Westheimer method would, however, be difficult to carry out for substituted naphthalenes and the method is in any case subject to uncertain errors through its treatment of the solvent as a uniform dielectric.

(b) The calculation of the π-inductive and mesomeric effects could be carried out by more refined procedures such as the SCF MO method. Calculation of this kind are in progress here though we doubt if the results will differ much from those given by the simple perturbation treatment.

(c) The charges set up in an adjacent conjugated system through polarization of the π-electrons by a substituent (π-inductive and mesomeric effects) should influence a reaction center directly by the field effect. Thus the charge set up in the positions *o:p* to a +E or −E substituent in benzene should in this way affect a reaction center at the *meta* position. This relayed mesomeric–field effect would simulate a resonance interaction directed to the positions *meta* to the substituent. Taft[20] has claimed that such interactions are important in benzene.

However, the main need at present is for more data on the effects of substituents in rigid molecules of known geometry, other than benzene. Any attempt to build up a more elaborate theory until such data are forthcoming seems to us a useless exercise.

Acknowledgment.—We are very grateful to Dr. L. C. Snyder for the calculated charge densities in substituted naphthalenes.

[20] See R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959); R. W. Taft, S. Ehrenson, I. C. Lewis and R. E. Glick, *ibid.*, **81**, 5352 (1959).

[CONTRIBUTION FROM THE CALIFORNIA RESEARCH CORPORATION, RICHMOND, CALIF.]

Carbon as a Hydrogen Bonding Base and Carbon–Hydrogen–Carbon Bonding

BY LOUIS L. FERSTANDIG

RECEIVED APRIL 27, 1962

One-to-one hydrogen bonding between hydrogen donors and the isocyanide group is demonstrated by infrared and nuclear magnetic resonance spectra and concentration dependencies of the bonded species. Electronic and steric arguments as well as experimental evidence are presented to prove that the hydrogen bond is at carbon. Proof is given for a carbon–hydrogen–carbon bond between an isocyanide and the C–H in an acetylene. Frequency shift and equilibrium data indicate that isocyanides (carbon sp-bonding) form hydrogen bonds of comparable strength to cyanides (nitrogen sp-bonding).

In an earlier communication a hydrogen bond to an isocyanide[1a,b] and a carbon–hydrogen–carbon[1a] bond were announced. Detailed evidence of the points made in the communication and new evidence are given in this paper to show that isocyanides form hydrogen bonds and that these bonds are at the carbon atom. In a similar manner carbon–hydrogen–carbon bonding is demonstrated. For both types of bonding data are presented to show first that bonding occurs; second that it is at carbon; and third that bonding at sp-carbon is comparable to bonding at sp-nitrogen.

Proof of Hydrogen Bond Formation.—The presence of equilibrium 1 is demonstrated by infrared spectral evidence. An intense, characteristic ν_s for bonded OH appears at 3483 cm.$^{-1}$

$$n\text{-}C_5H_{11}OH + C_6H_5CH_2NC = (n\text{-}C_5H_{11}OH)(C_6H_5CH_2NC) \quad (1)$$

when *n*-amyl alcohol is added to benzyl isocyanide although this band is absent in both reactants (Fig. 1). Furthermore, the intensity of the new band is directly proportional to the concentration of each of the reactants, indicating that one molecule of each participates in the bonded complex. With appropriate concentration changes the new band grows at the expense of free OH and alcohol–alcohol bonded OH bands.

Nuclear magnetic resonance (n.m.r.) spectra also demonstrate the existence of a hydrogen bond between alcohols and benzyl isocyanide. With methanol, at concentrations favoring bonding, the hydroxyl proton moves to lower field. But even more striking is the occurrence of splitting of the hydroxyl proton (quartet) and of the methyl protons (doublet) at about 1:1 methanol to benzyl isocyanide. This is good evidence for a long-lived bond between the two.

Bonding to isocyanides by a hydrocarbon is shown by similar evidence. Figure 2 shows the infrared data. Phenylacetylene dissolved in benzyl isocyanide shows an acetylenic C–H ν_s at 3284 cm.$^{-1}$. This band is 26 cm.$^{-1}$ lower than the normal acetylenic C–H ν_s at 3310 cm.$^{-1}$. This is a small shift[2] but it is similar to the shift in benzonitrile (32 cm.$^{-1}$). When a solution of phenylacetylene in benzyl isocyanide is diluted with carbon tetrachloride the normal band at 3310 cm.$^{-1}$ returns but a slight shoulder remains about 26 cm.$^{-1}$ lower than the major peak, characteristic of a mixture of free and bonded C–H.

In n.m.r. a hydrogen bond between phenylacetylene and benzyl isocyanide is shown by a shift of the acetylenic proton to lower field. In pure phenylacetylene this proton precesses at 153 cycles per second (2.53 δ) relative to tetramethylsilane. At a benzyl isocyanide concentration of 0.475 mole fraction this peak is at 163 cycles per second while the aromatic proton major peak moves only from 402 to 406 cycles per second. The acetylenic proton peak of phenylacetylene at infinite dilution in benzyl isocyanide occurs at 169 cycles per second. A plot of this shift *versus* mole fraction of the two

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[1] (a) L. L. Ferstandig, *J. Am. Chem. Soc.*, **84**, 1323 (1962). (b) Isocyanide hydrogen bonding was also discovered independently by P. v. R. Schleyer and A. Allerhand, *ibid.*, **84**, 1322 (1962).

[2] R. West and C. S. Kraihanzel, *ibid.*, **83**, 765 (1961).

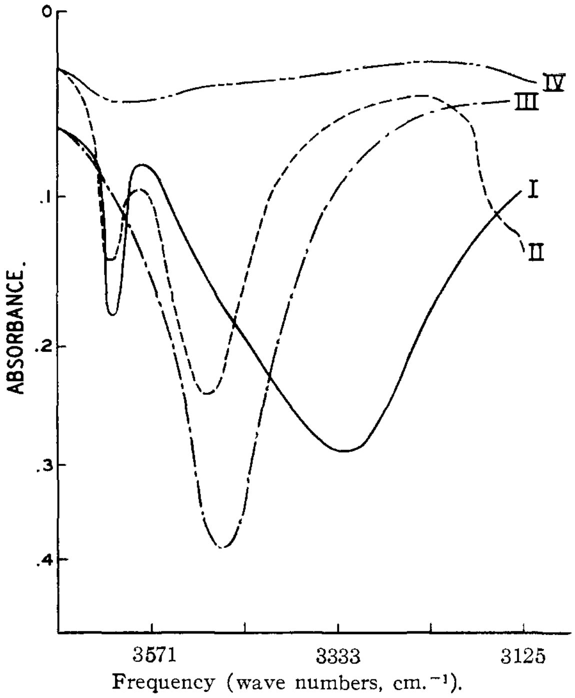

Fig. 1.—*n*-Amyl alcohol bonding to benzyl isocyanide (reference sample similar to mixture less alcohol): I, 5% *n*-amyl alcohol in CCl_4 (0.1 mm.); II, 0.5% *n*-amyl alcohol in 20/80 $C_6H_5CH_2NC/CCl_4$ (1.0 mm.); III, 5% *n*-amyl alcohol in $C_6H_5CH_2NC$ (0.1 mm.); IV, benzyl isocyanide *vs.* air (0.025 mm.).

components gives a curve with greater slope at high phenylacetylene concentrations. This is consistent with a rapidly changing percentage of bonded acetylenic proton at low benzyl isocyanide concentrations and a more static bonded percentage at high benzyl isocyanide concentrations.

There is also a shift for the acetylenic proton to lower fields in carbon tetrachloride solutions: from 153 to 178 cycles per second over the entire range for the two-component system. Unlike the benzyl isocyanide shift this one is a linear function of mole fraction which suggests only a simple solvent effect.[3]

The fact that only a small shift occurs for the acetylenic proton in benzyl isocyanide is not too surprising. The normal shift to lower field for hydrogen bonding is occurring in the face of the aromatic solvent effect toward high field.[3] With an aliphatic isocyanide a large shift should be observed.

Added evidence of bonding is seen in the temperature dependence of the acetylenic n.m.r. peak. In a dilute solution of the acetylene in benzyl isocyanide the peak occurs at 172 at 0° and at 167 at 55°. Under these same conditions the benzyl protons shift from 236 to 235. For a similar dilute solution of the acetylene in carbon tetrachloride the shifts caused by temperature changes are small and the same for all the protons: aromatic, benzylic and acetylenic.

Location of Hydrogen Bond.—The point of attachment of OH hydrogen bond to benzyl isocyanide

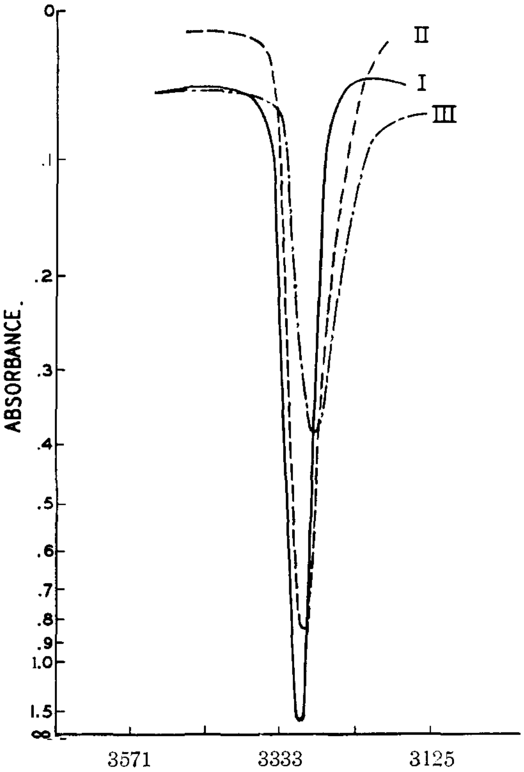

Fig. 2.—Phenylacetylene bonding to benzyl isocyanide (0.1-mm. NaCl cells; reference sample similar to mixture less phenylacetylene): I, 10% $C_6H_5C{\equiv}CH$ in CCl_4; II, 10% $C_6H_5C{\equiv}CH$ in 20:80 $C_6H_5CH_2NC$–CCl_4; III, 5% $C_6H_5C{\equiv}CH$ in $C_6H_5CH_2NC$.

can be deduced from general electronic and steric information with supporting spectral evidence. First the π electrons in the aromatic ring[4] and in the $N{\equiv}C$ bond can be ruled out as points of attachment on the basis of the magnitude of the $\Delta\nu_s$ from free to bonded OH and on the direction of n.m.r. shifts. For aromatic π-systems $\Delta\nu_s$ rarely exceeds 50–70[5,6] cm.$^{-1}$. The $N{\equiv}C$ bond can be compared to $C{\equiv}C$ where shifts of 30 to 40 cm.$^{-1}$ are to be expected.[5] The observed $\Delta\nu_s$ of 151 cm.$^{-1}$ (138 cm.$^{-1}$ in 20:80 isocyanide–carbon tetrachloride) argues against both π-systems. The shift in n.m.r. to lower field is opposed to that found for hydrogen bonding for aromatic π-electrons.[7] These data suggest either nitrogen or carbon bonding.

Electron distributions in the free isocyanide and of postulated structures for hydrogen bonded isocyanide are instructive in the question of acceptor site of nitrogen *versus* carbon. While the electron distribution of the free isocyanide does not dictate the location of the hydrogen bond, it certainly may indicate a probable site for bond formation. In the resonance view the ground state of the isocyanide is a hybrid with only two important contributing

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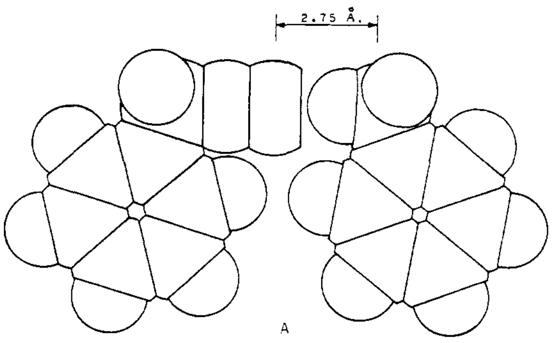
[3] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, 1959, p. 422.

[4] The work described in Ref. 1b includes isocyanide hydrogen bond formation with aliphatic isocyanides: no aromatic π electrons present.

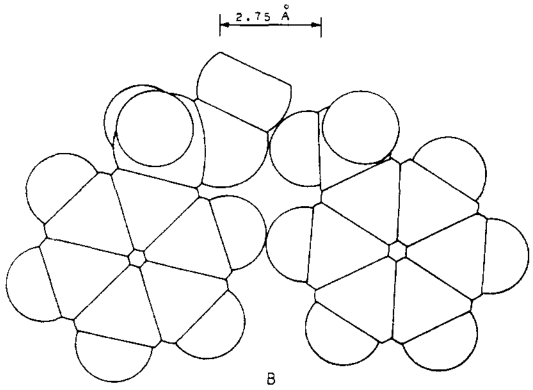
[5] P. v. R. Schleyer, D. S. Trifan and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

[6] M. Ōki and H. Iwamura, *Bull. Chem. Soc. Japan*, **34**, 1395 (1961), and references therein.

[7] Reference 2, pp. 412, 428.



CARBON BONDING OF BENZYL ISOCYANIDE TO ANILINE



NITROGEN BONDING OF BENZYL ISOCYANIDE TO ANILINE

Fig. 3.

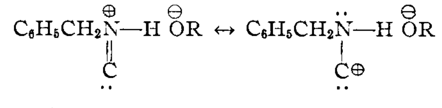
structures (2). For methyl isocyanide bond length data suggest that the dipolar or separated-charge form contributes 74% to the hybrid.[8] If the separated-charge form were, in fact, the isocy-

$$RCH_2\overset{\oplus}{N}\equiv\overset{\ominus}{C}: \leftrightarrow RCH_2N=\overset{..}{C}: \qquad (2)$$

anide structure the choice of site for hydrogen bonding would be clear: negative carbon, not positive nitrogen. If the other canonical form represented the actual molecule, then carbon again would be a possible site for bonding and only in this form would nitrogen be a possible site. Weighting the relative contributions of the two forms and the possibility of carbon bonding in both forms, carbon is the favored site.

For possible carbon and nitrogen bonded molecules, 3 and 4 show some of the important contributing structures.[9]

$$C_6H_5CH_2\overset{\oplus}{N}\equiv C—H\ \overset{\ominus}{O}R \leftrightarrow C_6H_5CH_2\overset{..}{N}=\overset{\oplus}{C}—H\ \overset{\ominus}{O}R \qquad (3)$$



$$C_6H_5CH_2\underset{\underset{\underset{..}{C}}{\|}}{\overset{\oplus}{N}}—H\ \overset{\ominus}{O}R \leftrightarrow C_6H_5CH_2\underset{\underset{\underset{..}{C^{\oplus}}}{|}}{\overset{..}{N}}—H\ \overset{\ominus}{O}R \qquad (4)$$

Nitrogen bonding requires resonance stabilization from structures which are themselves very low in stability. The carbon bonding structures resemble the stabilizing structures for isocyanides. It should also be noted that more energy would be required to change the isocyanide structure from the unperturbed isocyanide resonance hybrid to the nitrogen-bonded complex than from the unperturbed resonance hybrid to the carbon-bonded complex; that is, the carbon-bonded complex resembles the unbonded resonance hybrid more closely. In fact, the energy provided by the reaction to form the hydrogen bond may be insufficient to cause the necessary rearrangement of atoms in the isocyanide to an imine type structure for nitrogen bonding. Thus the over-all electronic argument, based on the more attractive site for bonding in the reactant and the more stable bond in the product, predicts carbon is much favored over nitrogen.

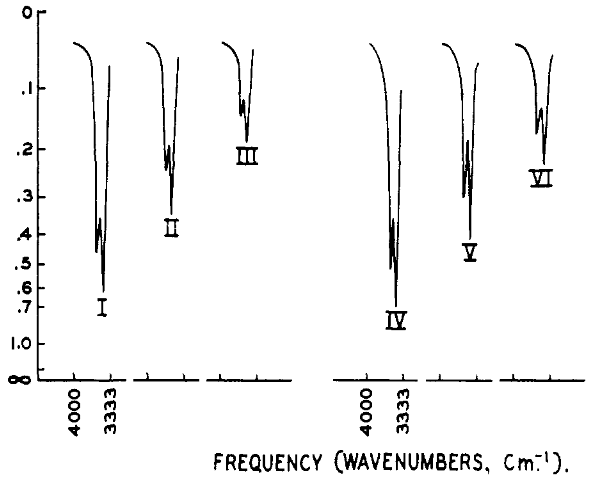


Fig. 4.—Aniline bonding to isocyanide and cyanide (0.1-mm. NaCl cells; reference sample similar to mixture less aniline): I, II and III, 10%, 5%, and 2.5% $C_6H_5NH_2$ in $C_6H_5CH_2NC$, respectively; IV, V and VI, 10%, 5% and 2.5% $C_6H_5NH_2$ in C_6H_5CN, respectively.

The steric factors are quite different for carbon and nitrogen bonding. For carbon bonding a straight line can be drawn through CH_2, N, C, H and O (see formula 3). With this linear structure the R group even if large is sterically free of the isocyanide substituent. For nitrogen bonding (imine form) both O and R may interfere with the isocyanide substituent and with the isocyanide carbon. In order to test this steric factor aniline was used as a hydrogen-bonding acid. Aniline not only has a large R (phenyl) but also can bond with two molecules of base. Thus, in addition to the steric factors already described there is the problem of bringing two isocyanide molecules and one aniline in close proximity.

Figure 3 shows drawings of two sets of models for hydrogen bonding of aniline at carbon and at nitrogen. For clarity only one isocyanide is shown. Another can be imagined attached to the remaining N–H in a plane with an angle of about 109° to the plane of the paper. Both models are constructed with acetylenic type carbon in the isocyanide group. Azide type nitrogen was used for the dipolar model with carbon bonding and imine type nitrogen was used for the nitrogen bonding model. The figure shows the model, 3A, at a typical hydrogen bonding distance[9] of 2.75 Å. between centers of isocyanide–carbon and aniline–nitrogen for carbon bonded isocyanide. The adjacent

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[8] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Third Edition, 1960, p. 270.

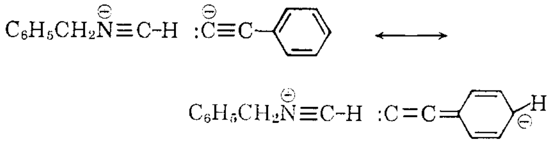
[9] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960.

groups do not touch. With the nitrogen bonded model, 3B, the centers of isocyanide–nitrogen and aniline–nitrogen cannot be brought within 2.75 Å. of each other without overlap of some atomic van der Waals radii.

Adding a second isocyanide to aniline brings the above factors to bear again; but even more important are the interactions between the two adjacent isocyanide substituents. With free rotation around the benzyl to isocyanide bond the two benzyl groups could interfere with each other seriously. The repulsive forces due to overlapping need be only 4 or 5 kcal./mole to exceed the hydrogen bond strength and preclude the formation of a second isocyanide–aniline bond. Keeping in mind that the methyl–methyl interaction in butane is 4–6 kcal./mole[10] any substantial overlap of benzyl groups should suffice. In the nitrogen-bonded model the volumes circumscribed by the two rotating benzyl groups overlap to a large extent. However, in the carbon bonded model the two volumes intersect little if at all. Therefore, only carbon bonding should permit two isocyanides per aniline. (This steric argument can also be extended to alcohol–isocyanide bonding with appropriate bonding examples.[1b])

The spectral evidence (Fig. 4) for aniline–isocyanide bonding shows two isocyanides for each aniline,[11] *e.g.*, carbon bonding. Both bands are proportional to aniline concentration and they are spectrally equivalent to the benzonitrile–aniline bands shown.

Electronic and steric considerations and spectral data all conspire to prove carbon bonding. Bonding of phenylacetylene to benzyl isocyanide is also undoubtedly to carbon. In this particular combination the negative charge on the acetylene can be delocalized (5) in the phenyl ring contributing to the strength of the bond.



(5)

Strength of the Hydrogen Bond to Carbon.—Qualitative inferences about the strength of hydrogen bonds are often made from the size of $\Delta\nu_s$.[12] This has its perils because $\Delta\nu_s$ is temperature[13] and solvent dependent.[14] The comparison is especially perilous when made among different types of base.[9] Nonetheless by this criterion isocyanides form stronger hydrogen bonds than cyanides. The $\Delta\nu_s$ for bonded *n*-amyl alcohol in benzyl isocyanide in carbon tetrachloride compared to the free OH in carbon tetrachloride is 138 cm.$^{-1}$, whereas for the same alcohol with benzyl cyanide $\Delta\nu_s$ is 95 cm.$^{-1}$.

A more exact comparison was made by determining the equilibrium for reaction 1 and its counterpart with benzyl cyanide. The intensity of ν_s for bonded OH was used as a measure of bonded material for a number of initial concentrations of reactants (Table I). Using a combination of the equilibrium expression and Beer's law, both the equilibrium constant and the apparent extinction coefficient can be determined. The validity of this approach has been demonstrated for ultraviolet spectra[15,16] and it should be applicable to infrared spectra. As shown in Table I at 26°, benzyl isocyanide and cyanide are quite similar in hydrogen bonding ability. However both are stronger bonding materials than benzonitrile: $K = 5.0$ at 26°.

TABLE I

EQUILIBRIUM CALCULATION AT 26°

Quantities, ml.[a]			Absorbance[b]	Base^{-1}, mole fraction^{-1}	K[c]	ϵ, l. m.$^{-1}$ cm.$^{-1}$
n-$C_5H_{11}OH$	C_6H_5-CH_2NC	CCl_4			5.8	87.3
0.0247	0.994	3.956	0.194	5.65		
.0247	1.992	2.959	.262	2.74		
.0247	2.986	1.965	.290	1.77		
.0118	0.994	0.982	.336	2.16		
n-$C_5H_{11}OH$	C_6H_5-CH_2CN	CCl_4			6.0	116
0.0247	0.994	3.956	0.252	5.78		
.0247	1.992	2.959	.319	2.79		
.0247	2.986	1.965	.379	1.80		
.0118	0.994	0.982	.428	2.19		

[a] Densities used to calculate mole fractions: *n*-$C_5H_{11}OH$, 0.8144 g./ml.; CCl_4, 1.595 g./ml.; $C_6H_5CH_2NC$, 1.047 g./ml.; $C_6H_5CH_2CN$, 1.015 g./ml. [b] Absorbance at peak maxima: benzyl isocyanide, 3490 to 3496 cm.$^{-1}$; benzyl cyanide, 3539–3542 cm.$^{-1}$; cell thicknesses: isocyanide, 0.0964 cm.; cyanide, 0.0929 cm. [c] K in units of mole fraction^{-1}.

Conclusions.—Carbon is capable of behaving as a hydrogen bonding base and a rather good one. Only a modest extension of the information presented is necessary to predict that carbanions should be excellent hydrogen bonding bases. Carbon–hydrogen–carbon bonding may well be an intermediate in hydrogen exchange *via* carbanions. This intermediate may even be long-lived where the exchange is slow. Also it is conceivable that hydrogen bonding plays a role in carbene reactions. Insertion by carbenes could be preceded by carbon–hydrogen–carbon bonding.

Carbons other than acetylenic ones may donate hydrogen to bonds. There is some evidence that vinyl hydrogens participate in hydrogen bonds.[17] It may be that hydrogen on carbon is not a shield for carbon but rather is a stepping stone *via* hydrogen bond formation to reactions at carbon.

Acknowledgment.—The author is indebted to Dr. J. R. Thomas and Mr. R. Bacskai for valuable discussions and to Dr. S. W. Nicksic for assistance in the n.m.r. determinations.

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[10] K. S. Pitzer, *Chem. Revs.*, **27**, 39 (1940).

[11] L. J. Bellamy and R. L. Williams, *Spectrochim. Acta*, **9**, 341 (1957). The criterion described in this reference for the relationship between the asymmetric and symmetric stretching frequencies for amines with two hydrogen bonds is met exactly by the observed frequencies: 3460 and 3373 cm.$^{-1}$.

[12] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

[13] E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961).

[14] Note $\Delta\nu_s$ in this work for *n*-amyl alcohol in benzyl isocyanide is 151 cm.$^{-1}$, but this value shifts to 138 cm.$^{-1}$ in a 20:80 benzyl isocyanide–carbon tetrachloride mixture.

[15] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

[16] L. L. Ferstandig, W. G. Toland and C. D. Heaton, *ibid.*, **83**, 1151 (1961).

[17] W. G. Schneider, H. J. Bernstein and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).

Experimental

Materials.—All the materials were reagent grade, freshly distilled with care taken to separate water in the forerun as an azeotrope. Benzyl isocyanide was prepared by the method of Corey[18] from benzylformamide; b.p. 92° (10 mm.),[19] strong infrared band at 2140 cm.$^{-1}$ characteristics of isocyanides.

Infrared Spectra.—Most of the spectra were measured on a Perkin–Elmer model 21 using a lithium fluoride prism under high resolution conditions with a chart speed of 10 inches/micron. Either 0.1-mm. or 1-mm. NaCl cells were used to maintain absorbances of about 0.2 to 0.7. Intensities were reproducible to about $\pm 2\%$; wave numbers were reproducible to about ± 3 cm.$^{-1}$, recording the water vapor band at 3566 cm.$^{-1}$ as an internal reference[20] for each critical spectrum. All measurements were made at $26 \pm 1.0°$.

The solutions were prepared using calibrated pipets and volumetric flasks. The *n*-amyl alcohol concentration was either 0.25 or 0.50 volume % introduced, for accuracy, as a more concentrated solution in carbon tetrachloride. The base concentrations varied from 20 to 60 volume %, the remainder being carbon tetrachloride. The solutions used in the reference beam were identical with the sample except that alcohol was omitted.

N.m.r. Spectra.—The n.m.r. spectra were measured using a Varian A-60. All n.m.r. values quoted are relative to tetramethylsilane at 60 mc./sec. Most runs were at room temperatures. The runs quoted at 0 and 55° were made with the samples initially at these temperatures but reverting slowly to room temperature while spectra were hastily determined.

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[18] W. R. Hertler and E. J. Corey, *J. Org. Chem.*, **23**, 1221 (1958).

[19] I. Ugi and R. Meyr, *Ber.*, **93**, 239 (1960).

[20] A. R. Downie, M. C. Magoon, T. Purcell and B. Crawford, Jr. *J. Opt. Soc. Am.*, **43**, 941 (1953).

[Contribution from the Department of Chemistry, Purdue University, Lafayette, Ind.]

Nucleophilic Displacement Reactions of Polyhalogenated Cyclopentadienes and Cyclopentenes. I[1,2]

By E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav and H. P. Braendlin

Received August 18, 1961

The reaction of hexachlorocyclopentadiene with methanolic base has been studied. The bimolecular reaction, first order both in halide and in base, led to the formation of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene exclusively. No monomethoxy derivative was obtained. Further reaction with base yielded 1,2,3-trichloro-4,5,5-trimethoxycyclopentadiene which, upon isolation and continued exposure to base, underwent two simultaneous reactions to give 1,2,5-trichloro-3,3,4,4-tetramethoxycyclopentene and a compound believed to be 1,4,5,5-tetramethoxy-2,3-dichlorocyclopentadiene. Octachlorocyclopentene reacted with methanolic base to give 1,2,4,4,5,5-hexachloro-3,3-dimethoxycyclopentene. The product did not undergo further substitution, whereas the isomeric 1,2,3,3,5,5-hexachloro-4,4-dimethoxycyclopentene yielded 1,2,4,4-tetrachloro-3,3,5,5-tetramethoxycyclopentene. The reaction of 1-methoxy-2-chloro-3,3,4,4,5,5-hexafluorocyclopentene with base gave mainly 1,3,3-trimethoxy-2-chloro-4,4,5,5-tetrafluorocyclopentene and a dimethoxy derivative believed to be 1,4,4,5,5-pentafluoro-2-chloro-3,3-dimethoxycyclopentene. Mechanistic aspects of these nucleophilic displacement reactions are discussed.

Reaction of hexachlorocyclopentadiene (I) with alcoholate or thiolate ion is known to give ketals[3] or thioketals[4] of 2,3,4,5-tetrachlorocyclopentadienone. However, beyond subjection of the products to subsequent reactions of different nature, no extensions or elucidations of this remarkable reactivity have been reported in the literature, and a closer investigation was attempted.

Results.—The reaction of I with equimolar quantities of potassium hydroxide in methanol, both at reflux and in the cold, gave II exclusively, with recovery of nearly 50% of I. Vapor phase chromatography of the reaction mixture showed the presence of I and II only. No intermediate, such as a monomethoxy derivative, $C_5Cl_5OCH_3$, could be detected. A kinetic investigation revealed the rate-determining step to be bimolecular in the cold, first order both in I and in base. Hence, the second chlorine atom is displaced in a fast step, unmeasurable by comparison with the first displacement. The ketal II, after further reaction with base, yielded the trimethoxy compound III which, after isolation and continued exposure to methoxide ion, underwent two simultaneous reactions. The main product isolated, resulting from alcohol addition, was the tetramethoxytrichlorocyclopentene IV, whose structure was proved by hydrolysis to the known[5] 3,4,5-trichloro-3-cyclopentene-1,2-dione (VI); nucleophilic displacement of chlorine in III yielded a tetramethoxy derivative to which the diene structure V was assigned. The reaction III → IV is base catalyzed; no reaction occurred on treating III with refluxing methanol in the absence of base. The sequence may be compared to the base-catalyzed addition of ethanol to ethoxyacetylene, where the only product isolated was ethyl orthoacetate.[6]

The trimethoxy derivative III gave 1:1 adducts with styrene and maleic anhydride and its ultraviolet spectrum showed characteristic absorption of a cyclopentadiene derivative: $\lambda_{\max}$ 310 mμ, log ϵ 3.282 (*viz.* for I: $\lambda_{\max}$ 322 mμ, log ϵ 3.170[7]; for II: $\lambda_{\max}$ 307 mμ, log ϵ 3.412). The ultraviolet spectrum of IV was consistent with that of a cyclopentene structure, $\lambda_{\max}$ 212 mμ, log ϵ 3.916, whereas

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[1] Part of a paper presented by E. T. McBee, R. D. Crain, D. L. Crain, J. O. Stoffer, L. R. Belohlav and H. P. Braendlin, 137th Meeting, Am. Chem. Soc., Cleveland, O., April, 1960, p. 31-O.

[2] This paper is based in part on portions of the theses submitted by Ronald D. Crain and Donald L. Crain to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] (a) J. A. Krynitsky and R. W. Bost, *J. Am. Chem. Soc.*, **69**, 1918 (1947); (b) J. S. Newcomer and E. T. McBee, *ibid.*, **71**, 946, 952 (1949); (c) J. W. Dawson and W. J. Croxall, U. S. Patent 2,562,893 (1952); *C. A.*, **46**, 1587 (1952).

[4] E. P. Ordas, U. S. Patent 2,697,102 (1954); *C. A.*, **49**, 15956 (1955).

[5] H. J. Prins, *Rec. trav. chim.*, **65**, 455 (1946).

[6] H. C. Volger and J. F. Arens, *ibid.*, **76**, 847 (1957).

[7] E. T. McBee, J. D. Idol, Jr., and C. W. Roberts, *J. Am. Chem. Soc.*, **77**, 4375 (1955).