

lute value of h is somewhat lower than that predicted by α -hydrogen bonding theory (0.85),¹⁶ but in view of the general crudeness of the theoretical calculations, this does not seem alarming. In particular, both h and $\Delta H\psi$ may be smaller than predicted due to an improper choice of the resonance integral for the carbon-carbon π -bond, while the ratio $h/\Delta H\psi$ was still correct. On the other hand, the agreement between calculated and observed ratios $h/H\psi$ may be fortuitous.

It is noteworthy that in this, as in previous work on aliphatic compounds,¹³ the approximation that Baker-Nathan effects are simply proportional to the number of α -hydrogen atoms seems adequate.

However, the data on non-conjugated acetylenes is insufficient to provide a very stringent test for any formulation of this effect. The question of whether alkyl groups attached to the α -carbon atom give rise to a similar, but smaller, effect also cannot be answered.

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Synthesis and Some Reactions of *cis*- and *trans*-Di-*t*-butylethylenes¹

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Improvements in the syntheses for *cis*- and *trans*-di-*t*-butylethylene, I and II, have been made. The rearrangement of I to II by acidic catalysis proved unusually difficult but was accomplished by heating over a palladium-on-alumina catalyst. The addition of chlorine to *trans*-di-*t*-butylethylene yielded a rearranged product, 2,4-dichloro-2,3,5,5-tetramethylhexane (III).

The strain in *o*-di-*t*-butylbenzene has been estimated to be at least 25 kcal. per mole.³ To date no authenticated synthesis of *o*-di-*t*-butylbenzene or a derivative thereof has been reported.⁴ Since syntheses of both *cis*-di-*t*-butylethylene⁵ (I) and *trans*-di-*t*-butylethylene⁶ (II) had been reported we thought it desirable to prepare quantities of each in order to study certain chemical and physical properties. The *cis* isomer represents an acyclic analog of *o*-di-*t*-butylbenzene and, as such, would be expected to be highly strained.

We have prepared quantities of *cis*- and *trans*-di-*t*-butylethylene by the methods described^{5,6} and were able to effect improvements in each synthesis. Samples of each isomer were supplied to Professor Rossini of Carnegie Institute of Technology for determination of the heats of combustion and to Professor Turner of The Rice Institute for determination of the heats of hydrogenation. The value for the difference in heats of combustion⁷ between the *cis* and *trans* isomer is 10.5 ± 0.5 kcal./mole, whereas the value for the difference in heats of hydrogenation⁸ is 9.3 kcal. Thus this energy difference is the largest yet

found for *cis-trans* isomer acyclic olefins, with the *cis* the higher in energy.⁸ In addition samples of I and II were sent to Dr. M. Szwarc of Syracuse University for studies of their behavior when treated with methyl radicals.⁹

We have found that the ease of acid-catalyzed and thermal isomerization of *cis*- to *trans*-di-*t*-butylethylene is not nearly as great as one might expect from the large difference in energy. For example, the *cis* isomer I was recovered unchanged after refluxing for 14 hours in acetic acid containing *p*-toluenesulfonic acid. In addition, the *cis* isomer was recovered unchanged after heating at 200° for 74 hours with 2,3-di-methyl-1,3-butadiene and hexachlorocyclopentadiene in unsuccessful attempts to effect a Diels-Alder reaction. A successful method of isomerization of *cis*- to *trans*-olefin was suggested by the fact that when di-*t*-butylacetylene was hydrogenated to prepare *cis*-di-*t*-butylethylene⁵ an appreciable amount of the *trans* isomer II also was produced. Accordingly, when the *cis* isomer was refluxed with 5% palladium-on-alumina for 2 hours, an 80% yield of *trans*-olefin was obtained.

An attempt to convert *trans*-di-*t*-butylethylene (II), to the *cis* isomer I by the method of Hoff, Greenlee and Boord¹⁰ failed when the addition of chlorine to *trans*-di-*t*-butylethylene (II) yielded a rearranged dichloride III. We assign the structure 2,4-dichloro-2,3,5,5-tetramethylhexane to III because on dehydrohalogenation with potassium amide III yielded 2,3,5,5-tetramethyl-1,3-hexadiene (IV) which afforded 2,3-butanedione (V) on ozonization. Furthermore, on removal of the two

(1) This research was supported by a grant from the National Science Foundation.

(2) Thiel College, Greenville, Pa.

(3) H. C. Brown, D. Gintis and L. Domash, *THIS JOURNAL*, **78**, 5387 (1956).

(4) The synthesis of *o*-phenylene-diisobutyric acid represents the first preparation of a highly hindered di-*o*-substituted benzene derivative; see H. A. Bruson, F. W. Grant and E. Bobko, *ibid.*, **80**, 3633 (1958).

(5) G. F. Hennion and T. F. Banigan, Jr., *ibid.*, **68**, 1202 (1946).

(6) F. L. Howard, T. W. Mears, A. Fookson and P. Pomerantz, *ibid.*, **68**, 2121 (1946).

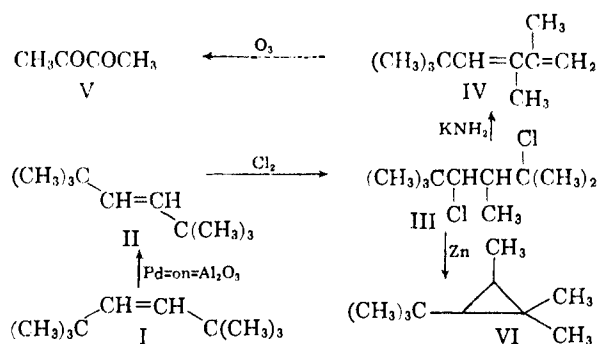
(7) Unpublished results by Rockenfeller and Rossini, Chemical and Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

(8) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *ibid.*, **80**, 1430 (1958).

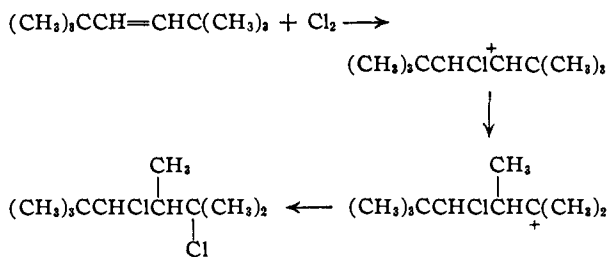
(9) A. R. Rader, R. P. Buckley, F. Leavitt and M. Szwarc, *ibid.*, **79**, 5621 (1957); the results reported therein are preliminary.

(10) M. C. Hoff, K. W. Greenlee and C. E. Boord, *ibid.*, **78**, 3829 (1951).

chlorines from III by treatment with zinc, the original olefin II was not regenerated. Instead, a new hydrocarbon, believed to be 1,1,2-trimethyl-3-*t*-butylcyclopropane (VI) was produced.



Although the formation of rearranged dihalides on the addition of halogens in the terpene series¹¹ and in bicycloheptene¹² is known, we believe that the above case is the first authenticated example in the acyclic olefin series. Interestingly, the addition of bromine to *t*-butylethylene in methanol led to unrearranged 2-bromo-1-methoxy-3,3-dimethylbutane,¹³ whereas the addition of chlorine to *trans*-di-*t*-butylethylene in the present instance led to rearrangement. In each case a carbonium ion adjacent to a *t*-butyl group is formed by nucleophilic attack of an olefin on a halogen molecule. In the previous case the reaction could be completed as shown¹³ by an attack of the solvent, but in the present case such a path is made less likely because of the increased steric hindrance. Accordingly, rearrangement of a methyl group to the electron-poor carbon occurs to yield a less sterically hindered carbonium ion which then reacts with chlorine (or chloride ion).¹⁴



Experimental¹⁵

2,2,5,5-Tetramethyl-3-hexyl Acetate.—The carbinol precursor of this acetate was prepared by the previously described¹⁶ reaction of methyl *t*-butylacetate with excess *t*-butylmagnesium chloride. The earlier workers used 6.2 moles of *t*-butylmagnesium chloride to 1 mole of ester to obtain a 79% yield of carbinol. We used 3.4 moles of Grignard reagent to one of ester and, by treating the reaction mixture with acetyl chloride, obtained the above acetate in 80% overall yield.

(11) H. Kwart, *THIS JOURNAL*, **75**, 5942 (1953).

(12) H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954); J. D. Roberts, F. O. Johnson and R. A. Carboni, *ibid.*, **76**, 5692 (1954).

(13) W. H. Puterbaugh and M. S. Newman, *ibid.*, **79**, 3469 (1957).

(14) If a three-membered chloronium ion were involved, its lack of reactivity would also be explained by steric hindrance.

(15) Analyses by Galbraith Laboratories, Knoxville, Tenn., except that marked "c" by Clark Microanalytical Laboratories, Urbana, Ill. Melting points and boiling points are uncorrected except where noted.

(16) F. L. Howard *et al.*, *J. Res. Nat. Bur. Stand.*, **38**, 365 (1947).

To the Grignard reagent,¹⁷ prepared from 172 g. (7.08 moles) of magnesium and 680 g. (7.35 moles) of *t*-butyl chloride in 1800 ml. of ether, was added 267.5 g. (2.06 moles) of methyl *t*-butylacetate in 150 ml. of ether during two hours. The mixture was stirred and refluxed 20 hours, cooled to room temperature, and 576 g. (7.35 moles) of acetyl chloride added dropwise over 3 hours. The pasty mixture was stirred without heating overnight, then decomposed with water. Rectification of the washed and dried reaction product yielded 330 g. (80%) of 2,2,5,5-tetramethyl-3-hexylacetate, b.p. 93–98° at 30 mm. The analytical sample boiled at 97° at 30 mm.

Anal. Calcd. for C₁₂H₂₄O₂: C, 72.0; H, 12.1. Found: C, 71.8; H, 12.2.

***trans*-Di-*t*-butylethylene (II).**—Previous workers¹⁶ obtained only a 25% yield of this olefin by dehydration of 2,2,5,5-tetramethyl-3-hexanol over alumina at 300°, due to the occurrence of considerable rearrangement. By pyrolysis of the acetate, we obtained this olefin in 90% yield (based on recovered acetate) with no evidence of rearrangement products.

The pyrolyses were carried out under conditions essentially as described.¹⁸ The acetate pyrolyzed at a lower temperature than ordinary acetates. Thus, at 425°, 92% of the theoretical acetic acid had been split out, whereas standardization runs on 2-ethylhexyl acetate gave only 27% cleavage at 485°. The optimum temperature for pyrolysis in terms of maximum yield was found to be 390°.

To the pyrolysis tube heated to 390 ± 10° was added dropwise at constant rate 138 g. (0.69 mole) of 2,2,5,5-tetramethyl-3-hexyl acetate during 2.5 hours. A constant flow of nitrogen through the apparatus at a rate of approximately 5 ml./minute was maintained during the addition. The product was extracted with four 75-ml. portions of water, and an aliquot of the water washings titrated to reveal 72% cleavage of acetic acid. The water washings were extracted with ether and the combined organic layers washed with saturated sodium bicarbonate solution to remove acetic acid, then with saturated sodium chloride solution and dried over Drierite. The solvent was removed and the residue distilled, first at atmospheric pressure to yield 63 g. (65.4%) of II, b.p. 124–126°, and then *in vacuo* to yield 38 g. (27.5%) of recovered 2,2,5,5-tetramethyl-3-hexyl acetate, b.p. 98–100° (30 mm.).

The combined products from nine runs were redistilled through a 2.5 × 60 cm. glass helices-packed column to give 230 g. of II, b.p. 125.0–125.7°, *n*_D²⁰ 1.4116, f.p. –4.8°. Reported values¹⁶ are b.p. 125.013°, *n*_D²⁰ 1.4115, f.p. –4.75°.

Chlorination of II.—Five chlorinations were carried out using a modification of a previously described¹⁰ procedure for chlorinating olefins. The yields of dichloride were found to be variable, ranging from 42–74%. The yield of dichloride decreased as the size of the run increased. The detailed procedure for the best run is given below.

In a 250-ml. three-necked flask equipped with Hershberg stirrer, gas inlet tube and a two-hole outlet holding a Drierite drying tube and a small addition funnel was placed 28 g. (0.2 mole) of II and 80 ml. of purified chloroform. The flask was partially immersed in a Dry Ice-acetone-bath which was adjusted so that the contents were cooled to a point just higher than that which caused a precipitate to form (presumably II). The stirrer was started and 14 g. (0.2 mole) of liquefied chlorine was allowed to evaporate into the reaction mixture over one hr. while 3 ml. (0.024 mole) of antimony pentachloride was added dropwise through the addition funnel during the same period. After completion of addition, the flask was fully immersed in the bath and stirred an additional 2 hr. The reaction mixture then was poured into a beaker containing 300 ml. of ice-water and 6.4 g. (0.06 mole) of sodium carbonate. Super-Cel filter aid was added and the mixture filtered with suction to remove precipitated antimony salts. The filtrate was taken up in 300 ml. of ether, washed with water, saturated sodium bicarbonate, sodium bisulfite and sodium chloride solutions, and dried over Drierite. The solvents were removed by distillation, first at atmospheric pressure, then under reduced pressure to a

(17) F. C. Whitmore and D. E. Badertscher, *THIS JOURNAL*, **55**, 1559 (1933).

(18) W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953); W. J. Bailey, *et al.*, *ibid.*, **76**, 2251 (1954); W. J. Bailey and C. King, *ibid.*, **77**, 75 (1955).

pot temperature of 60°. The residue was distilled *in vacuo* to yield 31 g. (74%) of dichloride, b.p. 84–87° at 3 mm.

The combined products from five runs were redistilled to give 124 g. of the decyl dichloride, b.p. 85–87° at 3 mm. The analytical sample, n_D^{20} 1.4750, boiled at 86° at 3 mm.

Anal. Calcd. for $C_{10}H_{20}Cl_2$: C, 56.9; H, 9.6; Cl, 33.6. Found: C, 57.2; H, 9.3; Cl, 33.3.

Structure of Dichloride Obtained from Chlorination of II.—The product obtained as described above was shown to be not the desired *meso*-3,4-dichloro-2,2,5,5-tetramethylhexane, but to be 2,4-dichloro-2,3,5,5-tetramethylhexane (III) by the following series of reactions.

(A) **Treatment with Zinc in Ethanol.**—A solution of 21 g. of dichloride in 60 ml. of 95% ethanol was stirred and refluxed for 1.5 hour with 19.6 g. of zinc dust. After working up in the usual manner there was obtained 7.8 g. (56%) of hydrocarbon, b.p. 66–68° at 47 mm.; 3.3 g. of chlorine-containing material, b.p. 84–86° at 24 mm.; and 2.4 g. (11%) of recovered dichloride, b.p. 86–90° at 4 mm. Redistillation of the hydrocarbon gave 7.0 g., b.p. 146–147° at 750 mm., n_D^{20} 1.4399. Thus, no *trans*-di-*t*-butylethylene was regenerated. The infrared spectrum of the product showed no olefin band in the region 6.0–6.2 μ , but instead showed a strong band at 10.05 μ , suggesting a cyclopropane ring. The material reacted extremely slowly with potassium permanganate. The product is believed to be 1,1,2-trimethyl-3-*t*-butylcyclopropane (VI), but no further structure proof was carried out.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.6; H, 14.4. Found: C, 85.5; H, 14.2.

(B) **Treatment with Potassium Amide.**—To 0.115 mole of potassium amide in liquid ammonia was added over 0.75 hour, 21 g. of dichloride in 50 ml. of ether. After stirring for 2 hours in liquid ammonia the ammonia was replaced by ether and the mixture refluxed one hour. After working up in the usual manner there was obtained 4.1 g. (30% as diene) of hydrocarbon, b.p. 50–53° at 15 mm.; 3.0 g. (17% as olefinic monochloride) of material giving a positive silver nitrate test, b.p. 69–85° at 5 mm.; and 8.4 g. (40%) of recovered dichloride, b.p. 85–88° at 3 mm. Redistillation afforded a sample of n_D^{20} 1.4480, b.p. 147° at 750 mm.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.9; H, 13.1. Found: C, 86.6; H, 13.0.

As the hydrocarbon product analyzed for either an acetylene or a diene, it was shown to be the latter by its physical constants, which do not correspond to di-*t*-butylacetylene⁸ (reported b.p. 111°, n_D^{20} 1.4055) and by its infrared spectrum, which showed typical conjugated olefin bands at 6.1 and 6.2 μ and a strong terminal double-bond band at 11.3 μ . Further, ozonolysis of 0.75 g. of the hydrocarbon and then decomposition with zinc in acetic acid and treatment with 2,4-dinitrophenylhydrazine yielded the di-2,4-dinitrophenylhydrazone of 2,3-butanedione, V, m.p. 313–315° cor. after one recrystallization from pyridine (reported¹⁹ m.p. 314–315°). Identity was further established by a mixed melting point with authentic material and by comparison of X-ray powder photographs. Derivatives of the other cleavage products were not isolated. Isolation of V, however, proves the rearrangement of a methyl group, and the diene is believed to be 2,3,5,5-tetramethyl-1,3-hexadiene (IV).

t-Butylacetylene was prepared by a modified procedure representing an improvement in both yield and ease of operation. Earlier workers²⁰ synthesized this material by treatment of pinacolone dichloride with powdered potassium hydroxide, moistened with ethanol, at 150–200°. In our hands this procedure gave a 37% yield of *t*-butylacetylene and a 42% yield of 2-chloro-3,3-dimethylbutene-1 over an 8-hour reaction period. Considerable difficulty was encountered in stirring the near-solid reaction mass. By the use of mineral oil as solvent, a fluid medium was obtained which greatly facilitated the reaction.

A 2-l. three-necked flask was equipped with Neoprene stoppers holding a thermometer, stainless steel hemispherical blade stirrer and a Liebig condenser, 40 cm. in length with an inside diameter of 1.5 cm. at its outlet into the flask. The top outlet of the condenser was connected to a distilling head permitting reflux-return control. The outlet from the distilling head led to a receiver immersed in an ice-bath, which in turn was connected *via* an outlet to a vapor trap

immersed in an ice-bath. During the reaction a slow stream of tap water was circulated through the Liebig condenser and a stream of ice-water, by means of a circulating pump, through the condenser in the distilling head. A mixture of 155 g. (1.0 mole) of pinacolone dichloride,²⁰ 300 ml. of mineral oil and 45 ml. of absolute ethanol was added to the flask and stirred into solution, followed by 450 g. (8.0 moles) of potassium hydroxide. The stirrer was started and heat applied through a Glas-Col mantle. At a pot temperature of 110° the potassium hydroxide pellets melted to give an easily stirred fluid mush. At 132° an extremely vigorous evolution of distillate began and it was necessary to lower the mantle for a short time to control the reaction. A fairly rapid take-off of distillate was permitted at first, with the stop-cock in the distilling head being adjusted to permit as much reflux return as possible and still minimize flooding of the condenser. The initial head temperature reached 75°, but then subsided and was maintained as much as possible in the range 40–60°. After about 10–15 minutes, most of the vigorous reaction had subsided, the mantle was replaced and heating and take-off of distillate continued over a one-hour period to a pot temperature of 200°. The distillate was washed with 50 ml. of water to remove ethanol, taken up in 150 ml. of xylene, washed with saturated sodium chloride solution and dried over Drierite. Distillation at atmospheric pressure yielded 60 g. (73%) of *t*-butylacetylene, b.p. 36–40°, and 24 g. (20%) of 2-chloro-3,3-dimethylbutene-1, b.p. 95–99°.

The 2-chloro-3,3-dimethylbutene-1 obtained as by-product was converted to *t*-butylacetylene by the same procedure. In this case, evolution of distillate began at 100° and was not as vigorous as with the dichloride. From 134 g. of chloride there was obtained 76 g. (82%) of *t*-butylacetylene, b.p. 35–37°, and 11 g. (8%) of recovered chloride b.p. 95–100°.

Di-*t*-butylacetylene.—*t*-Butylacetylene was converted into di-*t*-butylacetylene as described.⁴ *t*-Butylethynylmagnesium bromide was treated with acetone to give 2,5,5-trimethyl-3-hexyn-2-ol in 89% yield. This carbinol was treated with anhydrous hydrogen chloride at 0° in the presence of calcium chloride to give 2-chloro-2,5,5-trimethylhexyne-3 in 75% yield. Reaction of this chloride with methylmagnesium bromide gave di-*t*-butylacetylene in 66–76% yields. One attempt to increase the yield by adding the methylmagnesium bromide inversely to the chloride resulted in a 60% yield of acetylene.

As by-product from the latter run there was isolated a crystalline solid. Similar material was isolated in smaller amounts from the normal runs. Recrystallization from ethanol gave colorless needles, m.p. 112.5–113.0°. The compound was readily soluble in petroleum ether, benzene and chloroform, only slightly soluble in methanol and ethanol. The material is believed to be 2,2,5,5,6,6,9,9-octamethyldecadiyne-3,7 resulting from dimerization of the chloride by the Grignard reagent. The yield from the inverse addition run would correspond to 19%; from the normal runs, less than 5%.

Anal. Calcd. for $C_{18}H_{30}$: C, 87.7; H, 12.3; mol. wt., 246.4. Found: C, 87.6; H, 12.4; mol. wt., 219, 256, 229.

A 1.0-g. sample of this material was hydrogenated over 5% palladium-on-alumina to give, after consuming approximately 4 equivalents of hydrogen, a viscous liquid, b.p. 265–267.5° (cor.). This material is believed to be 2,2,5,5,6,6,9,9-octamethyldecane; analytical sample, b.p. 266° (cor.), f.p. 18°, n_D^{20} 1.4506.

Anal. Calcd. for $C_{18}H_{38}$: C, 85.0; H, 15.1. Found: C, 85.0; H, 15.2.

cis-Di-*t*-butylethylene (I) was prepared previously in 49% yield by hydrogenation of di-*t*-butylacetylene over Raney nickel.⁵ We obtained a 51% crude yield by reduction over 5% platinum-on-alumina. Attempted reduction with freshly prepared Lindlar catalyst²¹ failed to show any uptake of hydrogen.

A hydrogenation flask was charged with 41.5 g. of di-*t*-butylacetylene, 100 ml. of 95% ethanol and 2 g. of 5% platinum-on-alumina.²² After 1.75 hours the theoretical quantity of hydrogen had been consumed. The catalyst was removed by filtration and the filtrate worked up in the usual manner to give on distillation at atmospheric pres-

(19) H. H. Strain, *This Journal*, **57**, 758 (1935).

(20) M. P. Ivitsky, *Bull. soc. chim.*, [4] **35**, 357 (1924).

(21) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(22) Baker and Co., Newark, N. J.

sure 14.0 g., b.p. 115–133°, of a mixture of *trans*-olefin and acetylene, and 21.6 g. (51%) of crude I, b.p. 138–142°, n_D^{20} 1.4242.

The products from five runs were combined and redistilled through a 2.5 × 60 cm. glass helices-packed column to give 30 g., b.p. 143.0–143.6°, n_D^{20} 1.4263. To obtain samples for thermodynamic measurements, this fraction was redistilled on a spinning band column of 30-plate efficiency. This material had a practically constant boiling point at 143.0° on redistillation, and the mid-cut had n_D^{20} 1.4266. Its infrared spectrum was identical with that in the National Bureau of Standards file. Reported⁵ physical constants are b.p. 144.2–144.4°, n_D^{20} 1.4271.

Gas chromatographic analysis of the sample of I sent to Dr. Rossini showed it to be essentially homogeneous. However, the sample of I sent to Dr. Turner had about 5% of impurity judged to be 2,2,5,5-tetramethylhexane. For

the heat of hydrogenation experiments, Dr. Turner used I which had been purified by gas chromatography by Dr. W. Doering, Yale University.

Attempted isomerization by refluxing 1.5 g. of I with 0.075 g. of *p*-toluenesulfonic acid in 17 ml. of glacial acetic acid for 14 hours gave recovered material which was identical in refractive index and infrared spectrum. However, refluxing 1.5 g. of I with 0.8 g. of 5% palladium-on-alumina resulted in 80% isomerization to II after 2 hours, as estimated by refractive index and infrared spectra.

Various attempts to cause I, II and di-*t*-butylacetylene to undergo Diels-Alder reactions with 2,3-dimethylbutadiene and hexachlorocyclopentadiene²³ were unsuccessful.

(23) We are indebted to Hooker Electrochemical Corp., Niagara Falls, N. Y., for a generous sample of this material.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Hydrogen Bonding of Phenols to Olefins¹

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Evidence for the formation of weak intermolecular hydrogen bonds between phenols and olefins in solution has been obtained by infrared spectral studies in the 3400–3800 cm^{-1} region. A new O–H absorption band characteristic of the hydrogen bonded complex appears at 60–130 cm^{-1} lower frequency than the absorption due to unassociated phenol hydroxyl groups. The relative basicities of some olefins have been measured by determining the frequency shift on hydrogen bonding. The basicities of olefins are increased by increasing alkyl substitution at the double bond, and decreased by conjugation. Olefins are stronger hydrogen bonding bases than simple aromatic hydrocarbons. Intramolecular hydrogen bonding to ethylenic π -electrons has also been observed in the compound *o*-allylphenol.

Both olefins and aromatic hydrocarbons behave as bases toward electrophilic reagents such as certain transition metal ions.^{1a–4} The work of Jones and Badger⁵ and of Tamres⁶ on mixtures of aromatic hydrocarbons with alcohols and chloroform, and that of Brown⁷ on hydrogen chloride-arene systems, has established that the π -electron systems of aromatic rings can serve as hydrogen-bonding bases, toward both strong and weak acids. However, little evidence has been presented for hydrogen bond formation involving olefinic π -electrons as bases. Olefins are known to form complexes with hydrogen chloride at low temperatures,^{7,8} but no other examples of hydrogen bonding to olefins seem to have been reported.

This paper reports infrared studies of hydrogen bonding between hydroxyl compounds and olefins in carbon tetrachloride solution. The infrared absorption was observed in the 3000–3800 cm^{-1} region, near the fundamental O–H stretching frequency for the alcohols. In the presence of olefins the sharp absorption band due to non-bonded hy-

droxyl groups is diminished in intensity, and a broad new band at lower frequency appears, indicating that a hydrogen-bonded complex is formed. The hydroxyl association bands observed with olefins are generally of low intensity, which may account for the fact that this type of hydrogen bonding has not been reported previously.

In this work phenol, as suggested by Kuhn,⁹ was used as the principal hydroxyl compound, along with the slightly more acidic compound *p*-fluorophenol. Phenols have many advantages as reference acids in hydrogen bonding studies. In particular they are superior to methanol-*d* used by earlier workers^{1,2} for the following reasons: 1, the greater acidity of phenols leads to larger shifts of absorption position on hydrogen bonding; 2, phenols have a higher absorbency for the O–H vibration, so that the bands in question can be observed conveniently; and 3, phenols have less tendency to self-association than do aliphatic alcohols, and hence complications resulting from intermolecular association of hydroxyl groups with one another are minimized. At 0.020 *M* or less in carbon tetrachloride the self-association of the phenols which we used was negligible.

Experimental

Materials.—The phenol was Merck reagent grade material, fractionally crystallized and distilled in vacuum. *p*-Fluorophenol was used as obtained from the Pierce Chemical Co. The Pennsalt Chemicals Co. kindly donated a sample of 2,2,2-trifluoroethanol which was redistilled before use. 1-Methylcyclohexene and *o*-allylphenol were obtained from the Aldrich Chemical Co. Cyclohexene, isoprene and the aromatic hydrocarbons were from the Eastman Kodak Co., and all other olefins were from Matheson, Coleman and Bell Co. All of the olefin materials were dried and fractionally distilled through a short helix-packed column

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

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(2) H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **66**, 227 (1943).

(3) L. J. Andrews and R. M. Keefer, *ibid.*, **71**, 3644 (1949); **72**, 3113, 5034 (1950); and **74**, 640 (1952).

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(6) (a) S. Searles and M. Tamres, *ibid.*, **73**, 3704 (1951); (b) M. Tamres, *ibid.*, **74**, 3375 (1952).

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(9) L. P. Kuhn, *THIS JOURNAL*, **74**, 2492 (1952).