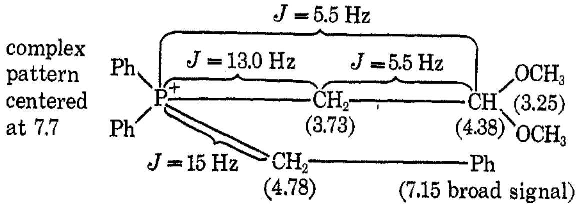
Nmr data for this compound, obtained in $CDCl_3$ solution at 60 MHz, were in good accord with this structure.



2,5-Dimethoxy-1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohexane Dibromide (5a).—Diphenylphosphinoacetaldehyde dimethyl acetal (12.0 g, 0.047 mol) was dissolved in 200 ml of glacial acetic acid and this solution was brought to reflux. Hydrogen bromide was then passed slowly through the refluxing solution for 1 hr. The acetic acid was stripped off under reduced pressure and the residue was triturated with acetone yielding 9.1 g (50%) of a white solid, mp 208–210° dec (from acetonitrile–methanol).

Anal. Calcd for $C_{30}H_{32}Br_2O_2P_4$: C, 55.77; H, 4.95; Br, 24.70. Calcd for $C_{30}H_{32}Br_2O_2P_4 \cdot H_2O$: C, 54.26; H, 5.12; Br, 24.06. Found: C, 53.66; H, 4.94; Br, 24.50.

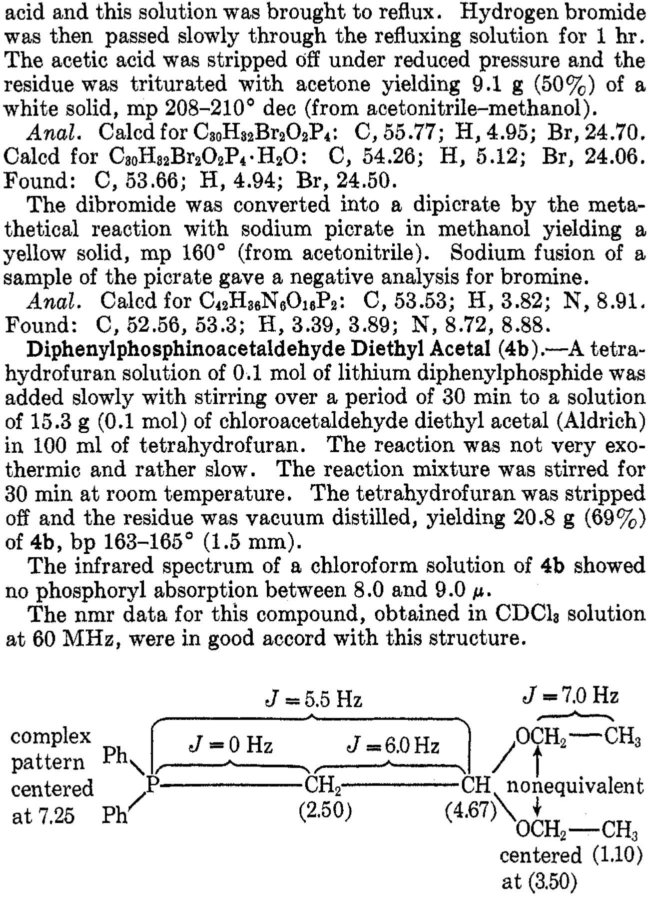
The dibromide was converted into a dipicrate by the metathetical reaction with sodium picrate in methanol yielding a yellow solid, mp 160° (from acetonitrile). Sodium fusion of a sample of the picrate gave a negative analysis for bromine.

Anal. Calcd for $C_{42}H_{36}N_6O_{16}P_2$: C, 53.53; H, 3.82; N, 8.91. Found: C, 52.56, 53.3; H, 3.39, 3.89; N, 8.72, 8.88.

Diphenylphosphinoacetaldehyde Diethyl Acetal (4b).—A tetrahydrofuran solution of 0.1 mol of lithium diphenylphosphide was added slowly with stirring over a period of 30 min to a solution of 15.3 g (0.1 mol) of chloroacetaldehyde diethyl acetal (Aldrich) in 100 ml of tetrahydrofuran. The reaction was not very exothermic and rather slow. The reaction mixture was stirred for 30 min at room temperature. The tetrahydrofuran was stripped off and the residue was vacuum distilled, yielding 20.8 g (69%) of **4b**, bp 163–165° (1.5 mm).

The infrared spectrum of a chloroform solution of **4b** showed no phosphoryl absorption between 8.0 and 9.0 μ.

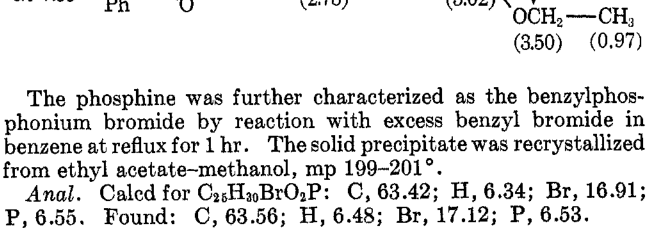
The nmr data for this compound, obtained in $CDCl_3$ solution at 60 MHz, were in good accord with this structure.



The above phosphine was characterized as the oxide by reaction of an acetone solution with 3% hydrogen peroxide in acetone. An exothermic reaction was noted, and evaporation of the solvent yielded a white crystalline solid, mp 101° (from hexane–cyclohexane).

Anal. Calcd for $C_{18}H_{23}O_3P$: C, 67.92; H, 7.23; P, 9.74. Found: C, 67.83; H, 7.01; P, 9.59.

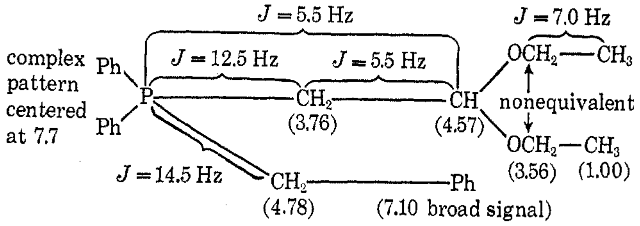
The nmr spectrum of this compound, obtained in $CDCl_3$ solution at 60 MHz, was in good accord with this structure.



The phosphine was further characterized as the benzylphosphonium bromide by reaction with excess benzyl bromide in benzene at reflux for 1 hr. The solid precipitate was recrystallized from ethyl acetate–methanol, mp 199–201°.

Anal. Calcd for $C_{25}H_{30}BrO_2P$: C, 63.42; H, 6.34; Br, 16.91; P, 6.55. Found: C, 63.56; H, 6.48; Br, 17.12; P, 6.53.

The nmr data for this compound, obtained in $CDCl_3$ solution at 60 MHz, were in good accord with this structure.



2,5-Diethoxy-1,1,4,4-tetraphenyldiphosphonia-1,4-cyclohexane Dibromide (5b).—Diphenylphosphinoacetaldehyde diethyl acetal (20 g, 0.066 mol) was dissolved in 150 ml of glacial acetic acid and hydrogen bromide was passed slowly through the solution at reflux for 2 hr and the solution allowed to stand at room temperature for 12 hr. The acetic acid was stripped off at reduced pressure and the residue was triturated with acetone yielding 13.5 g (61%) of **5b**, mp 208–210° (from acetonitrile–methanol).

Anal. Calcd for $C_{32}H_{36}Br_2O_2P_2 \cdot H_2O$: C, 55.49; H, 5.49; Br, 23.12. Found: C, 55.61; H, 5.68; Br, 23.16.

The infrared spectrum of a potassium bromide disk of **5b** showed absorptions at 6.98, 9.00, and 10.04 μ which are typical of aryl phosphonium salts. Strong absorption was also observed at 9.40 μ assigned to a carbon-to-oxygen single bond stretching frequency.

Picrate of 5b.—A sample of **5b** in methanol was mixed with an aqueous solution of sodium picrate and the immediate precipitation of a yellow solid resulted, mp 182–183° dec (from acetonitrile).

Anal. Calcd for $C_{44}H_{40}N_6O_{16}P_2$: C, 54.43; H, 4.12; N, 8.65; Br, 0.00. Found: C, 53.91; H, 3.73; N, 8.01; Br, 0.00.

Fluoroborate Salt of 5b.—A warm aqueous solution of **5b** and an aqueous solution of sodium fluoroborate were mixed and a white solid immediately precipitated, mp 260–262° (from ethyl acetate–methanol). The nmr spectrum of a trifluoroacetic acid solution of the fluoroborate salt was identical with that of the bromide.

Registry No.—**4a**, 24744-62-5; **4a** (oxide), 24744-63-6; **4a** (benzyl bromide salt), 24744-64-7; **4b**, 24744-65-8; **4b** (oxide), 24744-66-9; **4b** (benzyl bromide salt), 24744-67-0; **5a**, 24744-68-1; **5a** (dipicrate), 24744-69-2; **5b**, 24744-70-5; **5b** (picrate), 24799-52-8; **5b** (fluoroborate), 24806-55-1.

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^{19}F Nuclear Magnetic Resonance Spectra of Some Trifluoroacetanilides

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We have become interested in the transmission of electronic activation effects through the amide link from groups attached to the nitrogen atom to a reactive site on a carbon atom attached to the carbonyl

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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 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.

TABLE I

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

4 substituent	Registry no.	$\sigma^{+\,a}$	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.

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.

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.

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[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

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[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.