Quantitative Solubility–Structure Relationships for Some *meta*- and *para*-Substituted Benzoic Acids in Benzene and in Cyclohexane[1]

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The solubilities of benzoic acid and of 19 *meta*- and *para*-substituted benzoic acids in benzene and in cyclohexane at 30° have been determined. For 16 of these acids, there is a good correlation between log (X_B/X_C) and Hammett's σ, where X_B and X_C are the mole fraction solubilities in benzene and in cyclohexane. It is significant that there is no correlation between log X_B alone or log X_C alone and σ. These results indicate that log (X_B/X_C) is a measure of the tendency of the acid to interact with the π cloud of benzene. Deviations from these relationships for the other four acids are discussed.

The mutual solubility of two condensed phases has been described[2] as being governed by solvent–solvent, solute–solute, and solvent–solute attractive forces. In comparisons of the solubility of a series of solutes in a common solvent, only the solvent–solvent forces cancel. If, by experimental design, the effect of the different solute–solute forces present in a series of structurally related solutes can also be effectively cancelled or minimized, it would be of interest to determine whether the remaining solvent–solute forces conform to a Hammett-type relationship.[3] Usually, substituent constants[3] are applied to chemial reactions which are characterized by localized reaction sites. In contrast, a solubility "reaction" site is not localized, the gross structure of the entire molecule playing an important role in the solution process. However, correlations have been reported[4] between absorption maxima in electronic spectral excitations (where gross molecular structure is similarly important in the spectral "reaction") and Hammett and Taft[5] substituent constants.

Hildebrand[2] has shown that neglecting to correct solubilities to a common vapor pressure for the solutes may lead to completely erroneous conclusions about even the relative order of these solubilities. Unfortunately, because of a lack of sufficient physical data for many organic compounds, it is often not feasible to correct solubilities of structurally related compounds to a common vapor pressure. However, for saturated solutions in contact with excess solid solute, the ratio of solubilities in two different common solvents cancels the effect of varying vapor pressure among the member compounds of the solute series since the solute partial pressure is the same in both common solvents. In addition, different members of a series of solid solutes may have different crystalline structures. The ratio of solubilities in the two common solvents, since both solutions are in equilibrium with the same solid phase, makes comparisons of data independent of the nature of the solute crystal structure. It is also believed that

the use of the solubility ratios in two common solvents will tend to cancel out that part of the total solubility which is due to compositional similarity between the solute and the solvent. In summary, it is believed that the solubility ratios in two common solvents of a series of *meta*- and *para*-substituted benzene derivatives may be related to the Hammett effects of the *meta* and *para* substituents.

For a solid solute in equilibrium with its saturated solution in each of the two solvents (1 and 2), if the solute has the same mole fraction activity coefficient in the two solutions, then

$$\mu_2{}^* - \mu_1{}^* = RT \ln (X_1/X_2) \qquad (1)$$

where X_1, $X_2 = $ the mole fraction of the solute in saturated solutions in solvents 1 and 2, and $\mu_1{}^*$, $\mu_2{}^* = $ the chemical potential of the solute in its standard state[6] in solvents 1 and 2. The form of eq 1 suggests the possibility of a correlation between Hammett effects and the solubility ratio in two solvents expressed as log (X_1/X_2).

Previously,[7] solubilities at 25° in heptane and in water were determined for 2-nitrophenol and four 4-substituted 2-nitrophenols. Linear regression analysis[8] of the data gave[7] eq 2 with a correlation coefficient (r) of -0.853 and a standard deviation from regression (s) of 0.44. In eq 2, X_H and X_W are the mole fractions of solute in

$$\log (X_H/X_W) = 2.40 - 0.983\sigma \qquad (2)$$

saturated solutions in hepane and in water and σ is Hammett's *para*-substituent constant[9] for the 4 substituent. The r value indicates that eq 2 is significant at the 94% confidence level. The correlation afforded by eq 2 is not very satisfactory but does show some promise. In view of the marked difference between heptane and water as solvents (dielectric constants[10] at 20°: heptane, 4.3; water, 80), it is now believed that their choice for use in the above study was unfortunate and imposed a severely extreme test of a correlation such as that of eq 2.

Results and Discussion

In the present study, benzene and cyclohexane were chosen as solvents because they are similar

(1) (a) Abstracted in part from the M.S. thesis of J. N. P., Texas A & M University, Aug 1963. (b) Presented in part before the H. L. Lochte Symposium, The University of Texas, Austin, Texas, Oct 12, 1963.

(2) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold Publishing Corp., New York, N. Y., 1948, p 263; J. H. Hildebrand, *J. Phys. Colloid Chem.*, **53**, 973 (1949).

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p 184.

(4) L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960); L. E. Scoggins and C. K. Hancock, *ibid.*, **26**, 3490 (1961); M. Rapoport, C. K. Hancock, and E. A. Meyers, *J. Am. Chem. Soc.*, **83**, 3489 (1961); C. K. Hancock and A. D. H. Clague, *ibid.*, **86**, 4942 (1964).

(5) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 619.

(6) Extrapolated from infinite dilution to unit mole fraction. See F. Daniels and R. A. Alberty, "Physical Chemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 157, Convention II.

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(8) G. W. Snedecor, "Statistical Methods," 5th ed, The Iowa State College Press, Ames, Iowa, 1956, Chapter 6.

(9) H. H. Jaffé, *Chem. Rev.*, **53**, 222 (1953).

(10) N. A. Lange, "Handbook of Chemistry," 7th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1949, p 1419.

TABLE I

SOLUBILITIES AT 30° OF 20 *meta*- AND *para*-SUBSTITUTED BENZOIC ACIDS IN BENZENE AND IN CYCLOHEXANE

Acid	Benzoic acid substituents	Mole fraction solubility in—— Benzene, X_B	Cyclohexane, X_C	Grams of acid/100 g of satd soln in Benzene	Cyclohexane	Log (X_B/X_C)	σ (ref 9)
1	None	$8.32 \times 10^{-2\,a,b}$	$1.43 \times 10^{-2\,a}$	12.42	2.06	0.7643	0.000
2	p-CH$_3$	$9.20 \times 10^{-3\,a}$	$2.49 \times 10^{-3\,c}$	1.59	4.02×10^{-1}	0.5671	−0.170
3	m-CH$_3$	$1.06 \times 10^{-1\,a}$	$1.79 \times 10^{-2\,c}$	17.11	2.86	0.7730	−0.069
4	p-CH$_3$O	$1.66 \times 10^{-3\,a}$	$6.40 \times 10^{-5\,a}$	3.24×10^{-1}	1.16×10^{-2}	1.4147	−0.268
5	m-CH$_3$O	$4.42 \times 10^{-2\,a}$	$4.93 \times 10^{-3\,c}$	8.26	8.87×10^{-1}	0.9530	0.115
6	p-Br	$2.75 \times 10^{-4\,a}$	$3.62 \times 10^{-5\,c}$	7.08×10^{-2}	8.65×10^{-3}	0.8811	0.232
7	m-Br	$1.02 \times 10^{-2\,a}$	$1.60 \times 10^{-3\,c}$	2.58	3.81×10^{-1}	0.8049	0.391
8	p-Cl	$4.89 \times 10^{-4\,a}$	$7.19 \times 10^{-5\,c}$	9.79×10^{-2}	1.34×10^{-2}	0.8325	0.227
9	m-Cl	$9.48 \times 10^{-3\,a}$	$1.45 \times 10^{-3\,c}$	1.88	2.69×10^{-1}	0.8162	0.373
10	p-OH	$5.88 \times 10^{-5\,a}$	$3.70 \times 10^{-5\,a}$	1.04×10^{-2}	6.08×10^{-3}	0.2012	−0.357
11	m-OH	$5.04 \times 10^{-5\,c}$	$9.73 \times 10^{-6\,a}$	8.99×10^{-3}	1.69×10^{-3}	0.7144	−0.002
12	p-NH$_2$	$4.27 \times 10^{-4\,a}$	$1.16 \times 10^{-5\,a}$	7.49×10^{-2}	1.88×10^{-3}	1.5676	−0.660
13	p-NO$_2$	$1.66 \times 10^{-4\,a}$	$1.18 \times 10^{-5\,a}$	3.55×10^{-2}	2.42×10^{-3}	1.1461	0.778
14	m-NO$_2$	$8.24 \times 10^{-3\,c,d}$	$3.40 \times 10^{-4\,c}$	1.76	6.76×10^{-2}	1.3843	0.710
15	3-NO$_2$-4-Cl	$6.78 \times 10^{-4\,c}$	$2.18 \times 10^{-5\,c}$	1.75×10^{-1}	5.23×10^{-3}	1.4921	0.937
16	3,4-Cl$_2$	$7.34 \times 10^{-4\,a}$	$5.78 \times 10^{-5\,c}$	1.79×10^{-1}	1.31×10^{-2}	1.1038	0.600
17	3,5-(NO$_2$)$_2$	$4.54 \times 10^{-4\,a}$	$6.98 \times 10^{-6\,c}$	1.23×10^{-1}	1.76×10^{-3}	1.8134	1.420
18	m-NH$_2$	$7.71 \times 10^{-5\,e}$	$2.75 \times 10^{-5\,e}$	1.38×10^{-2}	4.48×10^{-3}	0.4483	−0.161
19	m-N(CH$_3$)$_2$	$1.06 \times 10^{-2\,e}$	$4.06 \times 10^{-4\,e}$	2.22	7.97×10^{-2}	1.4171	−0.211
20	p-N(CH$_3$)$_2$	$6.37 \times 10^{-4\,e}$	$1.52 \times 10^{-5\,e}$	1.35×10^{-1}	2.98×10^{-3}	1.6231	−0.600

a Average of values obtained by J. N. P. and J. P. I. *b* Value for $X_B = 0.0879$ (interpolated) at 30° for benzoic acid given in J. Chipman, *J. Am. Chem. Soc.*, **46**, 2445 (1924). *c* Value obtained by J. N. P. *d* Value for $X_B = 0.0080$ (interpolated) at 30° for *m*-nitrobenzoic acid given in A. R. Collett and C. L. Lazzell, *J. Phys. Chem.*, **34**, 1838 (1930). *e* Value obtained by J. P. I.

both in chemical composition and in polarity (dielectric constants[10] at 20°: benzene, 2.28; cyclohexane, 2.05). The solubilities of benzoic acid and of 19 *meta*- or *para*-substituted benzoic acids were determined in each of these solvents at 30°. The results are shown in Table I. For each of the 20 acids, the solubility in benzene is greater than that in cyclohexane. For six of the substituents [CH$_3$, CH$_3$O, Br, Cl, N(CH$_3$)$_2$, and NO$_2$], the solubility of the *meta*-substituted benzoic acid in either solvent is considerably greater than that of the corresponding *para*-substituted benzoic acid in the same solvent. On the other hand, the solubility of *m*-hydroxybenzoic acid in either solvent is less than that of *p*-hydroxybenzoic acid in the same solvent. Of the *m*- and *p*-aminobenzoic acids, the *para* isomer is more soluble in benzene while the *meta* isomer is more soluble in cyclohexane.

For all of the data of Table I, the correlation coefficient between log (X_B/X_C) and Hammett's σ is 0.287 which is significant at only the 78% confidence level. Omitting the data for acids **4, 12, 19**, and **20**, linear regression analysis[8] of the data from Table I for the other 16 acids gives eq 3 which is significant at the 100.0% confidence level.

$$\log (X_B/X_C) = 0.666 + 0.805\sigma,\ r = 0.953,\ s = 0.126 \quad (3)$$

In Figure 1, log (X_B/X_C) is plotted *vs.* σ and the line of eq 3 is shown.

It is significant that there is no appreciable correlation between either log X_B alone or log X_C alone and σ, as shown by the data of Table II.

In view of eq 1, it is perhaps interesting that the quantitative relationship given by eq 3 is slightly better than that given by eq 4 for the same 16 acids. In eq 4,

$$\log (MR_B/MR_C) = 0.675 + 0.796\sigma,\ r = 0.947,\ s = 0.133 \quad (4)$$

MR_B and MR_C are mole ratio solubilities (moles of solute per mole of solvent) in benzene and in cyclohexane.

TABLE II

CORRELATIONS BETWEEN SOLUBILITY IN A SINGLE SOLVENT AND HAMMETT'S σ

Acid	Dependent variable	Independent variable	Correlation coeff, r	Standard dev, s
20	Log X_B	σ	−0.021	1.06
16[a]	Log X_B	σ	−0.090	1.16
20	Log X_C	σ	−0.131	1.13
16[a]	Log X_C	σ	−0.413	1.10

a Data for acids **4, 12, 19,** and **20** (see Table I) omitted.

The positive sign of ρ (+0.805) in eq 3 shows that log (X_B/X_C) increases as the variable *meta* or *para* substituent becomes more strongly electron withdrawing, that is, the acids become relatively more soluble in benzene as they become stronger. This indicates that log (X_B/X_C) is a measure of the tendency of the acid to interact with the π cloud of benzene, this tendency increasing as the strength of the acid increases. At the same time, there is little if any, such effect on the solubilities of the acids in cyclohexane. The stronger acids are better able to interact with the π cloud of benzene because they are less extensively associated.[11]

The four acids (**4, 12, 19,** and **20**) that deviate most from the line of Figure 1 are included in the five weakest acids of the 20 studied, the fifth weak acid being **10**, *p*-hydroxybenzoic acid, Of these five weakest acids, **10** is most capable of self-association through intermolecular hydrogen bonding involving the phenolic hydroxyl group. Consequently, it might be expected that *p*-hydroxybenzoic acid would be least soluble in benzene relative to cyclohexane; that is, would have the smallest log (X_B/X_C) value, and this is the case.

It is apparent from Figure 1 that there is a fairly good linear relationship between log (X_B/X_C) and σ for 16 of the acids; that is, that these acids become less soluble in benzene relative to cyclohexane as they

(11) G. Allen and E. F. Calden, *Quart. Rev.* (London), **7**, 255 (1953).

become weaker acids. It is also apparent from Figure 1 that not only the strongest of these 16 acids but also four (**4, 12, 19**, and **20**) of the five weakest acids are the most soluble in benzene relative to cyclohexane. There is some indication in Figure 1 that the points for acids **4, 12, 19**, and **20** may fall on a different line with negative slope. Thus, it appears that the solubility "mechanism" for the weakest acids with the most strongly electron-releasing substituents may be different from that for the other 16 acids which have electron-withdrawing or weakly electron-releasing substituents. There are many complicated factors involved in these solubility data and it would be difficult to isolate the exact causes for such a dual solubility "mechanism." In spite of this, it appears that log (X_B/X_C) is a fairly good measure of Hammett effects on solubilities of benzoic acids in benzene and in cyclohexane.

Experimental Section

Reagent grade benzene and cyclohexane were refluxed over P_2O_5 for 24 hr and then distilled through a 3×80 cm column filled with 0.32-cm glass helices.

The 20 benzoic acids were procured from commercial sources. After two or more recrystallizations from aqueous ethanol, the acids were dried under vacuum over P_2O_5. The melting points agreed closely with previously reported values.

Equilibrium was approached from the sides of both undersaturation and supersaturation. Solvent and excess solute were mixed at room temperature (ca. 25°) in a ground-glass stoppered, 500-ml conical flask and left in a $30.00 \pm 0.02°$ water bath, with periodic manual agitation, for several days. In a second 500-ml flask, solvent and excess solute were mixed and shaken thoroughly at 50° and then left in the 30.00° bath as above. Equilibrium at 30.00° was indicated when the resulting solubilities obtained by these two methods agreed quite closely.

A Soxhlet thimble (25×80 mm, previously washed with acetone and dried *in vacuo* over P_2O_5), equipped with a one-hole cork stopper and an inverted, U-shaped delivery tube extending nearly to the bottom of the thimble, was half immersed in the saturated solution. Gentle suction was applied to the delivery tube in order to transfer an appropriate part of the saturated solution, free of excess solute, to a second ground-glass stoppered flask (25–250-ml capacity, depending on the solubility of the acid) suspended in the 30.00° bath. This second flask plus contents were weighed. Successive portions of the contents were evaporated at room temperature in a tared (ca. 1.5 g) aluminum foil weighing dish (57-mm diameter, 18-mm depth) under a bell jar through which a slow stream of dry air was passed. The second flask plus unused saturated solution and the aluminum foil dish plus residue were weighed.

From these data, solubilities at 30.00° were calculated as: (1) mole ratio of solute; (2) mole fraction of solute; and (3) grams of solute per 100 g of saturated solution. The average values for 2 and 3 are given in Table I, while 1 can be calculated from $MR = X/(1 - X)$, where MR is 1 and X is 2.

For each of the 20 acids, two or more solubility determinations were made in each of the two solvents. Based on mole fraction solubilities, the average deviation from the mean of replicate values exceeded 3% only in the case of 5.5% for m-hydroxybenzoic acid in cyclohexane. The maximum deviation from the mean of replicate values exceeded 5% only in the following two cases: m-aminobenzoic acid in benzene, 5.2%; m-hydroxybenzoic acid in cyclohexane, 9.1%.

As indicated in footnotes to Table I (1) J. N. P. determined the solubilities of the first 17 acids in both benzene and in cyclohexane, (2) J. P. I. determined the solubilities of the last three acids in both solvents, and (3) of the first 17 acids, the solubilities in benzene of 15 and the solubilities in cyclohexane of six acids were checked by J. P. I. Of the 21 solubilities determined by both J. N. P. and J. P. I., the average deviation of the duplicate values from their mean exceeded 3% in only the cases of the following in cyclohexane: p-aminobenzoic acid, 8%; m-hydroxybenzoic acid, 33%; p-nitrobenzoic acid, 44%. The last two of these solubilities are included in the lowest three of the

40 values given in Table I and their determination involved the evaporation of about 100 g of saturated solution to yield 1–2 mg of residual acid; consequently, their determination is subject to a considerable percentage error in both precision and accuracy. In view of the fact that the points for these two acids (**11** and **13**) lie close to the regresssion line in Figure 1, the solubilities of acids **11** and **13** in cyclohexane, as reported in Table I, are probably fairly reliable.
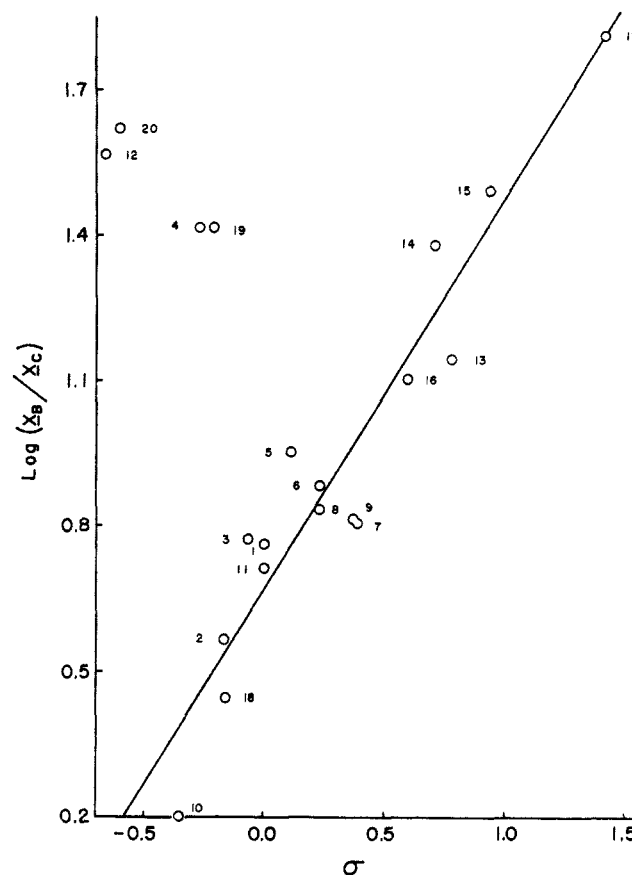

Figure 1.—Relationship between log (X_B/X_C) and σ for 20 benzoic acids.

The results of the below-described studies of potential errors show that (1) no appreciable loss of acid by sublimation occurs, (2) during evaporation of the saturated solution, no significant amount of the acid is swept out by the vaporized solvent, (3) there is no soluble, nonvolatile matter in the Soxhlet thimbles, (4) the Soxhlet thimbles do not adsorb acid from the saturated solution.

A weighed sample of each of 17 of the benzoic acids was left open at room temperature for 48 hr and then placed under a bell jar and swept with dry air for 1 hr. The losses in weight under these conditions were: benzoic acid, 0.02%; m-toluic acid, 0.01%; m-anisic acid, 0.01%. The other 14 acids showed no appreciable change in weight.

For each of the three lowest melting acids (benzoic, m-toluic, and m-methoxybenzoic acids), a weighed portion was dissolved in benzene or in cyclohexane. The solution was evaporated as in the solubility determination and the residue was weighed. None of the three acids showed a loss in weight in excess of the loss reported in the previous paragraph.

In quadruplicate, benzene alone was filtered through an unused Soxhlet thimble. The filtrate was evaporated at room temperature in a tared aluminum foil dish. This procedure was repeated, using cyclohexane alone. In no case did the gain in weight of the dish exceed 0.1 mg.

For m-CH$_3$, p-NH$_2$, m-Cl, p-Br, and m Br benzoic acids, a saturated solution at 30.00° in benzene or in cyclohexane was filtered through an unused Soxhlet thimble in two portions. Separate solubility determinations on the two portions agreed within 0.14% for p-aminobenzoic acid and within 0.04% or less for the other four acids.

Addition of Phosphorus Trihalides to Olefins[1]

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Phosphorus tribromide can be added to olefins to yield 1:1 adducts, with ultraviolet irradiation, peroxides, or heat as initiators. Asymmetrical olefins yield both isomers. Similar results are obtained with phosphorus trichloride.

The utility of free-radical addition reactions of compounds containing P–H bonds to olefins in the preparation of organophosphorus compounds is well recognized.[2] However, since the initial description of the free-radical addition of phosphorus trichloride to 1-octene,[3] little work has appeared on the potentially useful free-radical addition of P-halo compounds to olefins. A recent paper[4] describes the photochemical initiation of addition of phosphorus trichloride to olefins; 1:1 adducts were obtained with isobutylene and vinylcyclohexene.

An examination of bond energies[5] indicates that the addition of phosphorus tribromide or phosphorus trichloride to olefins should be an exothermic process. However, the lower bond strength of the

$$PX_3 + \diagdown C{=}C\diagup \longrightarrow {-}CX{-}C{-}PX_2$$

$$X = Cl, Br; \Delta H \sim -13 \text{ kcals.}$$
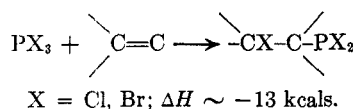
P–Br bond ($\bar{E} = 62$ kcal/mole) as compared with the P–Cl bond ($\bar{E} = 76$ kcal/mole) should make phosphorus tribromide more easily dissociated into radicals, and a better chain-transfer agent, than phosphorus trichloride. Accordingly, the free-radical initiated addition of phosphorus tribromide to olefins was examined initially.

Three types of initiation were employed: ultraviolet light, peroxide, and thermal. All were effective in producing the desired adducts (see Table I). In the reaction between ethylene and phosphorus tribromide, thermal initiation was more effective than ultraviolet light, while for the longer chain olefins, ultraviolet light gave better yields, and a cleaner product, than did peroxide or thermal initiation.

The structure of the product from phosphorus tribromide and ethylene was established as 2-bromoethylphosphonous dibromide by its conversion, on being treated with aqueous hydrogen peroxide, to the known 2-bromoethylphosphonic acid.[6] The adduct from phosphorus tribromide and cyclohexene must be 2-

bromocyclohexylphosphonous dibromide (probably a mixture of stereoisomers) but attempts to further characterize this compound by hydrolysis and oxidation to a phosphonic acid, or by reaction with amines to give a phosphonous diamide, invariably gave partially dehydrobrominated compounds, and it has not yet proved possible to obtain derivatives of the above kinds from this compound.

Similar difficulties were encountered with the phosphonous dibromides from 1-heptene and 1-octene, and again partial dehydrobromination occurred. The ¹H nuclear magnetic resonance (nmr) spectra of these compounds were extremely complex and not amenable to analysis. The compounds were, however, shown to be mixtures of both possible isomers (2-bromoalkyl-1-phosphonous dibromides and 1-bromoalkyl-2-phosphonous dibromides) by gas–liquid partition chromatographic analysis (see Experimental Section), and by ³¹P nuclear magnetic resonance spectroscopy (see Table II).

The ¹H nmr spectrum of the product from propylene and phosphorus tribromide proved amenable to analysis and confirmed the presence of both 2-bromopropylphosphonous dibromide and 1-bromopropyl-2-phosphonous dibromide. The CH₃ region of the spectrum showed a relatively intense quartet at $\delta = 2.25$ ppm with $J_{CH_3CH} = 7$ cps, and $J_{CH_3-C-P} = 17$ cps; the assignment of the CH₃CP coupling constant was confirmed by a spin-decoupling experiment. The large value of this coupling constant indicates the proximity of the methyl group and the phosphorus atom and confirms the assignment of this quartet to CH₃CH(PBr₂)CH₂Br. In addition, a weaker quartet was observed at $\delta = 2.67$ ppm with $J_{CH_3CH} = 7$ cps and $J_{CH_3CCP} = 1.5$ cps. The small value of this last coupling constant indicates the relatively remote position of the methyl group from the phosphorus atom and the formulation of the compound giving rise to it as CH₃CHBrCH₂PBr₂.

The relative intensities of the two quartets varied according to the method of initiation of the reaction, confirming the fact that a mixture of products was being produced. Ultraviolet irradiation of a mixture of refluxing propylene in phosphorus tribromide gave almost pure CH₃CH(PBr₂)CH₂Br, containing only about 5% of the isomeric product. Thermal reaction at 150° gave 70% of CH₃CH(PBr₂)CH₂Br and 30% of CH₃CHBrCH₂PBr₂.

Although the mechanism of the thermal addition reaction may be disputable, the ultraviolet light

(1) This investigation was supported by Public Health Service Research Grant CA 07182 from the National Cancer Institute. For a preliminary account of the phosphorus tribromide additions, see B. Fontal and H. Goldwhite, *Chem. Commun.*, 111 (1965).

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