The dianilide derivative of the diacid chloride XXI was prepared in benzene. It was obtained as colorless crystals from absolute ethanol, m.p. 244.5–245°.

Anal. Calcd. for $C_{18}H_{16}O_2N_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 73.80; H, 5.33; N, 9.46.

N,N,N′,N′-Tetramethyl-*trans*-1-methylenecyclopropane-2,3-dicarboxamide (XXII) was obtained by the procedure used to prepare the diamide XV. From 16.54 g. (0.0924 mole) of the diacid chloride XXI in 250 ml. of benzene, there was obtained *in toto* 14.48 g. (80%) of the diamide XXII. The first crop of crystals (11.23 g.) which deposited in the final crystallization from ether had m.p. 70–71°.

Anal. Calcd. for $C_{10}H_{16}O_2N_2$: C, 61.20; H, 8.22; N, 14.28. Found: C, 61.47; H, 8.45; N, 14.47.

***trans*-2,3-Bis-(dimethylaminomethyl)-1-methylenecyclopropane (XVII).**—The procedure used here was essentially the same as that followed in the reduction of the diamide XV to the diamine XI. From 13.6 g. (0.0693 mole) of the diamide XXII and 3.90 g. (0.1028 mole, *ca.* 50% excess) of lithium aluminum hydride there was ultimately isolated 6.65 g. (57%) of the colorless liquid diamine XVII, b.p. 77–79° (9.5 mm.), $n^{25}\text{D}$ 1.4600.

Anal. Calcd. for $C_{10}H_{20}N_2$: C, 71.37; H, 11.98; N, 16.65. Found: C, 71.54; H, 11.93; N, 16.75.

The dipicrate derivative of the diamine XVII was prepared and recrystallized from 95% ethanol, m.p. 167–169°.

Anal. Calcd. for $C_{22}H_{26}N_8O_{14}$: C, 42.17; H, 4.18; N, 17.89. Found: C, 42.31; H, 4.10; N, 17.84.

ITHACA, N. Y.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Reactions of Resonance Stabilized Anions. I. Neutralization of the α,α-Dimethylbenzyl Carbanion

BY GLEN A. RUSSELL[1]

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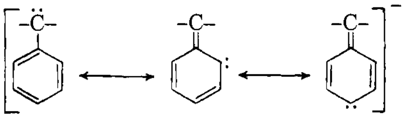
Reaction of α,α-dimethylbenzylpotassium with deuterium oxide, carbon dioxide or dimethyl sulfate yields only the product of alpha attack (α-deuteriocumene, *t*-butylbenzene, dimethylphenylacetic acid). Reaction of the anion with deuterium chloride in diethyl ether solution yields cumene containing deuterium in the α-, *o*- and *p*-positions and containing 0, 1, 2 and 3 atoms of deuterium per molecule. This result is interpreted in terms of the anion reacting with deuterium chloride at the α-, *o*- and *p*-positions to yield α-deuteriocumene or an unstable isopropylidenecyclohexadiene which in the presence of base or acid can rearrange to cumene containing deuterium in the ring. The effect of heterogeneity and of solvating power of ethereal solvents upon the products of the reaction with deuterium chloride are discussed.

Introduction

A number of highly colored benzyl-type carbanions are known which do not react readily with ethyl ether. The color and unreactivity of these carbanions is commonly attributed to resonance stabilization. If this is the case direct evidence for this resonance stabilization should be forthcoming from the reactions of these carbanions, preferably in the simplest of their reactions, *i.e.*, neutralization.



The neutralization of α,α-dimethylbenzylpotassium (potassium cumyl) has been studied by the use of various deuterio-acids. The results indicate that weak acids, such as deuterium oxide, react with the cumyl anion to produce only α-deuteriocumene. With strong acids, such as deuterium chloride in ethyl ether solution, neutralization involves attack of deuterium on the *o*-and *p*-positions of the anion. This finding presents direct chemical proof of the commonly accepted resonance stabilization mentioned previously.

Results

Potassium cumyl, a blood-red carbanion, is readily prepared by the reaction of sodium–potassium alloy with cumyl methyl ether in the presence of ethyl ether[2] or other diluents. In ethyl ether the anion has a solubility of about 0.07 *M*. Treatment of a filtered solution of the anion with hydrogen chloride yields potassium chloride containing less than 0.1% sodium chloride. There is therefore no question that the cleavage reaction should be formulated

$$C_6H_5C(CH_3)_2OCH_3 + NaK \xrightarrow{Et_2O} C_6H_5C(CH_3)_2{:}^-K^+ + NaOCH_3$$

Neutralization of the anion in ethyl ether solution 7 hours after the cleavage reaction had commenced (cleavage temperature, 25°) with > 99.5% deuterium oxide gave a deuteriocumene containing 90.8% d_1-cumene and 9.2% d_0-cumene (from mass spectra at reduced ionizing potential). Deuterium atoms in the *o*-, *m* or *p*-positions were absent as judged from the lack of infrared absorption at 15.8, 15.0 and 16.4 μ (the ring deuterated cumenes were found to have intense absorptions at these wave lengths). After storage for 161 hours a sample of the anion gave upon neutralization a cumene containing 74.4% d_1-cumene and 25.6% d_0-cumene. Ring deuteration was again absent. These results indicate that abstraction of a proton from ethyl ether by this anion must be extremely slow. For 0.1 mole of the anion in the presence of 700 ml. of ethyl ether, hydrogen abstraction cannot exceed 0.1% per hour and possibly is considerably less.

The formation of exclusively α-deuteriocumene from the reaction of deuterium oxide with potassium cumyl is in agreement with the previous report of Ziegler and Schnell that carbonation of the anion yields only dimethylphenylacetic acid.[2] Moreover, treatment of the anion with dimethyl sulfate at 0° gave *t*-butylbenzene whereas *p*-cymene could not be detected by gas–liquid chromatography. The ratio of *t*-butylbenzene to

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[1] Department of Chemistry, Iowa State College, Ames, Iowa.

[2] K. Ziegler and B. Schnell, *Ann.*, **437**, 222 (1934).

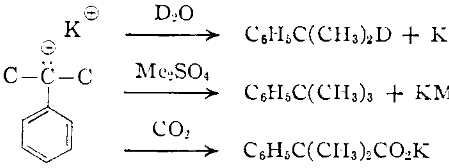
TABLE I

PRODUCTS OF THE NEUTRALIZATION OF THE CUMYL ANION AT 0°[a]

Expt.	Neutralizing agent	Solvent	Composition of cumene[b] d_0-	d_1-	d_2-	d_3-	α-d-	o-d-	p-d-
1	D_2O	Et_2O	9.2	90.8	<0.1	<0.1	90.8	<0.1	<0.1
2	D_2O	Et_2O[c]	25.6	74.4	< .1	< .1	74.4	< .1	< .1
3	DOAc	Et_2O	20.8	79.2	< .1	< .1	78.8	.2	1.2
4	DCl[d]	Et_2O	27.0	58.4	13.6	1.0	69.0	4.5	15.4
5	DCl[e]	Et_2O	32.8	52.0	14.0	1.3	62.0	4.7	15.5
6	DCl[c,d]	Et_2O[f]	35.1	50.8	13.1	1.0	51.0	3.2	11.3
7	DCl[d]	Et_2O[g]	31.0	57.6	10.8	0.55	63.5	3.6	12.1
8	DCl[d]	Et_2O[h]	26.4	64.8	8.3	0.4	75.5	2.65	8.8
9	DCl[d]	Et_2O[i]	30.0	51.8	16.6	1.6	62.5	5.4	19.4
10	D_2O	n-Pentane[i]	5.0	95.0	<0.1	<0.1	95.0	<0.1	<0.1
11	DCl	n-Pentane[j]	7.0	93.0	< .1	< .1	94.5	< .1	< .1
12	DCl	$MeOCH_2CH_2OMe$	38.9	60.8	.3	< .1	61.0	< .1	< .1

[a] 0.10 mole of anion in 700 ml. of solvent. 7-hour reaction period at 25° for preparation of anion. [b] Analysis by mass spectra at reduced ionizing potential and by infrared absorption at 4.63, 15.8 and 16.4 μ. [c] 168-hour reaction period for preparation of anion. [d] Deuterium chloride exactly equivalent to anion. [e] 100% excess of deuterium chloride. [f] Deuterium chloride added to filtered solution of anion. [g] 2000 ml. of ether used for 0.1 mole of anion. [h] 100 ml. of ether per 0.1 mole of anion. [i] Neutralized at −60°. [j] Solvent consisted of 700 ml. of n-pentane and 10 ml. of ethyl ether.

p-cymene in the reaction product must have been greater than 500:1.

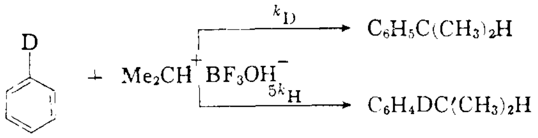


Although the three reagents mentioned above are very selective in their reaction with the cumyl anion, deuterium chloride in ethyl ether solution gives a variety of deuteriocumenes. The results summarized in Table I indicate that cumene molecules containing 0, 1, 2 and 3 deuterium atoms are formed and that deuterium atoms are present in the α-, o- and p-positions. Deuterium atoms could not be detected in the m-position.

The same product was obtained (ignoring isotopic dilution) in the neutralization of 0.1 mole of the cumyl anion in the presence of 700 ml. of ether (not completely homogeneous) as in the presence of 2000 ml. of ether (anion completely in solution). Moreover, the same product was obtained when a reaction employing 700 ml. of ether was filtered to remove sodium methoxide and undissolved potassium cumyl. Furthermore, in the presence of 700 ml. of ether the same product was obtained whether an exactly equivalent amount of deuterium chloride was used (as indicated by the disappearance of the blood-red color) or when a 100% excess of deuterium chloride was used. Trial experiments indicated no detectable exchange between cumene and deuterium chloride in ethyl ether solution at 0°, under conditions comparable with those employed in neutralization of the anion, even when a 2000% excess of deuterium chloride was employed. Thus, experiments 4, 5, 6 and 7 in Table I fairly represent the product of reaction between deuterium chloride and the cumyl anion in ethyl ether solution.

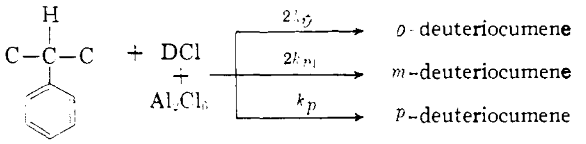
When only 100 ml. of ether was used as diluent for 0.1 mole of the anion (expt. 8) the amount of ring substitution was noticeably lower, and when a mixture of 700 ml. of n-pentane and 10 ml. of ether was used as diluent (expt. 11) no ring substitution was observed. A further complicating factor was the observation that in the presence of the dimethyl ether of ethylene glycol (expt. 12), in which the anion is soluble to the extent of at least 0.4 M, that again only α-substitution occurred and ring-deuterated cumenes could not be detected.

As part of the infrared calibration a sample of deuteriocumene was prepared by the reaction of an excess of d_1-benzene with isopropyl alcohol at 0° in the presence of boron trifluoride. The benzene contained 3.75% d_0-benzene and 96.25% d_1-benzene, whereas the cumene formed by isopropylation contained 14.0% d_0-cumene and 86.0% d_1-cumene. On the basis that the secondary



isotope effects would be very small it can be calculated that the primary isotope effect in this reaction, k_H/k_D is 1.69 . If the substitution occurred exactly as pictured, then o-, m- and p-deuteriocumenes should be present in the ratio of 2:2:1 or to the extent of 34.4, 34.4 and 17.2%. By analysis a p-deuteriocumene content of 14.9% was found. This value is 2.3% lower than the expected statistical value although 1% of the difference may well be attributed to experimental uncertainty. From the present data the possibility certainly exists that an aromatic deuterium atom may deactivate p-hydrogen atoms toward aromatic substitution although the effect is not large and not necessarily demanded by the data.

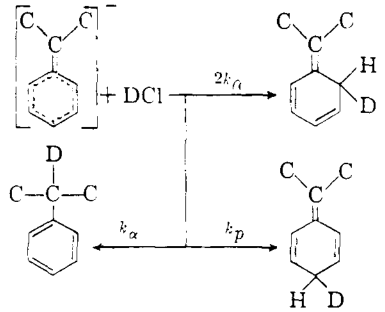
In another experiment cumene was allowed to react with a deficiency of deuterium chloride and aluminum chloride at −50°. Under the conditions used, benzene or diisopropylbenzene were not formed. The product contained 0.35 deuterium atom per molecule distributed as 26.6% d_1-, 4.2% d_2- and 0.2% d_3-cumene. The cumene contained no deuterium in the α-position, 9.1% o-deuterium, 6.1% p-deuterium and, by difference, 11.45% m-deuterium. The ratios of rate constants, $k_o:k_m:k_p$ are thus calculated to be 0.73:0.94:1.0. From the *meta/para* ratio of 0.94 the reaction is

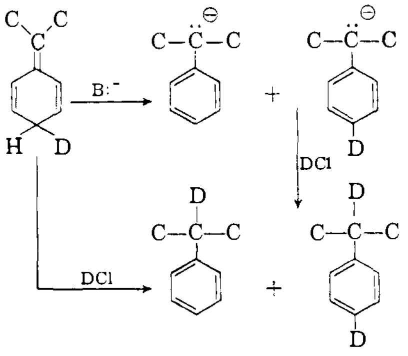


judged to be quite unselective with some *ortho-para* activation. The *ortho/para* ratio of 0.73 indicates *ortho* deactivation, presumably from steric hindrance. At the present time it cannot be stated to what extent the products of this exchange are equilibrium controlled.

Discussion

The formation of ring deuterated cumenes as well as cumene molecules containing 1, 2 and even 3 deuterium atoms from the reaction of the cumyl anion with deuterium chloride undoubtedly proceeds *via* the formation of an unstable isopropylidenecyclohexadiene intermediate. In the presence of base or acid these intermediates would be rearranged to cumene containing deuterium in the aromatic ring, *e.g.*

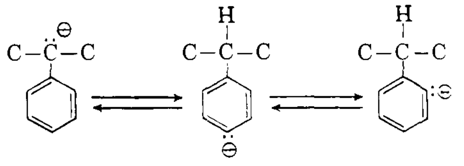




This mechanism explains the formation of d_2- and d_3-cumenes as well as the fact that the α-deuterium content of the deuterated cumene is lower when deuterium chloride is used as a neutralizing agent than when deuterium oxide is used. The addition of a deuteron to the aromatic ring results in isotopic dilution whenever substitution occurs and the yield of α-deuteriocumene is thereby reduced.

The results cannot be explained on the basis of exchange between deuterium chloride and initially formed cumene since trial experiments indicated that this exchange was undetectable under the reaction conditions. Moreover, the amount of ring substitution was independent of the amount of deuterium chloride used. Finally, this type of an exchange reaction would have been expected to give at least some exchange in the *m*-positions, whereas no exchange could be detected.

Another possible reaction course involving an equilibrium between ions can be eliminated on the basis that such an equilibrium can occur only slowly.[3] This equilibrium does not predict the observed difference between deuterium oxide and deuterium chloride as neutralizing agents nor does this equilibrium immediately explain the formation of d_2- and d_3-cumenes in the neutralization reaction.



The ratios of k_α, k_o and k_p for the reactions of deuterium chloride with the cumyl anion can only be approximated by the analysis of the product because not all of the deuterium which adds at the *o*- or *p*-position of the anion will be found in the product. If k'_o and k'_p are defined by the composition of the product it follows that at most k_p or k_o will be twice k'_p or k'_o (k_H/k_D = 1 for rearrangement of cyclohexadiene) or if the deuterium isotope effect for the rearrangement of the cyclohexadiene is 5 then k_p or k_o will be only 1.2 times k'_p or k'_o. Ratios of k_α/k'_p and k'_p/k'_o for neutralization under various conditions are summarized in Table II (note that k'_p/k'_o and k_p/k_o must be nearly identical).

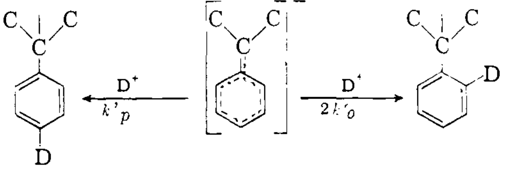


TABLE II

RATIO OF k_α/k'_p AND k'_p/k'_o IN THE NEUTRALIZATION OF THE CUMYL ANION[a]

Expt.	Neutralizing conditions Reagent, temp., °C., solvent	k_α/k'_p	k'_p/k'_o
1	D_2O, 0, Et_2O	>500	..
3	DOAc, 0, Et_2O	65	..
4	Eq. DCl, 0, Et_2O	4.5	6.9
5	100% excess DCl, 0, Et_2O	4.0	6.6
6	Eq. DCl, 0, filtered Et_2O sol.	4.5	7.1
7	Eq. DCl, 0, Et_2O (2000 ml.)	5.2	6.7
9	Eq. DCl, −60, Et_2O	3.2	7.2
8	Eq. DCl, 0, Et_2O (100 ml.)	8.6	6.7
11	Eq. DCl, 0, *n*-pentane	>500	..
12	Eq. DCl, 0, $MeOCH_2CH_2OMe$	>500	..

[a] 0.1 mole of anion in 700 ml. of solvent.

In ethyl ether solution (0.1 mole of anion, 700 ml. of ether) the value of k_α/k'_p is greater than 500 for deuterium oxide, 65 for *d*-acetic acid and about 4.5 for deuterium chloride. These results are readily interpreted in the terms of the Hammond postulate.[4] For a weakly acidic species, such as deuterium oxide, the neutralization reaction proceeds in such a manner as to yield the most stable product (α-deuteriocumene) exclusively. The stronger acid, *d*-acetic acid, reacts more readily with the anion and some

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[3] D. Bryce-Smith and E. H. Turner, *J. Chem. Soc.*, 1975 (1950); D. Bryce-Smith, *ibid.*, 1079 (1954).

[4] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

ring attack is observed. Finally, with the very strong acid deuterium chloride or its oxonium salt with ethyl ether, the reaction with the anion must occur with great rapidity and a significant proportion of the reaction leads to the formation of the least stable product, the isopropylidenecyclohexadiene. Reaction of a deuteron with the *o*- or *p*-position of the anion demonstrates the presence of a negative charge on these positions and affords a direct chemical verification of the commonly postulated resonance stabilization of benzyl-type carbanions.

The effect of solvents on the product of the reaction involving deuterium chloride is somewhat surprising. Replacement of the ethyl ether by either a very poor solvent (*n*-pentane) or a very good solvent for the anion (dimethyl ether of ethylene glycol) results in the formation of exclusively α-deuteriocumene. In Fig. 1 the ratios of $k\ /k'_p$ observed for the neutralization of 0.1 mole of the anion by deuterium chloride in the presence of various amounts of ethyl ether have been plotted. The data suggest that the heterogeneous reaction between the solid organometallic and deuterium chloride dissolved in the liquid phase is quite selective giving only α-deuteriocumene. The neutralization of 0.1 mole of the anion in 100 ml. of ether apparently proceeded partially *via* the neutralization of the undissolved anion. In the presence of 700 or 2000 ml. of ether only a homogeneous neutralization was observed and the ratio of k_o/k'_p was constant at about 4.5 and not affected by filtration of the ethereal solution of the anion.

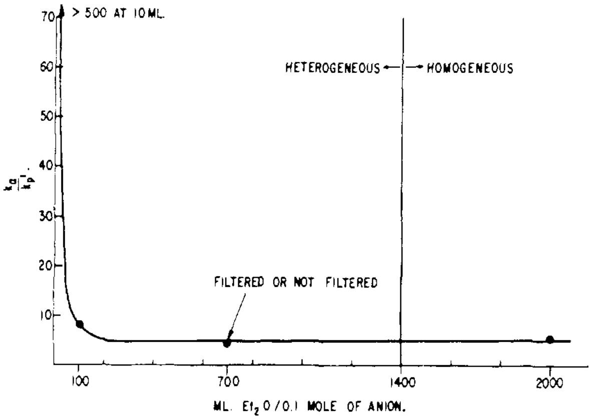

Fig. 1.—Effect of medium upon the products of the reaction of the cumyl anion with deuterium chloride.

In the excellent solvating agent dimethyl ether of ethylene glycol apparently the anion and the deuterium chloride are so stabilized by solvation that reaction gives only the most stable product, α-deuteriocumene. Thus, three conditions for selective deuteronation of the cumyl anion have been realized, (1) a weak acid such as deuterium oxide will give exclusively α-deuteriocumene under any conditions, (2) a strong acid such as deuterium chloride will give only α-deuteriocumene when it reacts with undissolved potassium cumyl, (3) in a powerful solvating agent, like the dimethyl ether of ethylene glycol, even a strong acid such as deuterium chloride will give only α-deuteriocumene.

The ratios of *ortho* to *para* attack summarized in Table II also deserve comment. The ratio, k'_p/k'_o is surprisingly high, about 7, and is relatively constant. The low reactivity of the *o*-position relative to the *p*-position probably does not represent a difference in electron density to the two positions. There is abundant evidence in aromatic electrophilic substitutions that in the absence of steric effects that activated *o*- and *p*-position have nearly equal reactivities. *Ortho* deactivation often results because of steric effects, but in the reaction of deuterium chloride with the cumyl anion such a large steric effect seems unlikely. It has already been argued that reaction with deuterium chloride occurs with great rapidity and that the transition state resembles the reactants. Therefore, the deuterium atom should not be particularly close to the *o*-position in the transition state for *ortho* attack and steric hindrance would not be expected to deactivate the *o*-position by the 7-fold factor observed.

A possible explanation of the low reactivity observed for the *o*-position relative to the *p*-position is that the reaction of the anion with deuterium chloride is a diffusion-controlled process. In this case the approach of the deuteron, or incipient deuteron, will be controlled simply by electrostatic attraction with the negative charge at the *o*-, *p*- and α-positions. In Fig. 2 a qualitative representation of the areas over which these positions exert a strong electrostatic force is presented. It is assumed that once a deuteron diffuses within one of the circles in Fig. 2 (actually a sphere in a three dimensional representation) that the probability is high that the deuteron will be captured by the atom at the center of this electrostatic attraction. The effect of this simple treatment is that if the α-position has a considerable higher concentration of negative charge than the *o*-position, it will essentially rob the *o*-positions of deuterons which would have otherwise diffused close enough to react. As pictured in Fig. 2, the α-position blankets the *o*-position and because of the stronger electrostatic attraction at the α-positions few deuterons will be able to diffuse into the reaction area of the *o*-position. The *p*-position is far removed from the α-position and once a deuteron diffuses close to the *p*-position it will be removed from the sphere of influence of the α-position.

This interpretation is consistent with the effect of temperature on the products of the reaction of the cumyl anion with deuterium chloride. At 0° and $-60°$ the ratio of k_p'/k'_o is the same, as would be expected on the basis of a diffusion controlled picture but not on the basis of steric hindrance. Moreover, the ratio k_α/k'_p is somewhat less at $-60°$ than at 0°. If the ratio of alpha to *para* attack was determined by a difference in energy of activation, more alpha attack would have been expected at the lower temperature. Actually less alpha attack (relative to *para* attack) was observed. This result is, however, in agreement with a model based on a diffusion-controlled process. On this basis the ratio k_α/k_p would be independent of temperature, whereas the deuterium-isotope effect in the rearrangement of the isopropylidenecyclohexadiene would be greater at $-60°$ than at 0°. Thus more of the deuterium adding to the aromatic nucleus would be found in the final product of the reaction at −60° than at 0° and the ratio of k_α/k'_p at −60° would be less than the same ratio at 0°.

Products of ring attack on numerous other organometallic derivatives of toluene are known.[5,6] Most of these reactions involve exclusive *ortho* attack, *e.g.*, the reaction of benzylmagnesium halides with formaldehyde to yield *o*-methylbenzyl alcohol,[7] and should be formulated as occurring *via* a cyclic intermediate.[8] A significant amount of *para* attack has been observed in only a few cases, namely in the reaction of benzyl-type Grignard reagents with chloromethyl ethers[9,10] or ethylene oxide.[9,11] Whether these products should be considered as arising *via* an incipient benzyl-type carbanion is not entirely clear since benzylmagnesium halides are known to react with deuterium chloride to produce solely α-deuteriotoluene.[12]

Experimental

General Technique.—Sodium–potassium alloy was prepared by melting 8 g. of potassium and 1.6 g. of sodium under mineral oil. The alloy was washed with ethyl ether, *n*-pentane or the dimethyl ether of ethylene glycol and added under a nitrogen atmosphere to a three-necked 1-l. flask containing an appropriate amount of solvent (usually 700 ml.) and equipped with a mercury sealed Hershberg stirrer, a reflux condenser and a pressure equalized dropping funnel containing 15 g. of cumyl methyl ether. The flask was thoroughly purged of oxygen by nitrogen dried by passage over beads coated with phosphoric pentoxide and the apparatus maintained under a positive pressure of about 10 mm. of nitrogen. The alloy was stirred with the solvent for at least one hour to destroy all hydroxylic impurities. The cumyl methyl ether was then added over a 0.5-hour period and the reaction mixture stirred at room temperature for a further period, usually 6.5 hours.

After the cleavage reaction had proceeded for the desired period of time, deuterium oxide or *d*-acetic acid was added directly to the organometallic as fine droplets through the dropping funnel. When deuterium chloride was used as the neutralizing agent the dropping funnel was replaced by a gas inlet tube and the deuterium chloride added above the surface of the liquid as it was generated. After the desired amount of neutralizing agent had been added, excess sodium-potassium alloy was destroyed by the careful addition of methyl alcohol. In the cases where *n*-pentane or ethyl ether were used as solvents the reaction mixture was thoroughly washed with water, dried over calcium chloride and concentrated by distilling the solvent through a 2-foot Vigreux column. The residue was distilled through a short Vigreux column and the cumene collected, usually as 4-fractions, boiling at 153–154°. The yield of cumene from 0.1 mole of the cumyl methyl ether was usually about 10 g. (0.083 mole), $n^{20}\text{D}$ 1.4905–1.4910. No attempt was made to recover the cumene quantitatively and highly efficient rectification was avoided because of the possibility of isotopic fractionation.

When the dimethyl ether of ethylene glycol was employed as solvent the excess alloy was destroyed by methanol and the solution reduced to 100-ml. volume by distillation. The residue was treated with 500 ml. of *n*-pentane, thoroughly washed with water and the cumene isolated as described previously.

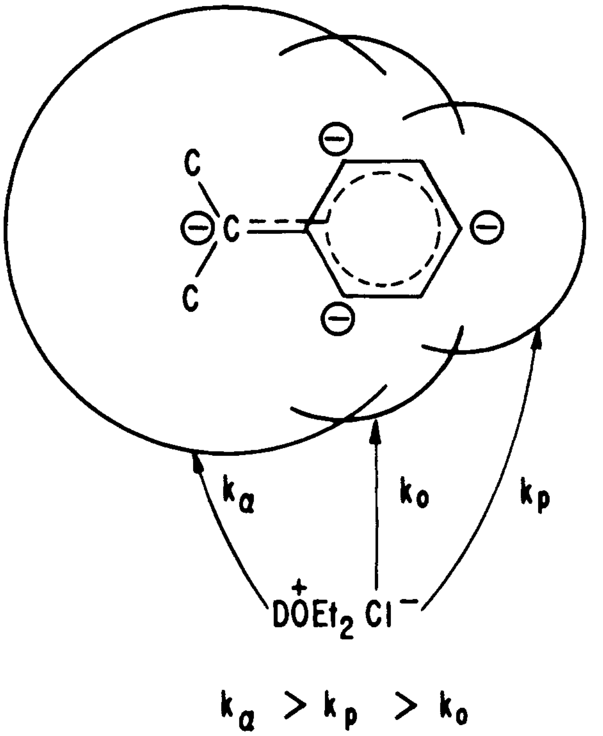

Fig. 2.—Electrostatic effects in the diffusion-controlled reaction of the cumyl anion with deuterium chloride.

In cases where the ethereal solution of the anion was filtered a flask was employed which contained a coarse sintered glass filter stick sealed in the bottom. Before filtration the solution was allowed to settle for approximately one hour after which the supernatant liquid was allowed to pass through the filter and was collected under positive nitrogen pressure in a second flask.

Analytical.—Samples of the cumene were analyzed for deuterium content by mass spectra at reduced ionizing potential such that for cumene itself the ratio of peaks for masses 120 and 119 was greater than 500 to 1. The isotopic concentrations were then calculated from the peak heights of the parent peaks for masses 120–125, the ratio of C_{13}/C_{12} being taken as 1.11/98.89. For a sample of normal cumene this procedure indicated that 0.15% of the molecules contained one deuterium atom, whereas from the natural abundance of hydrogen and deuterium it is calculated that 0.23% of the cumene molecules should contain one deuterium atom.

α-Deuteriocumene was analyzed by infrared absorption at 4.43 μ using a Perkin-Elmer model 21 spectrometer equipped with calcium fluoride optics. Samples of α-deuteriocumene prepared by treatment of the anion with deuterium oxide and known to be free of ring deuteration were used as standards, their purity being based on mass spectra. A linear relationship between absorbancy and concentration was found when α-deuteriocumene was diluted with cumene.

p-Deuteriocumene was prepared from the reaction of *p*-isopropylphenylmagnesium bromide and deuterium oxide. Infrared analysis indicated the absence of α-, *o*- or *m*-deuterium atoms. The *p*-deuteriocumene had an intense absorption at 16.4 μ suitable for analysis. Analysis was performed using a Baird spectrometer equipped with potassium bromide optics. Between 0 and 5% mixtures of cumene and *p*-deuteriocumene gave a linear relationship between absorbancy and concentration. For analysis unknown samples were diluted with cumene to give a *p*-deuteriocumene concentration of about 1%. The purity of *p*-deuteriocumene employed on a standard was obtained from its mass spectra.

Pure samples of *o*- and *m*-deuteriocumenes were never prepared. From experiments involving the exchange of deuterium chloride with cumene in the presence of aluminum

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(5) H. Gilman and F. Brewer, THIS JOURNAL, **56**, 1127 (1934); H. Gilman and J. F. Nelson, *ibid.*, **61**, 741 (1939).

(6) For an excellent summary of "abnormal" products in the reaction of benzyl-type Grignard reagents, see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, p. 1133.

(7) M. Tiffeneau and R. Delange, *Compt. rend.*, **137**, 573 (1903).

(8) J. R. Johnson, THIS JOURNAL, **55**, 3029 (1933); W. G. Young and S. Siegel, *ibid.*, **66**, 354 (1944); S. Siegel, W. M. Boyer and R. R. Joy, *ibid.*, **73**, 3237 (1951).

(9) H. Gilman and J. E. Kirby, *ibid.*, **54**, 345 (1932).

(10) L. Malm and L. Summers, *ibid.*, **73**, 362 (1951).

(11) M. Mousseron and N. P. Du, *Bull. soc. chim.*, [5] **15**, 91 (1948).

(12) H. C. Brown and G. A. Russell, THIS JOURNAL, **74**, 3995 (1952).

thloride and isopropylation of d_1-benzene, it was obvious that *o*-deuteriocumene had a sharp and intense absorption at 15.8 μ and *m*-deuteriocumene absorbed strongly at 15.0 μ. The isopropylation of d_1-benzene gave a product containing 86.0% d_1-cumene (by mass spectra). This material was used on an infrared standard with the assumption that two-fifths of the deuterium was in the *o*-position.

Products of the reaction of dimethyl sulfate with the cumyl anion were analyzed in the ethereal concentrate by gas-liquid chromatography employing a Perkin-Elmer model 154B Vapor Fractometer operating at 150° and using helium as a carrier gas. *t*-Butylbenzene and *p*-cymene were well separated by an "A"-column (purportedly di-*n*-decyl phthalate). *p*-Cymene would have been detected at a molar concentration $^{1}/_{600}$ that of the *t*-butylbenzene.

Solubility Measurements.—Treatment of 0.1 mole of cumyl methyl ether with sodium-potassium alloy for 7 hours in 700 ml. of ethyl ether at room temperature followed by filtration gave 550 ml. of an ether solution of the anion. Treatment of this solution with deuterium chloride gave a precipitate of alkali metal halide which was removed by filtration. The precipitate weighed 2.90 g. and was found to contain less than 0.03% sodium by flame photometry. From the ethereal solution 4.75 g. of cumene was recovered. The 550 ml. of filtrate thus gave 0.038 mole of potassium chloride and 0.039 mole of cumene and the solubility of the anion in ether is indicated to be 0.07 *M*.

Treatment of 0.1 mole of cumyl methyl ether with the alloy in the presence of 100 ml. of the dimethyl ether of ethylene glycol for 7 hours at room temperature did not give a homogeneous solution. The solution was allowed to settle and a sample of the homogeneous supernatant liquid was pipetted into methyl alcohol. The hydrolysate was analyzed for cumene, cumyl methyl ether and the dimethyl ether of ethylene glycol by gas-liquid chromatography at 100° in the "A"-column. The procedure was calibrated by prepared samples and the results indicated that more than 95% of the cumyl methyl ether had been destroyed. The ratio of cumene to dimethyl ether of ethylene glycol after hydrolysis indicated a solubility of the anion in this solvent of 0.42 *M*.

Reagents.—The cumyl methyl ether and *p*-bromocumene used have been described previously.[13] Deuterium oxide (>99.5%) was obtained from the Stuart Oxygen Co. Deuterium chloride was prepared by the reaction of deuterium oxide with benzoyl chloride[14] and should have possessed a purity of >95%. *d*-Acetic acid was prepared by the hydrolysis of acetyl chloride with deuterium oxide. The *d*-acetic acid was isolated by distillation. Its isotopic purity was never measured. Phillips 99 mole % minimum *n*-pentane was used without purification as was Mallinckrodt analytical grade ether (containing a trace of alcohol as a preservative). The dimethyl ether of ethylene glycol (Ansul Chem. Corp.) was refluxed over sodium until no further reaction occurred. Constant boiling material was stored over sodium and under nitrogen before use. All other solvents were dried by calcium hydride.

Acknowledgment.—Mass spectra were obtained by Mr. G. P. Schacher. Infrared absorptions were obtained by Mr. D. Harmes and Miss D. McClung. The Vapor Fractometer was operated by Mr. E. M. Hadsell. The cumyl methyl ether was prepared by Mr. W. Reuter.

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[13] G. A. Russell, THIS JOURNAL, **79**, 3871 (1957); **78**, 1047 (1956).

[14] H. C. Brown and C. Groot, *ibid.* **64**, 2223 (1942).

SCHENECTADY, N. Y.

COMMUNICATIONS TO THE EDITOR

INFRARED SPECTRA OF METAL CARBONYL HYDRIDES

Sir:

Several years ago this laboratory located the first vibration involving a hydrogen atom in metal carbonyl hydrides —703 cm.$^{-1}$ in $HCo(CO)_4$.[1] To take into account the range of possible consequences of the interaction expected between the hydrogen and the CO groups, a bonding model was proposed[1] containing a degree of freedom. In one limit the hydrogen was solely bonded to the metal and in the other limit to CO groups—the demonstration of the exact state requiring further experimentation.[1,2] Cotton has criticized this view and suggests that the 703 cm.$^{-1}$ band arises from a Co–H stretching vibration.[3,4]

This laboratory has now studied in detail the infrared spectrum of $DCo(CO)_4$, $H_2Fe(CO)_4$, $HDFe(CO)_4$, $HMn(CO)_5$, $DMn(CO)_5$, and a number of related compounds 2 to 33 μ obtained with appropriate prisms and small gratings. The 703 and 330 cm.$^{-1}$ bands of $HCo(CO)_4$ shift to 600 and 296 cm.$^{-1}$ in $DCo(CO)_4$ for frequency ratios of 1.17 and 1.12. These data establish that C and/or O atoms participate along with the H or D atom in the motions of this group of vibrations. Six vibrations of this character are observed between 300 and 800 cm.$^{-1}$ in $H_2Fe(CO)_4$, the typical hydrogen contribution being less than for $HCo(CO)_4$. Moreover, it appears that C–O bending motions primarily couple with the hydrogen motion in these modes.

The major components of the intense 5 μ band of $HMn(CO)_5$ are two overlapped bands with PQR structure apparently centering at 2028.8 and 2020 cm.$^{-1}$. A much weaker band has its Q branch at 1994.4 cm.$^{-1}$. Among the weaker satellites is a band at 1782 cm.$^{-1}$. The most intense bands at longer wave lengths occur at 735, 664, 615 and 458 cm.$^{-1}$. The stronger bands of $DMn(CO)_5$ are similar to those of $HMn(CO)_5$ except that the hydride bands at 735, 664 and 615 cm.$^{-1}$ seem to collapse into a deuteride band (doublet) at 676 cm.$^{-1}$; the weaker band at 1782 cm.$^{-1}$ is replaced by one at 1287 cm.$^{-1}$.

The 1782 and 1287 cm.$^{-1}$ bands are the Mn–H and Mn–D stretching vibrations! They correspond to a Mn–H force constant of *ca.* 1.87 md./Å. The following explanation is offered for the behavior of the bands near 15 μ. The 735 and 615 cm.$^{-1}$ bands result from the coupling of a weak, "pure" Mn–H bending mode with an intense C–O bending mode, both of which have (uncoupled) frequencies near a second C–O bending mode of different symmetry at 664 cm.$^{-1}$. The deuteration shift of the (uncoupled) Mn–H frequency (*ca.* $\sqrt{2}$) moves it

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[1] W. Edgell, C. Magee and G. Gallup, THIS JOURNAL, **78**, 4185 (1956).

[2] W. Edgell, *Ann. Rev. Phys. Chem.*, **8**, 353 (1957).

[3] F. Cotton and G. Wilkinson, *Chem. and Ind.* (*London*), 1305 (1956).

[4] F. Cotton, THIS JOURNAL, **80**, 4425 (1958).