group.[2] In addition to the study of rate effects, it was thought desirable to examine nonkinetic measurements of electronic effects in the amides.

Eight 4-substituted trifluoroacetanilides were prepared by reaction of the aniline with trifluoroacetic anhydride. The chemical shift of the fluorine resonance was measured in tetrahydrofuran solvent (5% concentration) at 56.4 MHz with trifluoroacetic acid as external standard.

The results are shown in Table I. The total spread

TABLE I

^{19}F CHEMICAL SHIFT OF 4-X-TRIFLUOROACETANILIDES

4 substituent	Registry no.	σ^+ [a]	Chemical shift[b]
OCH_3	332-34-3	−0.78	110.5
CH_3	350-96-9	−0.31	107.3
H	404-24-0	0	105.4
Br	24568-11-4	0.15	104.3
Cl	404-25-1	0.11	104.0
$COCH_3$	24568-13-6	0.50	104.2
$CO_2C_2H_5$	24568-14-7	0.48	103.0
NO_2	404-27-3	0.79	100.7

[a] Reference 5. [b] In Hz upfield from external trifluoroacetic acid, 0.021 *M* in tetrahydrofuran, 56.4 MHz.

of chemical shifts is less than 0.2 ppm. This value should be contrasted with the range of about 20 ppm obtained by Gutowsky[3] and Taft[4] for substituted fluorobenzenes and the range of about 2 ppm obtained for benzotrifluorides.[3] No measurements have been reported for trifluoroacetophenones. The present results indicate a very substantial compression of the chemical shift range in going from fluorobenzenes to trifluoroacetanilides. Within this narrow range, however, the ^{19}F chemical shifts of the acetanilides correlate well with Brown's σ^+ substituent constants.[5] The chemical shift for 4-acetyltrifluoroacetanilide is substantially removed from the best line, and the value for the 4-chloro compound shows minor deviation; these deviations have their parallels in measurements in the fluorobenzenes.[3] ρ for this set of data may be defined: $\rho = (a - a_0)/(a_0\sigma^+)$, where a is the chemical shift of substituted compound in Hz upfield from external trifluoroacetic acid, a_0 is the chemical shift of trifluoroacetanilide, and σ^+ is the constant associated with the substituent.[5] The value obtained is -0.058 ± 0.003, not including the acetyl value, or -0.054 ± 0.006, including the acetyl value.

It is clear that within the small range of chemical shifts reported a noninductive substituent effect is being observed. Several explanations such as resonance[6,7] or polarizability could adequately explain the observed data. The efficiency of transmission of electronic effects in the ^{19}F nmr chemical shifts of trifluoroacetanilides is substantially lower than that reported from reaction kinetics.[2] Presumably this difference reflects ground state *vs.* transition state sensitivity to substituent changes.

(2) H. W. Johnson, Jr., and M. Schweizer, *J. Org. Chem.*, **26**, 3666 (1961): H. W. Johnson, Jr., E. Ngo, R. C. Stafford, and Y. Iwata, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. ORGN 31; H. W. Johnson, Jr., E. Ngo, and V. A. Pena, *J. Org. Chem.*, **34**, 3271 (1969).

(3) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Amer. Chem. Soc.*, **74**, 4809 (1952).

(4) R. W. Taft, *ibid.*, **79**, 1045 (1956); R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

(5) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 285 (1957).

(6) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 281.

(7) P. Haake, W. B. Miller, and T. A. Tyssee, *J. Amer. Chem. Soc.*, **86**, 3577 (1964).

Experimental Section

The trifluoroacetanilides were synthesized from trifluoroacetic anhydride and the substituted aniline by standard methods.[8] Proton nmr spectra showed the usual pair of doublets ($J_{AB} \cong 9$ Hz) for the aromatic protons in a *para*-disubstituted benzene, and infrared spectra were consistent with the acetanilide structure. Melting point data follow: 4′ substituent (reported melting point, deg): $-OCH_3$, 113.5–114 (112.5–115);[8] $-CH_3$, 110–111 (111–112);[8] –H, 88–89 (88.5–90);[8] –Cl, 123–124 (123–124.5);[8] –Br,[9] 125.5–126; $-CO_2C_2H_5$,[9] 127.5–128.5; $-COCH_3$,[9] 160.5–161; $-NO_2$, 151.5–152.5 (151.5–153).[8]

Nmr spectra were measured in a Varian Associates HR spectrometer at 56.4 Mc at instrument temperature 35°; the instrument was equipped with the Varian superstabilizer. Frequency measurements were made by the audio side-band technique. Trifluoroacetic acid was used as the external standard and the trifluoroacetanilides were 2.1×10^{-2} *M* solutions in analytical reagent grade anhydrous tetrahydrofuran. The chemical shift of *p*-nitrotrifluoroacetanilide was measured as a function of concentration from 20 to 5% in THF; the fluorine resonance position changed 1 Hz in this concentration range. In some determinations *p*-nitrotrifluoroacetanilide was used as an internal standard; no appreciable difference between the internal and external standards was noted. Reproducibility (at least three measurements on each compound and ten measurements on the *p*-nitro derivative) was ±0.2 Hz.

(8) E. J. Bourne, S. H. Henry, C. E. M. Tatlow, and J. C. Tatlow, *J Chem. Soc.*, 4014 (1952).

(9) Satisfactory microanalysis (±0.3%) for this compound for C, H, and N were obtained from C. F. Geiger, 312 Yale St., Ontario, Calif. Melting points are uncorrected and were measured with a Thomas Unitemp bath.

Studies on the Antimicrobial Substances of Sponges. IV.[1a,b] Structure of a Bromine-Containing Compound from a Marine Sponge

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From a marine sponge *Verongia fistularis* and related species[3] we isolated four compounds: A, mp 195°; B, mp 191°; C, mp 132°; and D, mp 137°. The structure and synthesis of compound A, mp 195°, having a broad antibacterial spectrum, was reported in a recent paper.[4] A comparison of the ir, nmr, and mass spectra of compound C, molecular formula $C_{29}H_{50}O$, mp 132°, $[\alpha]^{20}D$ −38.7, with those of β-sitosterol[5] revealed them to be identical.

Now we wish to report the evidence leading to structure **1** for compound B, mp 191°. This compound was analyzed for $C_{10}H_{13}NO_4Br_2$ and showed infrared bands

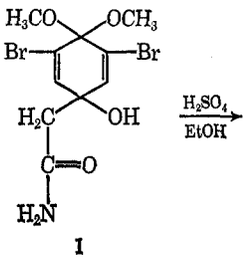
(1) (a) For part III in this series, see G. M. Sharma, B. Vig, and P. R. Burkholder, *Trans. Drugs Sea Symp., J. Ocean Technol.*, 119 (1968); (b) Lamont–Doherty Geological Observatory Contribution No. 1479.

(2) Postdoctoral research associate, 1967–1969.

(3) G. M. Sharma and P. R. Burkholder, *J. Antibiot.* (Tokyo), *Ser. A*, **20**, 200 (1967).

(4) G. M. Sharma and P. R. Burkholder, *Tetrahedron Lett.*, 4147 (1967).

(5) A pure sample of β-sitosterol was provided by Professor Maxwell S. Doty, University of Hawaii.



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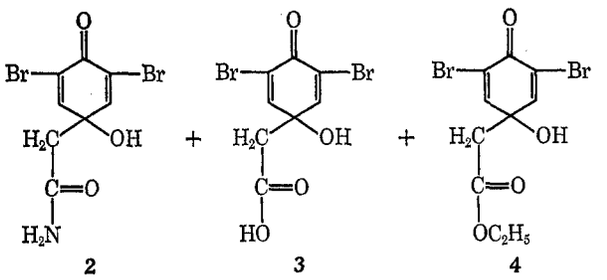
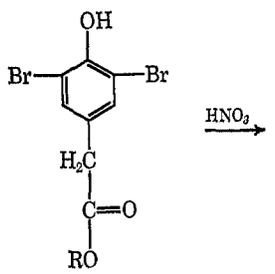
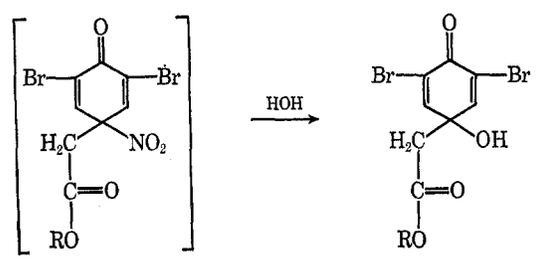
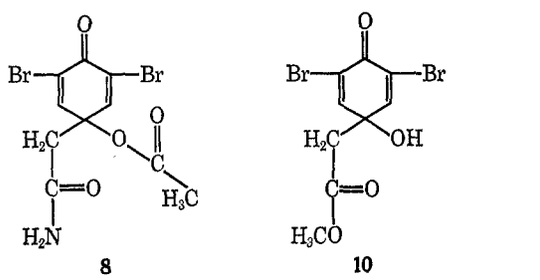


2 3 4



5a, R = H
b, R = C_2H_5



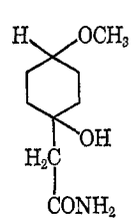


8 10

(KBr) at 3420, 3375, 3315, 1698, 1640 cm^{-1}, indicating the presence of hydroxyl group, amide function, and double bonds. The mass spectrum of this compound exhibited three weak molecular ion peaks at *m/e* 373, 371, 369, in the relative intensity ratio of 1:2:1, confirming the presence of two bromine atoms and the molecular weight corresponding to the formula stated above. Other prominent ions containing two bromine atoms occurred at *m/e* 342, 340, 338 (M − OCH_3); 324, 322, 320 [(M − OCH_3) − H_2O]; 315, 313, 311 (M − 58, loss of CH_2CONH_2). The presence of two methoxyl groups in the molecule was confirmed by functional group analysis. Formation of a mono-O-acetyl derivative indicated the presence of a single hydroxyl group.

Hydrolysis of B with sulfuric acid in ethanol produced three compounds having mp 195°, 192°, and 121°. The compound with mp 195° was confirmed to be dienone **2** by comparison with an authentic sample.[4] The other two products with mp 192° and 121° were assigned structures **3** and **4**, respectively, on the basis of spectral data. Further confirmation of these structures was obtained by their direct synthesis. Compounds **3** and **4** were synthesized by treating 4-hydroxy-3,5-dibromophenyl acetic acid **5a** and its ethyl ester **5b** with nitric acid.[4,6] It was later discovered that B could be quantitatively converted into **2** by heating with 70% acetic acid for 2 hr. Formation of dienone **2** from the compound B on acid hydrolysis supports the assignment of structure **1** for the latter.

On catalytic hydrogenation **1** absorbed 5.5 mol of hydrogen to furnish a mixture of products from which only one compound, mp 137°, could be obtained in an analytically pure state. On the basis of spectroscopic evidence (ir, nmr, and mass spectra) we have assigned structure **6** for this compound.



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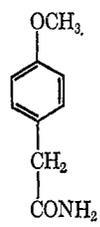

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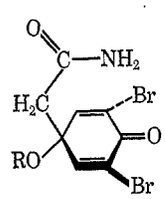
Since the total hydrogenation product showed aromatic absorption in the uv at 275 and 285 mμ, the presence of the expected product *p*-methoxyphenylacetamide **7** in the mixture was indicated, but this compound could not be isolated in the pure state.

The nuclear magnetic resonance spectrum[7] of B is fully in accord with the proposed structure **1**. In the nmr spectrum of the dienone **2** and of its acetyl derivative **8**, the protons attached to the amide nitrogen were found to resonate[4] at *ca.* 2.97 ppm instead of the expected values of 8 to 5 ppm. The marked excess shielding of the amide protons in **2** and **8** may be explained on the basis of the folded conformation **9**. In this con-



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formation, the amide group will not only be in the shielding zone of the dienone ring but may also be prevented from making intermolecular hydrogen bonds. Both these effects acting in concert may shift the amide resonance to the observed high-field position.

The amide group in the acetate of **1** also exhibits the unusual chemical shift (3.25 ppm) although no dienone moiety is present. It would seem, therefore, that the acetoxy group may also play a significant role in the shielding of the amide protons. Single crystal X-ray

(6) E. Muller, A. Shick, and K. Scheffler, *Chem. Ber.*, **92**, 474 (1959).
(7) Spectral data are recorded in the Experimental Section.

diffraction analyses of these compounds are being performed to check the validity of the above interpretations.

As the compounds **1** and **2** were isolated from the sponge by extraction with methanol, the possibility was considered that the former compound might have been obtained from the latter during isolation procedure. However, failure to convert **2** into **1** by reacting with methanol under various conditions supports the view that **1** is indeed a naturally occurring compound. Reaction of **2** with methyl orthoformate also failed to produce the acetal **1**.

Experimental Section

Melting points were determined on a Fisher-Johns melting point apparatus. Ultraviolet spectra were determined on a Beckman Model DK2A recording spectrophotometer and infrared spectra on a Model 337 Perkin-Elmer spectrophotometer; nuclear magnetic resonance spectra were determined on a Varian A-60A spectrometer in deuterated acetone (unless otherwise stated) using tetramethylsilane as internal standard. Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium im Max-Planck-Institut fur Kohlenforschung, 433 Mulheim (Ruhr), West Germany.

Isolation of 1.—The isolation of **1** from sponge *Verongia fistularis* has been described in a previous paper.[3] The molecular formula $C_{10}H_{15}NO_4Br_2$ reported in that publication is now revised to $C_{10}H_{13}NO_4Br_2$ on the basis of more accurate combustion analysis of a sample prepared by crystallizing three times from ethyl acetate to afford colorless prisms: mp 191°; ir (KBr) 3420, 3375, 3315, 1698 (amide C=O), 1640 cm^{-1}; nmr δ 6.75 (a singlet over a very broad amide resonance, 4 H, amide and olefinic protons, after addition of D_2O, 2 H), 5.75 (s, 1 H, OH), 3.04 and 3.06 (two singlets, 6 H, two OCH_3), and 2.56 (s, 2 H, CH_2—$CONH_2$).

Anal. Calcd for $C_{10}H_{15}NO_4Br_2$: C, 32.34; H, 3.5; N, 3.77; Br, 43.12; OCH_3, 16.71. Found: C, 32.18; H, 3.65; N, 3.79; OCH_3, 16.54.

Acetylation of 1.—Acetic anhydride (0.5 ml) was added to a solution of **1** (100 mg) in anhydrous pyridine. After 12 hr at 20°, the reaction mixture was worked up to give, after three crystallizations from ethyl acetate, fine colorless needles (60 mg): mp 184°; ir (KBr) 3460 (NH_2 of amide group), 1720 (ester C=O), and 1698 cm^{-1} (amide C=O); nmr δ 7.1 (s, 2 H, olefinic protons), 3.15 and 3.25 (two singlets, 8 H, two OCH_3 and $CONH_2$, after addition of D_2O, 6 H), 2.92 (s, 2 H, CH_2—CO), and 2.05 (s, 3 H, CH_3COO). Actually the $CONH_2$ resonance was found to shift between 2.95 and 3.2 ppm.

Hydrolysis of 1 with Sulfuric Acid.—To a solution of **1** (1.05 g) in ethanol (10.0 ml) was added 10% sulfuric acid (40 ml), and the reaction mixture was heated on a boiling water bath for 1 hr. The solution was cooled and 6 ml of 28% ammonium hydroxide solution was added. Approximately half the solvent was removed under reduced pressure and the remaining solution was extracted three times with ethyl acetate. The ethyl acetate extract after drying and evaporation gave a semisolid residue (800 mg) which was chromatographed over silica gel. Continuous elution with ether–benzene mixture ratio (1:4) first gave the ester **4** (38 mg, mp 121°) and then the acid **3** (295 mg, mp 195–196°). The structure of these compounds was established by synthesis from ethyl 4-hydroxy-3,5-dibromophenylacetate **5b** and the corresponding acid **5a**. Elemental analysis and spectral data are given later (**Synthesis of Dienones 3 and 4**).

Further eluting the column with ethyl acetate gave dienone **2**, mp 195°, identical with authentic[4] **2**.

Hydrolysis of 1 with Dilute Acetic Acid.—A solution of **1** (1.036 g) in acetic acid (14 ml) and water (7 ml) was heated for 2 hr on a boiling water bath. The solvent was removed under reduced pressure and the residue crystallized from ethyl acetate or water to give dienone **2** (600 mg), mp 195°.

Preparation of 4-Hydroxy-3,5-dibromophenylacetic Acid (5a).—A solution of *p*-hydroxyphenylacetic acid (7.6 g) in glacial acetic acid (250 ml) was stirred mechanically and bromine (16.5 g) dissolved in 5 ml of acetic acid was added dropwise over a period of 30 min. The bromination was allowed to proceed at room temperature for 72 hr. The solvent was then removed under reduced pressure, and the residue crystallized from water to afford pure **5a** (10 g): mp 195–196°; uv max (MeOH) 282 mμ (ϵ 2700) and 287 (2600); ir (KBr) 3350 (broad OH), 1650 cm^{-1} (-C=O); nmr δ 9 (broad OH), 7.5 (s, 2 H, aromatic protons), and 3.64 (s, 2 H, CH_2—C=O).

Anal. Calcd for $C_8H_6O_3Br_2$: C, 30.96; H, 1.93; Br, 51.61. Found: C, 31.01; H, 2.1; Br, 51.53.

Preparation of Ethyl 4-Hydroxy-3,5-dibromophenylacetate (5b).—This ester was prepared by refluxing (using Dean and Stark apparatus to remove water) a mixture of **5a** (2 g), ethanol (50 ml), benzene (125 ml), and concentrated sulfuric acid (0.5 ml) for 8 hr. The reaction mixture was cooled and diluted with water. The benzene layer was washed with sodium carbonate solution, dried, and evaporated to give ester **4**, 1.98 g (96%). Two crystallizations from hexane gave an analytical sample, mp 105°.

Anal. Calcd for $C_{10}H_{10}O_3Br_2$: C, 33.90; H, 2.80; Br, 45.19. Found: C, 38.81; H, 2.90; Br, 45.33.

Synthesis of Dienones 3 and 4.—A mixture of concentrated nitric acid and glacial acetic acid (1:9 v/v) was cooled to 10° and used for the syntheses of dienones **3** and **4** as described below.

A measured volume (2.1 ml) of the nitric acid–acetic acid mixture was added to a stirred solution of **5a** (330 mg) in glacial acetic acid (3 ml) at 10°. After stirring for 3 hr, the nitric acid was neutralized by adding sodium bicarbonate (600 mg), and the solvent was stripped off the reaction mixture under reduced pressure. The residue was suspended in water (10 ml) and extracted with ethyl acetate. The ethyl acetate extract was dried and evaporated to give a brown residue (250 mg). Chromatography of this material on silica gel and elution with ether–benzene mixture (1:4) gave pure dienone **3** (180 mg). Crystallization from ethyl acetate gave a white solid: mp 195–196°; uv max (MeOH) 255 mμ (ϵ 8600); ir (Nujol) 3475 (OH), 1700 (carboxylic C=O), 1670, 1600 cm^{-1} (dienone C=O); nmr δ 7.6 (s, 2 H, olefinic protons), 6.0 (broad, 2 H, exchanges with D_2O), and 2.88 (s, 2 H, $-CH_2$—CO_2H).

Anal. Calcd for $C_8H_6O_4Br_2$: C, 29.4; H, 1.84; Nr, 49.08. Found: C, 29.61; H, 1.98; Br, 49.38.

The dienone **4** was synthesized in 76% yield by reacting **5b** with nitric acid–acetic acid mixture in the manner described above. The ethyl acetate extract was evaporated to give a residue which was crystallized from hexane to afford pure **4** as colorless needles: mp 121°; uv max (MeOH) 253 mμ (ϵ 8632); ir (Nujol) 3460 (OH), 1720 (ester C=O), and 1680 cm^{-1} (dienone C=O); nmr ($CDCl_3$) δ 7.42 (s, 2 H, olefinic protons), 4.24 (quartet, 2 H, O—$CH_2 \cdot CH_3$), 2.78 (s, 2 H, CH_2—C=O), and 1.28 (t, 3 H, O—$CH_2 \cdot CH_3$).

Anal. Calcd for $C_{10}H_{10}O_4Br_2$: C, 33.9; H, 2.82; Br, 45.19. Found: C, 33.81; H, 2.90; Br, 45.33.

Catalytic Hydrogenation of 1.—A mixture of **1** (556 mg), sodium acetate (400 mg), and 10% Pd-C (80 mg) in methanol (50 ml) was hydrogenated. After 1.5 hr the absorption of the hydrogen had stopped and approximately 5 mol equiv of hydrogen had been consumed. The reaction mixture was filtered and evaporated to give a white residue. Water was added to the residue and the aqueous suspension was extracted with ethyl acetate. The ethyl acetate extract was dried and evaporated to give a mixture (280 mg) which could not be separated into its components by column chromatography or preparative tlc. Since the total hydrogenation product showed uv absorption at 275 and 285 mμ, the presence of *p*-methoxyphenylacetamide **7** was indicated.

The hydrogenation product was heated with benzene (4 ml) and the insoluble material was collected by suction. The insoluble compound was crystallized four times from ethyl acetate to give **6** (25 mg): mp 137°; uv max (MeOH) only end absorption; ir (KBr) 3525, 3310 (OH, $CONH_2$), 3000, 2950 (methylenes), and 1675 cm^{-1} (amide C=O); nmr ($CDCl_3$) δ 6.15 (broad, 2 H, $CONH_2$), 3.75 (m, 1 H), 3.4 (s, 3 H, OCH_3), 2.4 (s, 2 H, CH_2—CO), 1.7 (broad envelope, 9 H, methylenes of cyclohexane and OH); mass spectrum (70 eV) *m/e* 187 (M^+) is not observed, 169 (M − 18), 153, 122 (150 − OCH_3).

Anal. Calcd for $C_9H_{17}O_3N$: C, 57.75; H, 9.09; N, 7.48. Found: C, 57.66; H, 9.04; N, 7.53.

Attempted Synthesis of 1 from 2.—(a) The dienone **2** (100 mg) was dissolved in anhydrous methanol (10 ml), and the solution was kept at room temperature for 2 days. Examination of the uv and nmr spectra indicated the absence of **1** in the reaction mixture.

(b) To a solution of dienone **2** (100 mg) in anhydrous methanol, a catalytic amount of *p*-toluenesulfonic acid (10 mg) was added and the reaction mixture refluxed for 24 hr. Removal of solvent gave 105 mg of a material which was dissolved in ethyl acetate and washed with water. The ethyl acetate extract was dried and evaporated to give a semisolid (100 mg). Uv and nmr spectra of this material indicated the absence of **1**. The nmr spectrum instead indicated the presence of dienone **10**. Chromatography over silica gel gave pure **10** (25 mg, liquid) on elution with ether–benzene mixture (1:4). Further eluting the column with ethyl acetate gave the starting material, dienone **4**.

For combustion analysis the solid acetyl derivative of **10** was prepared. The acetyl derivative was crystallized from hexane to give colorless needles: mp 140°; uv max (MeOH) 258 mμ (ε 8420).

Anal. Calcd for $C_{11}H_{10}O_5Br_2$: C, 34.55; H, 2.61; Br, 41.88. Found: C, 34.74; H, 2.59; Br, 41.50.

(c) The dienone **2** was treated with methyl orthoformate using the conditions reported in literature.[8] Spectroscopic identification of the reaction product failed to reveal the presence of acetal **1**.

Registry No.—**1**, 24742-01-6; **1** (acetate), 24742-02-7; **3**, 24742-03-8; **4**, 24744-57-8; **5a**, 24744-58-9; **5b**, 24744-59-0; **6**, 24744-60-3; **10** (acetate), 24744-61-4.

Acknowledgment.—This work has been supported in part by National Institutes of Health Grant GM-11735 and in part by Sea Grant Project GH-16.

(8) L. F. Feiser and M. Feiser in "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, N. Y., 1967, pp 1206–1207.

Synthesis of Secondary Amines *via* Triphenylphosphinimines

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Received October 10, 1969

In continuation of our investigation utilizing triphenylphosphinimines (I) as tools in organic and inorganic synthesis,[2a–c] we investigated further the use of I in the preparation of mixed secondary amines. Our attention was mainly directed toward (a) the synthesis of secondary amines containing a cycloalkyl group and (b) establishing the scope and limitations of this method for the preparation of such amines. The synthesis followed the sequence of reactions of eq 1 and 2.

$$Ph_3\overset{+}{P}-\overset{-}{N}R \longleftrightarrow Ph_3P{=}NR + R'X \longrightarrow [Ph_3P{-}NRR']^+X^- \quad (1)$$

$$[Ph_3PNRR']^+X^- \xrightarrow{H_2O} Ph_3P{=}O + HNRR'^+X^- \quad (2)$$

R = Me, Et, *n*-Pr, *i*-Pr, *i*-Bu, *t*-Bu, 1-Adamantyl
R′ = Me, Et; X = I, Cl, Br

No difficulties were encountered in preparing the corresponding I with R = cyclopropyl, -pentyl, -hexyl, -heptyl, and adamantyl. However, again as reported previously,[2a] only MeI and EtI could be added according to eq 1. Use of any higher alkyl groups, including cyclopropyl, resulted in HX elimination from the alkyl halide and yielded alkylaminotriphenylphosphonium halides according to eq 3.

$$Ph_3P{=}NR + R'X \longrightarrow [Ph_3P{-}NHR]^+X^- + \text{olefin}^{2d} \quad (3)$$

R′ = any C_3 and higher alkyl; X = I

Alkylaminotriphenylphosphonium halides needed for the preparation of I were obtained by treating triphenyldibromophosphorane with the corresponding alkylamine in the presence of triethylamine.[2a,3] Dehydrohalogenation of these phosphonium salts was easily accomplished by treatment with sodium amide in liquid ammonia.[2a] The resulting triphenylphosphinecycloalkylimines were very sensitive to moisture and were used without further purification for the subsequent syntheses. These were carried out according to eq 1 by refluxing the corresponding triphenylphosphinimines in excess alkyl halide. Data on the resulting compounds are compiled in Table I.

All the dialkylaminophosphonium iodides obtained could be hydrolyzed as shown in eq 2. The mixed secondary amines were formed in good yields and were characterized as hemioxalates. Pertinent data are reported in Table II.

In conclusion it can be stated that alkyl addition to triphenylalkylphosphinimines, to give after hydrolysis mixed secondary amines, is limited to addition of methyl and ethyl groups.

Experimental Section

Melting points are uncorrected. Microanalysis was performed by A. Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut, Mülheim/Ruhr, Germany, and by Galbraith Laboratories, Knoxville, Tenn.

Cycloalkylaminotriphenylphosphonium Bromides.—To an ice-cooled suspension of triphenyldibromophosphorane (0.1 mol) in benzene was slowly added a solution of triethylamine (0.1 mol) and the appropriate cycloalkylamine (0.1 mol) in 50 ml of dry benzene. The reaction was stirred for 3 hr before filtering. The collected precipitate was washed with ether and then with ice water. After drying it was dissolved in 100 ml of chloroform, treated with Norit, and filtered. Excess anhydrous ether (200 ml) was added to the chloroform solution and the precipitated bromide was filtered off. The mother liquors yielded a second crop on refrigerating overnight. The cycloalkylaminotriphenylphosphonium bromides were recrystallized from chloroform–ether to give analytically pure samples.

Cyclopropylaminotriphenylphosphonium bromide: yield 82%; mp 204°. *Anal.* Calcd for $C_{21}H_{21}BrNP$: C, 63.31; H, 5.31; N, 3.52. Found: C, 63.10, H, 5.34; N, 3.50.

Cyclopentylaminotriphenylphosphonium bromide: yield 89%; mp 188°. *Anal.* Calcd for $C_{23}H_{25}BrNP$: C, 64.79; H, 5.91; N, 3.29. Found: C, 65.27; H, 5.96; N, 3.35.

Cycloheptylaminotriphenylphosphonium bromide: yield 85%; mp 194–195°. *Anal.* Calcd for $C_{25}H_{29}BrNP$: C, 66.07; H, 6.43; N, 3.08. Found: C, 66.14; H, 6.22; N, 3.24.

Adamantylaminotriphenylphosphonium Bromide: yield 79%; mp 261–263°. *Anal.* Calcd for $C_{28}H_{31}BrNP$: N, 6.30. Found: N, 6.32.

Triphenylphosphinecycloalkylimines.—To a stirred suspension of the appropriate cycloalkylaminotriphenylphosphonium bromide (0.05 mol) in anhydrous ammonia was added 2.2 g of sodium amide (0.055 mol) and the resulting mixture was stirred for 1 hr in a Dry Ice–acetone bath. Ammonia was then evaporated by removing the cold bath and continuing the stirring. The solid remaining in the flask was extracted repeatedly with anhydrous ether. Evaporation of the combined extracts gave the desired phosphinimines which were recrystallized from anhy-

(1) M. Jayawant, Ph.D. Thesis, University of Cincinnati, Cincinnati, Ohio, 1967, and P. Gutsch, 1970, respectively.

(2) (a) H. Zimmer and G. Singh, *J. Org. Chem.*, **28**, 483 (1963); (b) H. Zimmer and G. Singh, *Angew. Chem., Int. Ed. Engl.*, **2**, 395 (1963); (c) H. Zimmer and G. Singh, *J. Org. Chem.*, **29**, 3412 (1964). (d) The olefins were qualitatively identified by decolorization of bromine–water reagent. The stoichiometry and exact mechanism of the olefin forming reaction are presently being investigated.

(3) L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956).