 (q, J = 7 Hz, carbamate CH_2) and 4.28 (q, J = 7 Hz, *N*-bromo- and *N,N*-dibromocarbamate CH_2), 5.41 (broad s, carbamate NH_2), and 6.55 (broad s, *N*-bromocarbamate NH) with the following relative integrations—7.7 (the two overlapping triplets), 5.0 (the two overlapping quadruplets), 1.0, and 1.6.

The other *N*-bromoamides listed in Table I were prepared in exactly the same way except that for water-insoluble amides, longer reaction time was needed (up to 30 min) for the reaction with NaOBr. The ir and nmr absorptions of the crude *N*-bromocarbamates **18** and **19** are given below.

Crude **18**: ir ($CHCl_3$) 3400, 3200 (broad), 1745 (broad, strong), 1390, 1325, 1230, 1185, 1110, and 1045, and weak bands at 3530 and 1585 cm^{-1} (nonbrominated carbamate); nmr (CCl_4) δ 4.75 (s, carbamate CH_2), 4.81 (s, *N*-bromo- and *N,N*-dibromocarbamate CH_2), 5.60 (broad s, carbamate NH_2), 6.40 (broad s, *N*-bromocarbamate NH) with a relative integration of 1.9:8.7:1.0:4.6.

Crude **19**: ir (CCl_4) 3400, 3240 (broad), 1720 (broad, strong), 1395, 1325, 1210, 1180 (shoulder), and 1050, and weaker bands at 3500 and 1590 cm^{-1} (nonbrominated carbamate); nmr (CCl_4) δ 5.05 (s, carbamate CH_2), 5.85 (s, *N*-bromocarbamate CH_2), 5.35 (broad s, carbamate NH_2), 6.48 (broad s, *N*-bromocarbamate NH), 7.30 and 7.33 (s, aromatic H of the carbamate and the *N*-bromo derivative) with a relative integration of 1.0:2.3:1.1:1.2:7.7.

Registry No.—**1**, 16844-21-6; **2**, 52175-97-0; **3**, 52175-98-1; **4**, 30830-84-3; **5**, 30830-85-4; **6**, 30830-47-8; **7**, 52175-99-2; **8**, 598-49-2; **9**, 36448-95-0; **10**, 52176-00-8; **11**, 35070-76-9; **12**, 35070-77-0; **13**, 35077-08-8; **14**, 35077-09-9; **15**, 35077-10-2; **16**, 52176-01-9; **17**, 52176-02-0; **18**, 52176-03-1; **19**, 52176-04-2; **20**, 3699-17-0; **21**, 3699-20-5; **22**, 52176-05-3; **23**, 52176-06-4; **24**, 35077-11-3; **25**, 36015-63-1; **26**, 52259-82-2; **27**, 35077-12-4; **28**, 359-45-5; **29**, 627-12-3; **30**, 1616-88-2; **31**, 2114-18-3; **32**, 107-69-7; sodium hypochlorite, 7681-52-9; sodium hypobromite, 13824-96-9.

Supplementary Material Available. Characteristic ir absorptions (position of the NH and C=O bands) of the *N*-chlorocarboxamides **9–16** and of the *N*-bromocarboxamides **20–26**, and the nmr absorptions of these *N*-haloamides and of the *N*-chlorocarbamates **2–6** will appear in Table II (ir) and Table III (nmr) following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-74-3136.

References and Notes

(1) (a) Supported by a grant from the National Research Council of Canada; (b) Arts Council of Canada Predoctoral Fellow, 1969–1971; (c) NRCC Postdoctoral Fellow, 1968–1970; (d) France-Quebec Predoctoral Fellow, 1970–1972.
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Liquid Crystals. V. Molecular Structural Effects on the Mesomorphism of Phenylene Esters[1]

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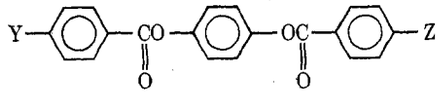
In an earlier paper,[1b] we reported the effects on the mesomorphism (liquid crystallinity)[2-4] of terminally substituted *p*-phenylene dibenzoates (**1**) caused by changing the



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end groups. It was shown that this molecular system has a marked tendency to exhibit nematic mesomorphism, which survives major variations of Y and Z. Since then, we have investigated the effects of more drastic alterations in structure: halogen and methyl substituents on the central phenylene ring, methyl substituents in the 3 and 5 positions of the benzoyl groups, replacement of the central *p*-phenylene with *m*-phenylene and of benzoyl with cinnamyl, and the combination of central chloro substitution with dissimilar acyl groups.

The esters that were prepared have the following structures.