[Contribution from the George Herbert Jones Laboratory, University of Chicago]

THE RAMAN SPECTRA OF SOME HYDROCARBONS CONTAINING TERTIARY C—D LINKAGES

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In the Raman spectra of compounds of the type R_3CH[1] there appears in each case one line which is to be associated with a vibration of the hydrogen atom along the line of the C—H bond at a frequency which is theoretically nearly, but not entirely, independent of the masses of the substituent groups R. Nevertheless, it is evident from an inspection of the limited available data relating to this point that the magnitude of this C—H frequency is by no means constant, that, in fact, it varies over a considerable range according to the nature of the substituent groups. It occurs in the spectrum of chloroform[2] at 3018 cm^{-1}, and in the spectrum of isobutane[3] ($R = CH_3$) at 2868 cm^{-1}. Tetrachloroethane[4] and pentachloroethane[4] each give rise to a Raman line at 2985 cm^{-1}. That the effect is not primarily a mass effect is clear, not only from the above data, but also from the fact the frequencies for chloroform and for bromoform[5] are identical within the limits of experimental errors. In view of the relatively simple nature of this vibration, the obvious conclusion is that these differences in frequency of vibration arise through variations in the binding force brought about by changing the character of the substituent groups. In this event the phenomenon becomes of interest in relation to the effect of substitution on the chemical reactivity of carbon-to-hydrogen linkages, an effect which, with properly chosen substituent groups, may be very striking indeed. In particular, it would be of interest to determine whether the effects of various organic groups on the binding force of tertiary hydrogen atoms can be differentiated in this way, and, if so, whether the variations thus produced are at all related to the chemical properties of the substances.

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[1] For a theoretical discussion, and pictorial representations, of the modes of vibration of molecules of this type, see Kohlrausch, *Z. physik. Chem.*, **B28**, 340 (1935).

[2] Kohlrausch, "Der Smekal-Raman-Effekt," Julius Springer, Berlin, **1931**, p. 304.

[3] Reitz and Sabathy, *Monatsh.*, **71**, 103 (1937).

[4] Kohlrausch, "Der Smekal-Raman-Effekt," p. 306.

[5] Kohlrausch, *ibid.*, p. 308.

One can readily envisage a number of different mechanisms whereby the binding force in a compound of the type under consideration might be subject to variation according to the nature of the substituent groups. The first would be a direct electrostatic effect producing a resultant force of attraction, or repulsion, which would be superimposed on the normal covalent binding force. In all probability this effect is largely responsible for the higher C—H binding force in chloroform, as compared with isobutane, which is revealed by the difference in Raman frequencies. A second mechanism, which might be operative even in the absence of any appreciable direct electrostatic interaction, involves an indirect or inductive effect operating through the bonds by which the substituent groups are attached. The magnitude of this effect would depend upon the electron affinity of the groups, and the resultant contribution to the C—H binding force would be in most cases, but not always, opposite in sign to that produced by direct interaction. Finally, it is conceivable that the shape of the potential energy surface for the normal state of the molecule, and hence the binding force, may be altered by an interaction of typically quantum-mechanical character between the normal electronic state and low-lying excited electronic states, the position of which, and hence the extent of interaction, would be greatly influenced by the substituent groups. This circumstance is probably common enough, and the phenomenon is of fundamental importance to chemistry, but, except in extreme cases, the effect on the binding force would be quite small. The chief result of such an effect would be a displacement of the potential energy surface in the neighborhood of the minimum without very much distortion in this region. Insofar as carbon-to-hydrogen bonds are concerned, the phenomenon will undoubtedly be of greater significance in molecules which are more definitely acidic than those dealt with at this time.

The whole question of the relationship between chemical reactivity, or what is loosely termed chemical bond strength, and physical bond strength rests in a highly unsettled state. This is largely because the magnitude of the latter, which refers to the energy required to dissociate the molecule at this bond into neutral unexcited components, is experimentally inaccessible in all but the simplest of cases. The most pessimistic view would be that even if such data were available their utility in the solution of chemical problems would be limited to the relatively few reactions in which the simple process of dissociation actually occurs. In the more general case it appears that the energy of formation of new bonds becomes available, in part at least, during the process of dissolution of the old bonds rather than after it so that the critical energy of activation is less than the bond energy and is not related to it in any simple way. The mechanism of such processes has been greatly clarified by Eyring,[6] who has given the name "activated complex" to the transition state, and it is the great virtue of the activated complex theory that it enables us for the first time to see precisely how the various physical characteristics of molecules enter into the determination of the activation energy and of the rate at which the barrier may be traversed. In this theory the bond energies appear as an important set of parameters, so also, implicitly, do the binding forces, but these alone are insufficient to determine the chemical behavior of the system.

But although a knowledge of the bond energies, or of the binding forces, must leave something to be desired in this respect, there would still seem to be a reasonable expectation of finding in the values of these constants some manifestation of the various electrical influences which organic chemists have come to speak of as decisive factors in chemical reactivity. There is, perhaps, less reason to expect significant variations to occur in the binding force for bonds of a given type than in the energy of dissociation. The former refers to the force of binding at the equilibrium positions of the atomic nuclei whereas certain factors which may affect the energy of dissociation, such as interactions with higher electronic states and also structural resonance in the products of dissociation may make their appearance only at greater distances of separation. Presumably just such a situation arises in the hexaarylethanes where, according to Pauling and Wheland,[7] the C—C bond in the unexcited molecule is a normal one and its instability arises as a consequence of resonance phenomena appearing at large distances of separation. However, such a bond could only be described as normal on the basis of binding force if the underlying assumptions are correct, or with reference to a hypothetical electronic state of the dissocation products, as the term bond strength is generally used, and as we have defined it above, the C—C bond in a compound of this type is without question a weak one. The concept of binding force may then prove useful in either event, and it has the distinct advantage of relating to a quantity which is experimentally more readily ascertainable.

In the determination of C—H binding force by the method of Raman spectra, we may anticipate the experimental difficulty of recording and identifying the particular C—H line, in which we are interested, in the spectrum of a compound which may contain several C—H bonds and which may give rise to a number of C—H lines in the same spectral region. Without some means of uniquely identifying this line we should be confined at the outset to the study of very simple molecules. The

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[6] EYRING, *J. Chem. Phys.*, **3**, 107 (1935).

[7] PAULING AND WHELAND, *ibid.*, **1**, 362 (1933).

Raman spectrum of isobutane, for example, contains six lines in the region from 2718 cm^{-1} to 2959 cm^{-1}, the identification of which in the absence of any other data presents a very difficult problem. With the aid of the hydrogen isotope, however, this difficulty can be easily overcome. Substitution of deuterium for hydrogen in a tertiary position shifts the corresponding Raman line to a much lower frequency without influencing appreciably the positions of other C—H lines which may be present. A particular C—H line may therefore be identified by its disappearance on making this substitution, or, if it happens to be obscured by adjacent or coincident lines, its position may be determined approximately, at least, with reference to the new C—D line.

Making use of this device, we have examined the Raman spectra of a number of hydrocarbons containing tertiary C—H bonds and the corresponding deutero compounds in which only the tertiary hydrogen is replaced by deuterium. Fortunately the C—D lines occur in a region which is quite free of other lines, and were observed in each case with no other difficulty than that of producing Raman spectra in small samples of material. We were not able in any instance to observe the disappearance of a C—H line on substituting deuterium due to the obscuring influence of very much more intense C—H lines of different origin, and our conclusions, therefore, are based on the variations in position of the C—D lines. For the purpose at hand, this makes little or no difference as the force constants for isotopic molecules are negligibly different.

The series of hydrocarbons selected provides a considerable range in the chemical behavior of the tertiary C—H linkages, and extends from triphenylmethane by successive substitution of methyl groups for phenyl groups to isopropylbenzene and finally, as a compound comparable in this respect with isobutane, which we could not handle in the apparatus at hand, isobutylbenzene. This series does not represent by any means the maximum possible range in behavior, as the choice was governed by the desirability of working with substances of low melting point which could be obtained in a high state of purity without undue difficulty, and also we wished to reserve for later investigations some of those cases where the enhanced reactivity of hydrogen is connected with the possibility of tautomerism. There is to be observed in the series we have selected a transition from the weakly acidic properties of the aliphatic C—H group in triphenylmethane, and the high susceptibility of the molecule to attack at this point by oxidizing agents, to the complete absence of acidic properties in isobutylbenzene and its lesser sensitivity toward oxidizing agents.

The observed C—D Raman lines (*cf.* Fig. 1) were as follows: triphenylmethane 2132 cm^{-1}, 1,1-diphenylethane 2122 cm^{-1}, isopropylbenzene 2152 cm^{-1}, and isobutylbenzene 2147 cm^{-1}, the experimental error being ±5

cm^{-1} in each instance. Thus there are small variations which are definitely beyond the limits of experimental error, and there is also perhaps a slight trend in the direction to be expected but it is by no means as clear-cut as might be desired, and the overall difference is not more than one per cent. The conclusions to be drawn are that the C—H binding force remains essentially constant within this group of compounds, that in this respect the bonds are in each case of normal strength and comparable with the corresponding bond in isobutane, and that the factors which give rise to their differences in chemical behavior exert a scarcely appreciable influence on the normal state of the molecules.

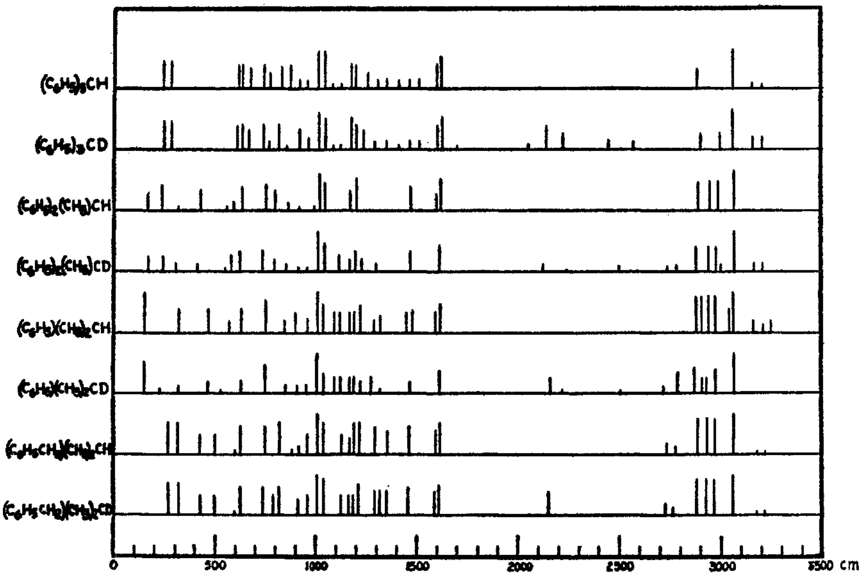

FIG.1.-THE RAMAN SPECTRA OF SOME SUBSTITUTED METHANES

FIG. 1

This result seems especially significant in the case of triphenylmethane as we could have predicted that the aliphatic carbon to hydrogen bond in this molecule is a relatively weak bond, from the standpoint of dissociation energy, for the same reason that the carbon-to-carbon bond in hexaphenylethane is weak, that is, the occurrence of resonance in the triphenylmethyl radical, although in the case of triphenylmethane the effect could only be half as large. However, it may be noted in this connection that there is no chemical evidence, of which we are aware, of any striking differences in the thermal stability of tertiary C—H groups, and that this is not necessarily in contradiction of the supposition that this bond in triphenylmethane is abnormally low in dissociation energy. A reduction in the bond energy of as much as 25 kcal. would still, in all probability, not enable the simple dissociation process to compete with the more complicated type of reaction mechanism pictured by the activated complex theory. The precise mode of thermal decomposition is not known. Jaeger[8] reports simply that it begins to decompose, with the appearance of a brown coloration, at 165°. The decomposition is evidently rather slow, even at the boiling point, 359°.

For the purposes of comparison, the frequencies of the C—D lines in some other types of compounds may be given. These lines occur in the spectra of deuterochloroform[9] and of deuterotetrachlorethane[10] at 2256 cm^{-1} and 2240 cm^{-1}, respectively. The increase in these frequencies over those from the hydrocarbons mentioned above, is to be attributed, in our opinion, largely to electrostatic effects. The C—D line in the spectrum of deuterodichlorethylene[10] occurs at 2325 cm^{-1}, and there is thus present in this molecule a still greater enhancement of the binding force which is to be associated with the presence of unsaturation. This effect is well known and appears not only in ethylenic compounds but also in the acetylenes and aromatic compounds.

EXPERIMENTAL

The experimental arrangement for the excitation of Raman spectra was essentially that described by Wood,[11] and by Wood and Rank.[9] Light from a mercury arc is focused on the tube containing the material to be examined by means of a cylindrical glass container filled with 33% sodium nitrite solution. This solution is effective in removing the Hg λ 4047 lines while allowing the Hg λ 4358 group to be transmitted.[12] In order to remove the Hg λ 4916 line and other lines in this region emitted by the source, a Wratten 34 filter was placed between the condensing lens and the Raman tube. This Wratten filter reduces the intensity of the Hg λ 4358 line appreciably, but without it the region in which the C—H Raman lines occur is badly obscured. The Raman tubes were of the conventional shape, that is, with one end horn-shaped, and blackened on the outside, the other end being closed by a plane window which was fused in. The straight part of the tube was silvered on the outside except for a broad slit through which the exciting radiation entered. For the work with triphenylmethane a jacketed tube was used, the material being maintained in a molten state by passing steam through the jacket. The Raman spectra were recorded on Eastman Type IJ plates, with iron arc spectra for comparison, using a Steinheil spectrograph in the three prism, short arm, arrangement.

We experimented briefly and unsuccessfully with the high-voltage spiral discharge

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[8] JAEGER, *Z. anorg. Chem.*, **101**, 111 (1917).

[9] WOOD AND RANK, *Phys. Rev.*, **48**, 63 (1935).

[10] TRUMPY, *Z. Physik*, **98**, 672 (1936).

[11] WOOD, *Phys. Rev.*, **45**, 392 (1934).

[12] PFUND, *ibid.*, **42**, 581 (1932).

tube recommended by Glockler and Davis[13] for the excitation of Raman spectra, the chief difficulty being the removal of traces of nitrogen, and finally adopted a simple form of low-voltage mercury arc which was very kindly suggested to us by Dr. Ralph Munch. This is a vertical arc of Pyrex glass, the cathode being a pool of mercury in the lower end, and the anode is a tungsten spiral sealed in the upper end. These arcs were found to be simple and inexpensive to construct and completely satisfactory in operation.

Of the four hydrocarbons included in this study, two have been previously investigated. The Raman spectrum of isopropylbenzene is described by Kahovec and Reitz,[14] and an attempt to obtain the Raman spectrum of triphenylmethane was made by Petrikaln and Hochberg.[15] The latter authors, using an ether solution of triphenylmethane, observed an intense continuous emission spectrum, *i.e.* a fluorescence spectrum, and were not able to record the Raman scattering. In our first attempts, using molten triphenylmethane, we also observed this intense fluorescence, but it was discovered that the impurities responsible for the fluorescence could be removed by distillations in very high vacua. Baker,[16] and also Orndorff and coworkers,[17] observed the presence of spurious bands in the ultraviolet absorption spectra of both diphenylmethane and triphenylmethane which they attributed to anthracene. However, Capper and Marsh[18] concluded that the fluorescent emission in the visible region up to λ 4750, which they observed in anthracene, was not due to anthracene but to traces of the compound chrysogen. Our experience with triphenylmethane would indicate that the fluorescent impurity is not anthracene, but a substance considerably less volatile. To guard against further difficulties of this kind, and also to preclude the possibility of photochemical oxidation, the final purification in all cases was effected by a series of high-vacuum distillations, the Raman tube being the receiver in the final distillation so that it could be filled and sealed without exposure of the material to air.

The preparation of the desired isotopic hydrocarbons presented, as might be expected, a problem in itself. A useful survey of previous work in this field has been published recently by Erlenmeyer.[19] In our work two factors were of paramount importance in the selection of methods, namely, the necessity of minimizing the consumption of heavy water, and the necessity of avoiding the introduction of deuterium in any position other than that desired. The first requirement weighed heavily because of the relatively large amounts of material needed, and the fact that the deuterium, once used, was for all practical purposes unrecoverable. The second requirement imposed certain limitations as to reagents and experimental conditions if exchange reactions, and consequently undesirable substitution of deuterium, were to be avoided. In fulfilling both of these specifications, methods involving the use of metalloörganic compounds as intermediates seemed to offer the greatest promise.

Normally, the preparation of a monodeutero hydrocarbon could be carried out by forming the Grignard reagent from the corresponding halide and treating the Grignard reagent with heavy water or with a deutero acid. This method was used for

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[13] Glockler and Davis, *J. Chem. Phys.*, **2,** 881 (1934).

[14] Kahovec and Reitz, *Monatsh.*, **69,** 363 (1936).

[15] Petrikaln and Hochberg, *Z. physik. Chem.*, **B3,** 217 (1929).

[16] Baker, *J. Chem. Soc.*, **91,** 1490 (1907).

[17] Orndorff, Gibbs, McNulty, and Shapiro, *J. Am. Chem. Soc.*, **49,**

[18] Capper and Marsh, *J. Chem. Soc.*, **129,** 724 (1926); *J. Am. Chem. Soc.*, **47,** 2847 (1925).

[19] Erlenmeyer, *Z. Elektrochem.*, **44,** 8 (1938).

the preparation of benzyldimethylmethane-*d*; the Grignard reagent was formed from benzyldimethylchloromethane and treated with deuteroacetic acid. However, the preparation of Grignard reagents from tertiary chlorides which are structurally able to form olefines by the loss of HCl, and which do so readily, is generally an unsatisfactory process, and we were unable to prepare isopropylbenzene and 1,1-diphenylethane by the Grignard method. The Raman spectrum of our sample of benzyldimethylmethane-*d* shows unmistakably the presence of a small amount of olefine, notwithstanding the fact that it had been carefully fractionated.

It is, however, in precisely such cases that Ziegler's ether cleavage method[20] for the preparation of alkali metal compounds is applicable, and although the experimental operations are somewhat more troublesome the process is free from side reactions. The preparation of phenyldimethylmethane-*d* by way of the potassium compound formed by the cleavage of the methyl ether of phenyldimethylcarbinol by sodium-potassium alloy was found to be completely satisfactory. The preparation of methyldiphenylmethane-*d* was accomplished by forming the potassium compound from the methyl ether of diphenylmethylcarbinol and subsequent treatment with deuteroacetic acid.

Samples of triphenylmethane-*d* were prepared in two different ways, one being the treatment of the sodium compound, formed from triphenylchloromethane and sodium amalgam by the method of Schlenk,[21] with deuteroacetic acid, the other being the reduction of triphenylchloromethane by zinc dust in deuteroacetic acid. The latter is an adaptation of Gomberg's method[22] for the preparation of triphenylmethane, and it is the most convenient method of preparing this hydrocarbon from the chloride. It requires an excess of acetic acid but since the excess acid can be recovered and used again this did not constitute an objection to its use. However it, was found that, while the Raman spectrum of the material prepared from triphenylmethyl sodium exhibited a single new C—D line, the material prepared by reduction of chloro compound with zinc showed this line and also a number of other new lines in the same region. These additional lines are almost certainly due to aromatic C—D linkages, for they check as well as could be expected with lines occurring in the Raman spectra of deuterated benzenes.[23] This indicated that some exchange of hydrogen had occurred during the preparation of the compound, a result which should not be surprising in view of the fact that zinc chloride is formed during the reaction and could exert a catalytic influence on the exchange reactions similar to that observed with aluminum chloride acting on other aromatic compounds.[24]

In order to determine the extent to which exchange of nuclear hydrogen had taken place samples prepared by the two methods were analyzed. The total deuterium content was first determined by measuring the density of water resulting from the combustion of the material. The combustions were carried out according to the usual macro-combustion procedure using samples of 1.5 to 2.0 grams, but the water was collected by freezing in traps, and the adsorbed water in the catalyst was brought into equilibrium with the heavier water resulting from these combustions by previous combustions of larger amounts of the same material. The water was purified first by heating in a sealed tube with a small amount of potassium permanganate and

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[20] Ziegler and Thielmann, *Ber.*, **56**, 1740 (1923).

[21] Schlenk, in Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, **1923**, Vol. 4, p. 974.

[22] Gomberg, *Ber.*, **36**, 383 (1903).

[23] Wood, *J. Chem. Phys.*, **3**, 444 (1935).

[24] Klit and Langseth, *Z. physik. Chem.*, **A176**, 65 (1936).

sodium carbonate for 12 hours, and subsequently by a series of vacuum distillations as described by Kharasch, Brown, and McNab.[25] The density determinations* were made by the temperature-float method. Two determinations on triphenylmethane prepared by the zinc reduction method gave 5.34 and 5.38 mole % deuterium, and for triphenylmethane prepared from triphenylmethyl sodium 5.20 and 5.10 mole % deuterium; theoretical for triphenylmethane-*d* 6.25 mole % deuterium. To determine the extent of substitution in positions other than the tertiary position, samples of triphenylmethane were chlorinated with phosphorus pentachloride according to the method of Auwers,[26] the chloro compound was hydrolyzed in hot alkaline solution, and the resulting carbinol was analyzed for deuterium. The deuterium content of triphenylcarbinol obtained from triphenylmethane which had been prepared by the zinc reduction method was found to be 0.48 mole %, while the triphenylmethane prepared from sodium triphenylmethyl yielded a carbinol containing 0.16 mole % deuterium. These results, therefore, confirmed the conclusion that there had occurred a greater amount of hydrogen exchange during the preparation of triphenylmethane by Gomberg's method. The extent of such substitution is, however, in both cases quite small.

The analytical results show that in our preparations the tertiary hydrogen has been replaced by deuterium to the extent of somewhat more than eighty percent. Our failure to obtain complete substitution of deuterium is probably to be attributed to insufficient drying of reagents and solvents and possibly also to some exchange of hydrogen between acetic anhydride and acetic acid (or water) during the formation of deuteroacetic acid.

The possibility of forming 1,1-diphenylethane and isopropylbenzene by reduction of the chloro derivative with zinc and acetic acid was investigated and found to be wholly unsatisfactory. 1,1-Diphenyl-1-chloroethane, on treatment with zinc dust in acetic acid, gave a practically quantitative yield of the olefine, while phenyldimethylchloromethane yielded a small amount of isopropylbenzene and a larger amount of a mixture of two solids which were not positively identified.

DATA

Triphenylmethane (*ordinary*).—Sixty grams of triphenylmethane from the Eastman Kodak Company was refluxed for two hours with zinc and glacial acetic acid, filtered hot through a 200-mesh sintered glass plate, and precipitated by the addition of cold water. The white crystalline product was recrystallized from absolute alcohol and vacuum dried. The crystals melted sharply at 92.5°. The material was then distilled four times in high vacuum and finally sealed off under vacuum in a jacketed Ramen tube.

Raman lines:† 240 (7), 280 (7), 612 (6), 627 (6), 667 (5), 736 (6), 763 (4), 824 (6), 867 (6), 911 (2)*b*, 952 (2)*c*, 1009 (10), 1037 (9), 1079 (1), 1117 (1), 1170 (8), 1192 (6), 1255 (4), 1300 (2), 1348 (2), 1407 (2), 1460 (2), 1506 (2), 1598 (6), 1613 (8), 2879 (5), 3059 (10), 3155 (1), 3201 (1).

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[25] KHARASCH, BROWN, AND MCNAB, J. ORG. CHEM., **2**, 36 (1937).

* We are indebted to Mr. W. R. Sprowls for carrying out the density measurements.

[26] AUWERS, *Ber.*, **40**, 2163 (1907).

† *Note:* All frequencies have been calculated assuming excitation by Hg λ 4358. Lines designated by the letters *b* and *c* are probably due to excitation by Hg λ 4339 and Hg λ 4347, respectively. Visual estimates of the intensities are given in parentheses following the numerical values of the frequencies in cm^{-1}.

Triphenylmethane-d—First method: Triphenylmethylsodium was prepared according to the method of Schlenk.[21] The entire reaction was carried out in a long-necked 1-l. flask with side-arm which served as an outlet for nitrogen gas and for the introduction of reagents. Commercial nitrogen was used after purification by passage over a copper spiral heated to 450°, through three gas bubblers containing Fieser's solution,[27] a bubbler containing sulfuric acid, and a series of towers containing potassium hydroxide, calcium chloride, and phosphorus pentoxide, in order. An ether solution containing 25 grams of recrystallized triphenylchloromethane was poured quickly into the reaction flask, and ether was added to make a total volume of 800 cc. To this was added 1200 grams of 1 % sodium amalgam. The flask was then closed, disconnected, and shaken for two hours. The theoretical amount of deuteroacetic acid, prepared by the addition of 99.6% D_2O to acetic anhydride, was then added, and the ether layer was decanted. After evaporation of the ether a yellow residue remained which, on recrystallization from alcohol, yielded 15 grams of triphenylmethane-*d*, m.p. 91–92°.

Second method—Fifteen grams of finely powdered triphenylchloromethane was stirred continuously in 60 g. of deuteroacetic acid with 15 g. of zinc dust for 30 minutes, the reaction being conducted in an atmosphere of nitrogen. Control experiments using ordinary acetic acid indicated that this time of reaction, rather than a period of several hours as Gomberg allowed, did not affect the yield adversely and resulted in a better quality of product. The excess deuteroacetic acid was removed by distillation, and the residue was extracted with ordinary hot glacial acetic acid from which the triphenylmethane-*d* was precipitated by the addition of cold water. After recrystallization from alcohol the product was colorless; m.p. 92°. This material, and also that prepared by the first method, was distilled three times in high vacuum, with discard, each time, of a small residue, before being collected in jacketed Raman tubes.

Raman lines: 239 (7), 278 (7), 605 (6)*i*, 628 (6), 664 (5), 736 (6), 760 (2), 811 (6)*i*, 851 (1)*i*, 912 (5)*b*, 953 (3)*c*, 1008 (9), 1038 (8), 1080 (1), 1118 (1), 1167 (8), 1191 (6), 1228 (5)*i*, 1283 (2)*i*, 1342 (2), 1401 (1), 1458 (2), 1506 (2), 1598 (6), 1616 (8), 2132 (6)*i*, 2894 (4), 3055 (10), 3153 (3), 3200 (3). There were present in the spectrum of the material prepared by the second method the following lines in addition to those listed above: 1694 (1)*i*, 2042 (1)*i*, 2214 (4)*i*, 2439 (2)*i*, 2565 (2)*i*.

1,1-Diphenylethane (ordinary).—Approximately 85 g. of diphenylmethylcarbinol, m.p. 80–81°, was converted to the olefin by refluxing for 5 hours, according to the method of Tiffeneau.[28] The heavy viscous oil was dried over potassium carbonate and then distilled under reduced pressure, the fraction boiling at 152–153° at 19 mm. being collected. Eighty-five cubic centimeters of the olefin was dissolved in 115 cc. of absolute alcohol, 3 g. of platinum oxide catalyst[29] was added, and the mixture was shaken under a pressure of two atmospheres of hydrogen for two hours at room temperature. After separation from the catalyst by filtration, the alcohol was removed by fractional distillation. The remaining colorless oil was dried over potassium carbonate, and then distilled under reduced pressure. All of the material distilled between 135 and 138°, and a 10-cc. fraction, b.p. 137–138° at 12.5 mm., was collected in a Raman tube and sealed off. The material did not give a positive test for unsaturation.

Raman lines: 162 (5), 234 (7), 313 (1), 424 (5), 551 (1), 586 (2), 628 (6), 742 (7), 789

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[27] Fieser, *J. Am. Chem. Soc.*, **46**, 2639 (1924).

[28] Tiffeneau, *Ann. chim.*, [8], **10**, 359 (1907).

[29] Adams, *Organic Syntheses* **8**, 92.

(5), 852 (2), 918 (1), 986 (1), 1011 (9), 1039 (7), 1164 (5), 1196 (8), 1461 (6), 1590 (4), 1612 (8), 2882 (7), 2940 (7), 2981 (7), 3060 (10).

Methyldiphenylmethane-d.—Unsuccessful attempts were made to develop a procedure for the preparation of this compound from 1,1-diphenyl-1-chloroethane by way of the Grignard reagent and by reduction with zinc in ordinary acetic acid. The chloro compound was prepared by passing dry hydrogen chloride into a benzene solution of diphenylmethylcarbinol at −10°, according to the method of Schoepfle and Ryan.[30] Employing a variety of forms of activated magnesium, no reaction could be obtained at temperatures below 40°. The action of zinc dust in acetic acid resulted in the formation of 1,1-diphenylethylene. To a solution of 25 g. of the chloro compound and 60 g. acetic acid, 8 g. of zinc dust was added in small portions over a period of 30 minutes, the mixing being carried out at −10°. The mixture was then allowed to warm to room temperature, and after filtration the liquid was subjected to fractional distillation at 12 mm. pressure. The acetic acid distilled at 20°, and practically all of the remaining liquid at 126°. This fraction (18 g.) was identified as 1,1-diphenylethylene by examination of the Raman spectrum. About 0.5 g. of a colorless solid, m.p. 124° was isolated from the residue. This substance, soluble in benzene, slightly soluble in ether and in alcohol, was not definitely identified, but may be 2,2,3,3-tetraphenylbutane, m.p. 126–127°.[31]

The successful preparation of methyldiphenylmethane-*d* was accomplished by treatment of 1,1-diphenylethylpotassium with deuteroacetic acid. The potassium compound was prepared by the reaction of diphenylmethylcarbinol methyl ether with sodium-potassium alloy, according to the procedure of Ziegler and Schnell,[32] the only important modification being in the method of purifying the ether. Fifty grams of diphenylmethylcarbinol was dissolved in a solution containing 12 g. of sulfuric acid in 100 g. of methanol, and after standing overnight at room temperature, the mixture was poured onto crushed ice and then extracted with ether. The ether solution was washed with dilute sodium hydroxide solution, dried over sodium sulfate, and fractionated at 12 mm. pressure. Forty-five grams of an impure product, boiling at 135° at 12 mm., was collected, the impurity being largely 1,1-diphenylethylene. This product was dissolved in 200 cc. of anhydrous diethyl ether and shaken with 2 g. of sodium-potassium alloy (1 part sodium, 5 parts potassium) in an atmosphere of nitrogen. A blue color appeared first, which on continued shaking gave way to an intense red coloration. At this point the shaking was discontinued, and dry carbon dioxide was passed into the liquid until the color was discharged. The material was then filtered, and the liquid was distilled at 12 mm. pressure. A fraction of 32 g., boiling at 140° at 12 mm., was collected; m.p. 37° (Lit.[32] m.p. 35–36°). Thirty grams of this material was placed in a nitrogen-filled flask together with 300 cc. of anhydrous diethyl ether and 10 g. of sodium-potassium alloy. The flask was then closed and placed in a shaker for 24 hours. Deuteroacetic acid (6.85 g.), dissolved in 20 cc. of diethyl ether, was then added, whereupon the red color of the mixture was immediately discharged. The material was filtered, and the liquid was distilled under reduced pressure; yield, 22 g. methyldiphenylmethane-*d*; b.p. 136–137°, at 12 mm.

Raman lines: 164 (4), 236 (4), 298 (2)*i*, 408 (2)*i*, 548 (1), 576 (4)*i*, 620 (5)*i*, 733 (6)*i*, 790 (3), 850 (2), 907 (1)*b*, 950 (1)*c*, 1008 (10), 1034 (7), 1108 (4)*i*, 1161 (3), 1194 (5), 1219

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[30] SCHOEPFLE AND RYAN, *J. Am. Chem. Soc.*, **52**, 4027 (1930).

[31] ZIEGLER AND SCHNELL, *Ann.*, **437**, 235 (1924).

[32] ZIEGLER AND SCHNELL, *ibid.*, p. 242.

(3)*i*, 1293 (2)*i*, 1461 (5), 1606 (8), 2122 (1)*i*, 2240 (0)*i*, 2494 (1)*i*, 2736 (1), 2777 (2), 2875 (6), 2935 (6), 2974 (6), 2994 (2), 3061 (10), 3162 (2), 3206 (2). Our photographs of this spectrum show a considerable number of lines not present in the spectrum of the light compound. These additional lines are not all due to isotopic effects, but in several cases to the fact that the photographs of the heavy compound were more fully exposed. There was materially less continuous background (fluorescence) from the deutero compound than from the ordinary, which indicated that the former was of higher purity.

Isopropylbenzene (*ordinary*).—Isopropylbenzene was prepared from isopropyl chloride and benzene by the Friedel-Crafts reaction according to the procedure recommended by Boedtker.[33] It was purified by fractional distillation at atmospheric pressure; b.p. 150.6–150.9°. A fraction, boiling at 150.7°, was collected for the Raman investigation.

Raman lines: 148 (10), 318 (6), 466 (6), 569 (3)*c*, 628 (6), 748 (8), 842 (3), 895 (5), 952 (3)*c*, 1007 (10), 1034 (7), 1087 (5), 1114 (5), 1161 (5), 1188 (5), 1219 (7), 1286 (3), 1313 (4), 1448 (5), 1471 (6), 1589 (5), 1610 (8), 2874 (9), 2905 (9), 2938 (9), 2968 (9), 3039 (6), 3059 (10), 3159 (3), 3208 (2), 3246 (3).

Phenyldimethylmethane-d.—As in the case of methyldiphenylmethane-*d*, unsuccessful attempts were made to utilize the Grignard procedure and the zinc–acetic acid reduction method before resorting finally to the use of the potassium compound. We were unable to form the Grignard reagent from 2-phenyl-2-chloropropane, and an attempt to prepare isopropylbenzene from the chloro compound by treatment with zinc dust and acetic acid, according to the procedure outlined above, resulted in a mixture containing small amounts of isopropylbenzene, 2-phenylpropene-1, and larger amounts of two solid substances which melted at 117° and 96°, respectively, after recrystallization from alcohol.

The methyl ether of phenyldimethylcarbinol, which was needed for the preparation[34] of the potassium compound, was prepared from 2-phenyl-2-chloropropane. One hundred forty grams of the halide was mixed with 400 g. of anhydrous methanol and 300 g. of potassium hydroxide, and the solution was allowed to stand at room temperature overnight. The solution was then poured onto a large quantity of crushed ice, extracted with ether, and the ether solution after drying over sodium sulfate was subjected to fractional distillation. Yield, 100 g., b.p. 78–82° at 17 mm. This material was further purified, as in the previous case, by treatment with a small quantity of sodium-potassium alloy. Yield of pure product, 2-phenyl-2-methoxypropane, 65 g., b.p. 82° at 20 mm. Ten grams of this material, dissolved in 500 cc. of anhydrous diethyl ether, was treated with 10 g. of sodium-potassium alloy by shaking in a closed flask, filled with nitrogen, for 24 hours. Four grams of deuteroacetic acid was then added, the mixture was filtered, and the liquid was combined with that obtained from two further batches. Fractional distillation yielded 20 g isopropylbenzene-*d*, b.p. 149–151°, of which a 10-g. fraction boiling at 151.0° was used in the Raman work.

Raman lines: 144 (8), 222 (1)*i*, 313 (2), 461 (3), 528 (1)*i*, 625 (4), 745 (7), 847 (2), 902 (2)*b*, 950 (2)*c*, 1005 (10), 1034 (5), 1089 (4), 1117 (4), 1163 (4), 1185 (3), 1218 (4), 1270 (4)*i*, 1313 (1), 1461 (3)*i*, 1610 (6), 2152 (4)*i*, 2216 (1)*i*, 2500 (1)*i*, 2717 (2), 2785 (6), 2865 (7), 2906 (4), 2928 (4), 2968 (6), 3059 (10).

Isobutylbenzene (*ordinary*).—Benzyldimethylcarbinol was prepared from benzyl

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[33] BOEDTKER, *Bull. soc. chim.*, [3], **25**, 845 (1901).

[34] ZIEGLER AND SCHNELL, *loc. cit.*, p. 255.

magnesium chloride and acetone according to the method of Tiffeneau,[35] b.p. 100–104° at 10 mm., and dehydrated[36] by heating on a steam bath with acetic anhydride and a few drops of sulfuric acid. Sixty-five cubic centimeters of the olefin, b.p. 182°, dissolved in absolute alcohol, was treated with platinum oxide catalyst and hydrogen at two atmospheres pressure for 1.5 hours. After separation of the liquid by the catalyst by filtration, and removal of the alcohol by distillation, the material was subjected to fractional distillation, yielding isobutylbenzene, b.p. 170–173°. A fraction boiling at 170–170.3° was collected for the Raman work.

Raman lines: 262 (8), 313 (8), 422 (5), 496 (5), 594 (1), 625 (7), 742 (7), 815 (8), 879 (1), 909 (2)*b*, 953 (5)*c*, 1006 (10), 1034 (8), 1122 (5), 1160 (4), 1183 (4), 1210 (8), 1286 (6), 1344 (6), 1455 (7), 1591 (6), 1609 (8), 2729 (3), 2768 (2), 2881 (9), 2925 (9), 2968 (9), 3063 (10), 3176 (1), 3212 (1).

Benzyldimethylmethane-d.—β-Chloroisobutylbenzene was prepared by saturating the carbinol at 0° with dry hydrogen chloride, and purified by distillation under reduced pressure, b.p. 86–89° at 10 mm. The Grignard reagent was formed from 7 g. of magnesium and 50 g. of the chloro compound at 50°, using a drop of methyl iodide to start the reaction. It was found desirable to begin with a relatively concentrated solution of the halide in ether, about 1:1, and to dilute the halide further during the addition so that the final volume was about 1 l.; otherwise the mixture becomes too viscous for smooth reaction. The halide was added over a period of three hours, after which stirring was continued for an additional hour. Five and nine-tenths grams of deuteroacetic acid, dissolved in 100 cc. ether, was then added slowly with stirring. The reaction mixture was filtered, and the filtrate was shaken successively with small amounts of sodium carbonate and silver nitrate. After a preliminary distillation at low pressure, and removal of the ether, the product was fractionated at atmospheric pressure, yielding benzyldimethylmethane-*d*, b.p. 170.5–171.5°. The Raman spectrum of this material exhibited a number of lines which were recognized, with reference to the work of Savard,[37] and also of Prevost, Donzelot, and Balla,[38] as lines due to dimethylstyrolene and are indicated below by the letter *o* following the numerical value of the shift. The line at 1658 cm^{-1} is especially characteristic of olefins and is generally very intense so that its presence here does not necessarily indicate a high proportion of olefine in the product.

Raman lines: 264 (8), 312 (8), 424 (5), 497 (5), 597 (1), 624 (7), 737 (7), 788 (5)*i*, 815 (7), 841 (5)*o*, 906 (4)*b*, 952 (5)*c*, 1003 (10), 1035 (9), 1122 (5), 1161 (5), 1181 (5), 1208 (8), 1287 (6), 1318 (6)*i*, 1346 (6), 1453 (7), 1586 (6), 1606 (8), 1658 (7)*o*, 2147 (6), 2720 (3), 2760 (2), 2880 (9), 2925 (9), 2925 (9), 2965 (9), 3059 (10), 3172 (1), 3212 (1).

SUMMARY

1. It is pointed out that the position of the C—H line (longitudinal or "valence" vibration) in the Raman spectra of compounds of the type R_3CH is determined largely by the C—H binding force, and that a comparison of the influences of various types of substituents (R) may be made on this basis. The available data indicate that, when R is a halogen, the C—H binding force is considerably greater than in the case where R is a

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[35] Tiffeneau, *Compt. rend.*, **137**, 575.

[36] Tiffeneau, *Bull. soc. chim.*, [4], **29**, 815 (1921).

[37] Savard, *ibid.*, [5], **2**, 633 (1935).

[38] Prevost, Donzelot, and Balla, *Compt. rend.*, **198**, 1041 (1934).

methyl group. The present work was undertaken to determine whether the influence of various organic groups could be differentiated.

2. Since it is not ordinarily possible to identify the tertiary C—H lines in the spectra of compounds which contain a large number of C—H groups of different types, use has been made of the isotope effect, and the comparisons were made on the basis of lines due to tertiary C—D linkages. The deutero compounds, in which only the tertiary hydrogen was replaced by deuterium, were prepared by treatment of sodium, potassium, or magnesium compounds with deuteroacetic acid.

3. The compounds examined were triphenylmethane-*d*, methyldiphenylmethane-*d*, phenyldimethylmethane-*d*, and benzyldimethylmethane-*d*. Variations of about 1 per cent. in the frequency of the C—D Raman shift were observed.

4. These variations are held to be of little significance, and it is concluded that the binding force is, in each case, normal. It follows that the factors which give rise to the variations in the chemical reactivity of the tertiary C—H groups in this series of compounds do not appreciably influence the character of the binding in the normal states of the molecules. It is concluded also that the enhancement of the C—H binding force in halogen-substituted methanes is due primarily to electrostatic attraction between halogen and hydrogen.

5. The Raman spectra of the analogous hydrocarbons of normal isotopic composition (triphenylmethane, 1,1-diphenylethane, isopropylbenzene, and isobutylbenzene) are also described. Of these, only the spectrum of isopropylbenzene has been previously reported. It has been shown that previous failure to obtain the Raman spectrum of triphenylmethane has been due to the presence of a fluorescent impurity which is less volatile than triphenylmethane and which may be removed by distillation in high vacuum.