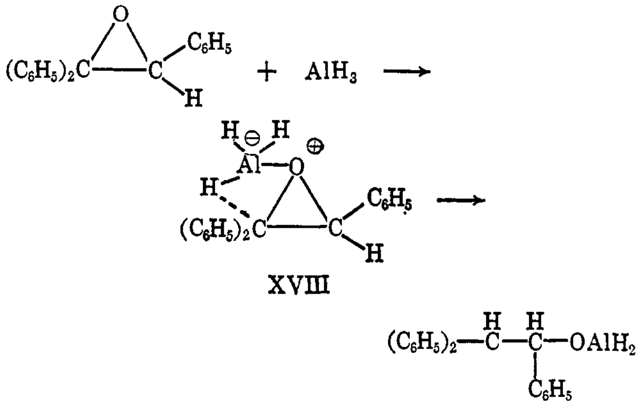
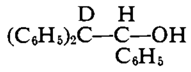
attacking Lewis acid is a strong acid such as $AlCl_3$ or $HAlCl_2$, the epoxide ring opening to form a carbonium ion should be fast and thus reduction and migration are competing reactions (Scheme I and II). Eliel has shown that the product formed through migration of the phenyl group (2,2,2-triphenylethanol) is the major one indicating that carbonium ion formation and subsequent phenyl migration is faster than reduction.

On the other hand if the attacking species is a much weaker Lewis acid than $HAlCl_2$, such as AlH_3, complexation at the epoxide oxygen atom is expected; however, ring opening should not be nearly so rapid.[15] In this case reduction could be the major reaction *via* a four-center transition state. This proposal is consistent with a report by Eliel that triphenylethylene oxide is reduced by $3LiAlD_4 + AlCl_3$, which produces AlD_3 *in situ*, to XX.



XVIII

XIX



$(C_6H_5)_2\overset{D}{C}—\overset{H}{\underset{C_6H_5}{C}}—OH$

XX

Thus it appears that the reaction of $LiAlH_4$ and $AlCl_3$ in 3:1, 1:1, 1:3, and 1:4 ratio produces AlH_3, H_2AlCl, $HAlCl_2$, and $HAlCl_2 + AlCl_3$, respectively, and that the first step in the reduction of an organic functional group such as an epoxide involves complexation of the aluminum species at the oxygen atom. If the aluminum species is a strong Lewis acid such as $HAlCl_2$ or $AlCl_3$, then ring opening to form a carbonium ion is very rapid followed by migration and then reduction. However, if the complexing Lewis acid is weak such as AlH_3, then the resulting complex is relatively stable and thus reduction proceeds by a four-center transition state to produce the expected alcohol. Whether or not AlH_3, reduces epoxides through a four-center transition state or a carbonium ion could be easily tested by reduction of optically active 1-phenyl-1-ethyl ethylene oxide. Reduction *via* a four-center transition state should result in the formation of optically active 2-phenyl-1-butanol whereas reduction *via* a carbonium ion should result in the formation of racemic 2-phenyl-1-butanol.

Since we have prepared the hydridoaluminum halides in pure form as the diethyl etherates and triethyl aminates, we are now studying the effect of both the halogen and solvating species of $H_nAlX_{3-n}\cdot$solvent on the product distribution by reaction with styrene oxide and triphenylethylene oxide. By reducing these compounds with different combinations of $HAlCl_2$, LiCl, and $AlCl_3$ and comparing the product ratio to what is observed by the "mixed hydride" reagent, we hope to determine the nature of the attacking species.

Acknowledgment. We would like to acknowledge financial support by the National Aeronautics and Space Administration under Grant NsG-657. Also we thank Dr. Sidney Gordon of Georgia Institute of Technology for assistance in our efforts to detect $LiAlCl_3H$ in solution by nmr analysis.

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[15] Strong Lewis acids such as $AlCl_3$ and BCl_3 are known to cleave ethers such as diethyl ether and tetrahydrofuran much more rapidly than AlH_3 and B_2H_6.

A Polarographic and Spectroscopic Study of Dibenzothiophene and Some of Its Isologs

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Contribution from the Cyanamid European Research Institute, Cologny, Geneva, Switzerland.

Received April 17, 1965

Abstract: The polarographic reduction potentials and ultraviolet absorption spectra of dibenzofuran, dibenzothiophene, dibenzoselenophene, and various derivatives of these compounds have been measured. The effects of methyl substituents on the reduction potentials of dibenzofuran and biphenyl have been shown to be in accord with the predictions of LCAO–MO theory. For dibenzothiophene agreement *is not* obtained if the 3d orbitals of the sulfur are included in the conjugated system in the way originally suggested by Longuet-Higgins, and this is in accord with a previous interpretation of the esr spectra of the radical anion of this compound. The shifts in the positions of the ultraviolet spectral bands, produced by methyl substitution, are discussed.

In an earlier paper[1] we reported the electron spin resonance spectra of the radical anions of dibenzofuran, dibenzothiophene, and certain of their methyl derivatives and obtained good agreement between their ring proton hyperfine splitting and the predictions of LCAO–MO theory. Two models were used to describe the sulfur atom in dibenzothiophene, one in which only its occupied $3p_z$ orbital entered into con-

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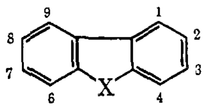
[1] R. Gerdil and E. A. C. Lucken, *J. Am. Chem. Soc.*, 87, 213 (1965).

jugation with the benzene system (p model) and another in which the vacant 3d orbitals were taken into account after the manner originally suggested by Longuet-Higgins (d model). Only the first model provided agreement between theory and experiment while the d model predicted both a qualitatively and quantitatively different spin distribution. *Within the framework of the LCAO–MO method* it was, therefore, possible to definitely exclude the Longuet-Higgins d model as a suitable representation of the sulfur atom in dibenzothiophene.

Obviously such a conclusion requires some confirmation and in support of it we here report the results of measurements of the polarographic reduction potentials of the compounds previously studied and of a number of structurally related molecules. The polarographic data are mainly interpreted in terms of the variations occurring in the half-wave potentials when hydrogen atoms are substituted by methyl groups. Certain regularities in the ultraviolet absorption spectra of methylated derivatives of dibenzothiophen seem also to be in accord with the p model of the sulfur atom. We would like to make it clear, however, that we do *not* maintain, either in ref 1 or in the present paper, that the vacant 3d orbitals of the sulfur atom do not interact *at all* with the conjugated system but only that their contributions to the ground states of the neutral molecule and the radical anion are not significant. The Longuet-Higgins d model of the divalent sulfur atom, which has been extensively used in LCAO calculations, therefore is inappropriate.

Results

Polarographic Reduction Potentials. The half-wave reduction potentials (HWP) of dibenzothiophene (I), dibenzofuran (II), and dibenzoselenophene (III), and of the structurally related compounds are reported in Table I. No polarographic reduction of simple sulfur heterocycles without an extracyclic reducible group has been reported previously. A single, well-defined wave was observed for each compound in anhydrous dimethylformamide (DMF) when we used a capillary with regulated drop time. The polarography of the heterocycles conducted with an ordinary dropping electrode without controlled drop time gave rise to somewhat distorted waves with a tendency to form maxima. As for aromatic hydrocarbons, the single reduction wave is presumably associated with the transfer of one electron and the formation of the corresponding radical ion.[2] This was demonstrated in the case of biphenyl and dibenzofuran by electrolyzing a DMF solution of each of these compounds in the resonance cavity of an esr spectrometer. Spectra were recorded which displayed the expected hyperfine structure of the radical ions.



I, dibenzothiophene (X = S)
II, dibenzofuran (X = O)
III, dibenzoselenophene (X = Se)

Table I. Polarographic Reduction Potentials of Some Isologous Heterocycles and Their Parent Hydrocarbons in Anhydrous DMF

Compound	$-E_{1/2}$, V[a]	I_d[b]
Fluorene	2.627	2.10
9,10-Dihydrophenanthrene	2.563	2.27
Biphenyl	2.525	2.37
2,2′-Dimethyl	Not reducible	...
3,3′-Dimethyl	2.555	2.03
4,4′-Dimethyl	2.665	2.08
Dibenzofuran (II)	2.459	2.20
2,8-Dimethyl	2.482	2.04
4,6-Dimethyl	2.558	2.09
Dibenzothiophene (I)	2.432	2.18
2,8-Dimethyl	2.452	2.05
3,7-Dimethyl	2.563	2.08
4,6-Dimethyl	2.501	2.08
Dibenzoselenophene (III)	2.418	2.18
Phenanthrene	2.397	2.21

[a] *Vs.* saturated Ag/AgCl electrode. [b] ma l. mole^{-1} mg$^{-2/3}$ sec$^{-1/6}$.

The logarithmic analysis of the polarogram of dibenzofuran gave a fairly good straight line of slope 0.085. This value compares well with the values 0.07–0.09 observed for monoelectronic reduction of aromatic hydrocarbons in DMF.[3] Since the diffusion constants are of comparable magnitude, we therefore assume that all the compounds in Table I are reduced by a one-electron transfer. A shift $\Delta E_{1/2}$ to more negative HWP was observed for all the methylated derivatives, and the magnitude of the shift depends markedly on the position of substitution.

Electronic Absorption Spectra. The spectra of dibenzofuran, dibenzothiophene, and their derivatives consist of three main absorption bands located in the ultraviolet region and displaying fine structure. Table II shows the positions of the first maximum for two absorption bands and the values of their extinction coefficients. Both bathochromic and hypsochromic shifts are observed in the dimethyldibenzothiophene series.

Discussion

Molecular Orbital Calculations. The LCAO-MO's of dibenzofuran and dibenzothiophene were calculated with the parameter values for oxygen and sulfur (p model) used in the previous discussion of the electron spin resonance spectra of the radical anions,[1] *i.e.*, $\alpha_O = \alpha + 2\beta$, $\beta_{CO} = \beta$; $\alpha_S = \alpha + \beta$, $\beta_{CS} = 0.566\beta$ (the value of β_{CS} given in ref 1 has been misprinted and should read 0.566β) where α and β are the Coulomb integral of the carbon $2p_z$ orbital, and the carbon $2p_z$–carbon $2p_z$ resonance integral, respectively. The Longuet-Higgins d-orbital model of the sulfur atom has been described and discussed in ref 1, and this discussion will not be repeated here. It will suffice to state that from the $3p_z$, $3d_{xz}$, and $3d_{yz}$ orbitals of the sulfur atom three hydrides are constructed h, g, and f, two of which, h and g, overlap well with one of the $2p_z$ orbitals on the adjacent carbon atoms while f overlaps negligibly and is not further considered in the conjugated system. The parameter values suggested by Longuet-Higgins were employed in the molecular orbital calculations, *i.e.*, $\alpha_h = \alpha_g = \alpha$, $\beta_{Ch} = \beta_{Cg} = 0.8\beta$, $\beta_{hg} = \beta$. It has been shown previously that these

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(2) G. J. Hoijtink, J. Van Schooten, E. de Boer, and J. J. Aalbersberg, *Rec. Trav. Chim.*, 73, 355 (1954); R. Pointeau, *Ann. Chim.*, 7, 680 (1962).

(3) P. H. Given, *J. Chem. Soc.*, 2684 (1958).

Table II. Ultraviolet Spectra[a]

	$^1A \rightarrow {}^1L_b$ transition[e]			$^1A \rightarrow {}^1L_a$ transition[e]		
	λ,[b] mμ	$\bar{\nu}$, cm^{-1}	Log ϵ	λ,[b] mμ	$\bar{\nu}$, cm^{-1}	Log ϵ
Dibenzofuran	301.7	33,146	3.71	249.2	40,128	4.35
2,8-Dimethyl	311.4	32,113	3.64	252.4	39,620	4.31
4,6-Dimethyl	304.5	32,841	3.77	254.0	39,370	4.33
2-Methyl	308[c]	32,470	3.70	...	...	...
2,8-Dibromo	316[d]	31,645	3.51	253.2	39,494	4.22
Dibenzothiophene	324.2	30,845	3.46	285.8	34,990	4.06
2,8-Dimethyl	332.2	30,102	3.46	291.7	34,282	4.16
3,7-Dimethyl	321.4	31,114	3.30	292.8	34,153	4.06
4,6-Dimethyl	325.1	30,760	3.59	284.2	35,186	3.99
4-Methyl	324.3	30,836	3.52	285.8	34,990	4.12
2,8-Dibromo	337.9	29,595	3.39	295.3	33,864	4.11
3,7-Dibromo	326.6	30,618	3.43	297.1	33,659	4.37

[a] Solvent ethanol. [b] First maximum on the long wavelength side of absorption band. [c] Reference 12. [d] Shoulder. [e] Classified according to ref 12.

two sets of parameter values give identical molecular orbitals for both models of the sulfur atoms when such orbitals are symmetric with respect to a plane containing the sulfur atom or atoms.[4]

The effect of a methyl group on a conjugated system is potentially twofold, inductive and hyperconjugative, but the relative significance of these two effects has been the subject of much discussion. However it can be shown by perturbation theory that if a methyl group changes the Coulomb integral or the carbon atom, r, to which it is attached by an amount $\delta\alpha_r$ then the energy of a MO Φ_i of the conjugated system is changed by an amount[5]

$$\delta\epsilon_i = c^2{}_{ir}\delta\alpha_r$$

and that for multiple substitution these effects are additive. It can further be shown that hyperconjugation produces normally only a second-order effect on the energy of Φ_i, unless its energy ϵ_i is close to that of either the bonding or antibonding carbon–hydrogen σ orbitals. For the orbitals under discussion in the compounds to be considered here this is not likely to be the case so in what follows we have treated the methyl group as a purely inductive substituent.

Polarographic Reduction Potentials. As usual, it is assumed that the additional electron occupies the lowest antibonding MO Φ_{j+1} and therefore that $E_{1/2}$ is proportional to the eigenvalue $\epsilon_{j+1} = \alpha + m_{j+1}\beta$. Since the inductive perturbation of ϵ_{j+1} is proportional to $c^2{}_{j+1,r}$, one might expect that the changes observed in $\Delta E_{1/2}$ according to the position of substitution would closely parallel the odd-electron distribution in Φ_{j+1} if the hyperconjugative effect is of second-order magnitude. The p and d model of dibenzothiophene display odd electron distributions which are entirely different from each other as can be seen in Figure 1. A good linear relationship is obtained when $\Delta E_{1/2}$ is plotted against $c^2{}_{j+1,r}$ for the set of compounds studied here when the c^2 values from the p model of dibenzothiophene are incorporated. The regression line, shown in Figure 2, is represented by the relation

$$-\Delta E_{1/2}\,(\text{mv}) = (369 \pm 39) \sum_r c^2{}_{j+1,r} + (23 \pm 7)$$

and also includes the data for a group of methylated sulfones. The odd-electron distribution of the radical anions of diphenyl sulfone, dibenzothiophene S,S-dioxide, and of thianthrene S,S,S',S'-tetroxide was studied by means of esr spectroscopy.[6] We also observed that the same set of MO parameters which was used for all sulfones to interpret the esr data gave the best interpretation of the HWP shifts measured on the methylated derivatives. Moreover, the calculated polarographic relationship was not significantly different from the one obtained independently for the molecules studied in the present paper. Inspection of Figure 2 shows clearly that the c^2 values calculated from the d model are not consistent with the experimental data.

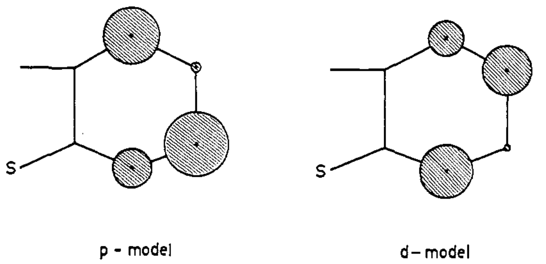

Figure 1. Odd-electron distribution in the lowest antibonding molecular orbitals of the p and d models of dibenzothiophene. The area of the circles are proportional to $c^2{}_{j+1,r}$.

The slope of the regression line allows an estimate of the magnitude of the inductive perturbation $\partial\alpha_r = h_r\beta > 0$, if it is assumed that the effect is independent of the site of the substitution ($h_r = h$ for all r). From the empirical relationship:[7] $E_{1/2} = bm_{j+1} + a$ the shift in the HWP is determined when the eigenvalue is changed by an amount Δm_{j+1}. As $\Delta m_{j+1} = h\sum_r c^2{}_{j+1,r}$, and using the slope of the regression line on Figure 2, one can write the equalities

$$\Delta E_{1/2} = b\Delta m_{j+1} = bh\sum_r c^2{}_{j+1,r} = 0.37 \sum_r c^2{}_{j+1,r}$$

It is usually admitted[8] that b is close to the true value for $-\beta$, so one obtains

$$\vartheta\alpha_r = h\beta \simeq 0.37 \text{ ev}$$

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(4) E. A. C. Lucken, *Theoret. Chim. Acta*, **1**, 397 (1963).
(5) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A191**, 39 (1947).
(6) R. Gerdil and E. A. C. Lucken, *Mol. Phys.*, **9**, 529 (1965).
(7) I. Bergman, *Trans. Faraday Soc.*, **50**, 829 (1954).
(8) G. J. Hoijtink, *Rec. Trav. Chim.*, **74**, 1525 (1955); A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1962, p 177.

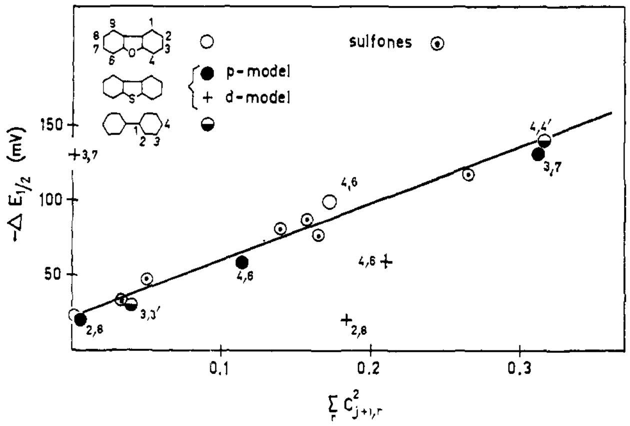

Figure 2. Dependence of the half-wave potential shifts on the inductive effect. Each number refers to the site of the substitution by a methyl group. The experimental data for dibenzothiophene are plotted *vs.* $c^2_{j+1,r}$ values calculated from both quantum mechanical models. The results for a group of related sulfones[6] are also included in the diagram.

In the prediction of the reduction potential of 9,10-dimethylbenzanthracene, Pullman, *et al.*,[9] used a Coulomb integral perturbation of the methylated carbon atoms equal to 0.285 ev.

Probably due to steric inhibition, 2,2′-dimethyl biphenyl was not reducible within the attainable potential range. This is not surprising when it is considered that the interplanar angle θ between the phenyl nuclei has been evaluated to 70° for the molecule in solution.[10] 9,10-Dihydrophenanthrene ($\theta \simeq 20°$;[11] the same as for biphenyl) may be regarded as a close representative of a "semiplanar" 2,2-dimethylbiphenyl molecule if the methylene groups are supposed to be equivalent to two methyl groups. However, the HWP shift observed for dihydrophenanthrene with regard to biphenyl is about 50 mv smaller than the one expected from Figure 2, ($c^2_{j+1,2}$ of biphenyl is 0.090). This is a fairly large discrepancy even in the present approximation.

For fluorene the expected HWP shift is observed if the methylene group is considered to be equivalent to two methyl groups.

Ultraviolet Absorption Spectra. The origin of the absorption bands of dibenzofuran, dibenzothiophene, and dibenzoselenophene has been discussed by Passerini, *et al.*[12] In the present study we attempt to correlate the shift in position of the long wavelength maximum of the parent compounds on methylation with the change in energy difference of the highest occupied and lowest unoccupied orbitals, $\epsilon_{j+1} - \epsilon_j$. This approach has often been used with success, for example by Heilbronner in his studies on the spectra of the methylazulenes.[13] According to our previous discussion on the effect of a methyl group this energy change is given by

$$\Delta(\epsilon_{j+1} - \epsilon_j) = \delta\alpha\sum_r(c^2_{j+1,r} - c^2_{j,r})$$

For the d-orbital model of dibenzothiophene $c^2_{j+1} = c^2_j$ and only second-order shifts in the spectra of the methyl derivatives should be observed. This arises because, as shown by Longuet-Higgins, the sulfur atom in the d model becomes a pseudo-ethylene molecule so that in this model dibenzothiophene is pseudo-alternant and the pairing properties of the molecular orbitals persist since $\alpha_h = \alpha_g = \alpha$, In fact, as Table III shows, quite large shifts occur and these shifts are reasonably in accord with the calculations for the p-orbital model of dibenzothiophene.

Table III. Comparison of the Shifts of the Long-Wave Absorption Band with the Calculated Δc^2 Values

Methylated derivatives	r	$\Delta\bar{\nu}$, cm^{-1}	$\sum_r(c^2_{j+1,r} - c^2_{j,r})$
Dibenzofuran[a]	2	−678	−0.117
	2, 8	−1038	−0.234
	4, 6	−305	−0.116
Dibenzothiophene	4	−9	−0.048
	2, 8	−743	−0.177
	3, 7	+269	+0.310
	4, 6	−85	−0.096

[a] For the MO parameters of dibenzofuran see Discussion.

LCAO MO calculations have shown that the magnitude of $(c^2_{j+1,r} - c^2_{j,r}) = \Delta c^2$ $(r = 2, 3, 4)$ is very sensitive to the variations of the parameter h_X in $\alpha_X = \alpha + h_X\beta$, for the range $1.5 < h_X < 2$. It is found that the spectral shifts of dibenzofuran are better accounted for if a Coulomb integral of $\alpha_O = \alpha + 1.5\beta$ is used (Table III) instead of the value $\alpha + 2.0\beta$ employed in the esr and polarographic calculations. This dependence of Δc^2 on h_X decreases enormously for $h_X < 1.5$ (case of dibenzothiophene).

Experimental Section

Materials. The samples of the heterocycles and their derivatives have the same origin as those already described.[1] Fluorene, mp 117° (Fluka, purum), phenanthrene, mp 100° (Fluka, puriss), and 4,4′-dimethylbiphenyl, mp 122° (Fluka, purum), were recrystallized and sublimed; 9,10-dihydrophenanthrene (Fluka, purum), mp 35°, was recrystallized before use. 3,3′-Dimethyl- and 4,4′-dimethylbiphenyl were prepared according to procedures given in the literature.[14,15]

Polarography. The data were obtained at 25.0° on a Polarecord Metrohm E 261 R with a capillary attached to a polarography stand E 354 for controlled drop time. The cathodic reductions were carried out in anhydrous DMF (<0.05% H_2O) with 0.15 *M* tetra-*n*-butylammonium iodide as supporting electrolyte. The reference electrode was a KCl saturated Ag–AgCl cell separated from the cathodic compartment by an agar plug and a glass frit. The resistance of the assembly which sometimes varied slightly during a single run, was measured before and after each test. We observed an average resistance of about 2000 ohms. For each compound polarograms were obtained from at least two solutions of different concentrations (10^{-3} to 3.10^{-3} *M*). The dissolved oxygen was removed by bubbling dry nitrogen through the solution during 15 min. The dropping electrode had a regulated drop time of 0.269 sec and the $m^{2/3}t^{1/6}$ value was 1.644 mg$^{2/3}$sec$^{1/6}$. The polarograms were recorded with a potential scanning of 1.000 v/min and at a chart drive speed of 250 mm/min (rapid polarography). The HWP were corrected for the *iR* drop and their mean deviation is ±0.004 mv. They were found to be independent of the

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[9] A. Pullman, B. Pullman, and G. Berthier, *Bull. Soc. Chim. France*, 591 (1950).

[10] H. Suzuki, *Bull. Chem. Soc. Japan*, 32, 1340 (1959).

[11] G. H. Beavan, D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 854 (1952).

[12] A. Mangini and R. Passerini, *Gazz. Chim. Ital.*, **84**, 606 (1954); A. Cerniani, R. Passerini, and G. Righi, *Boll. Sci. Fac. Chim. Ind. Bologna*, 75 (1954); A. Cerniani and R. Passerini, *ibid.*, 66 (1954).

[13] E. Heilbronner in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 171.

[14] N. Kornblum, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 296.

[15] M. S. Kharasch and E. K. Fields, *J. Am. Chem. Soc.*, **63**, 2316 (1941).

concentration within the range of concentrations from 0.8 × 10^{-4} to 6 × 10^{-3} *M* (observed on dibenzofuran and dibenzothiophene). The diffusion currents were corrected for the residual current and were found to be reproducible within 5% of their mean value.

Electron Spin Resonance Spectra. These were measured on a modified Microspin X-band spectrometer at room temperature. The radicals were generated within the cavity by electrolysis at mercury pool cathode, the anode and cathode compartments being separated by a Grade 3 fritted glass disk. The solvent and supporting electrolyte were the same as those employed in the polarographic measurements.

Ultraviolet Spectroscopy. The ultraviolet absorption spectra were determined in spectral grade 95% ethanol using a Cary Model 11 spectrophotometer.

Proton Magnetic Resonance Spectroscopy. Configurational Stability of Neohexyl(3,3-dimethylbutyl) Organometallic Compounds[1]

Michal Witanowski and John D. Roberts

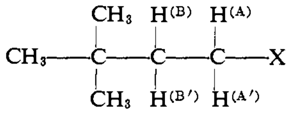
Contribution No. 3251 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California.

Received September 27, 1965

Abstract: The proton resonance spectra of dilute ether solutions of neohexyl(3,3-dimethylbutyl) organometallic compounds have been investigated as a function of temperature as a means of determining their configurational stabilities. Neohexyllithium, dineohexylmagnesium (free from magnesium chloride), and dineohexylzinc appear to undergo the inversion of configuration at the α-methylene groups at various temperatures. The activation energies for inversion are approximately 15, 20, and 26 kcal. for the lithium, magnesium, and zinc compounds, respectively. Inversion appears to be a first-order process for the lithium and magnesium compounds. This fact and the general dependence of the inversion rate on the nature of the metal suggest a dissociation–recombination mechanism (SE1). Trineohexylaluminum and dineohexylmercury were found to be configurationally stable up to 150–160°. The chemical shifts of the CH_2–CH_2 groupings in these organometallic compounds can be correlated with the electronegativity of the metal atoms.

In an extension of previous work[2] on the configurational stability of primary Grignard reagents, we have studied other kinds of organometallic compounds and also carried out a more detailed investigation of dineohexylmagnesium prepared free of magnesium halides.

The *modus operandi* was the same as before, being based on the fact that neohexyl compounds (I) which are configurationally stable at the α carbon show proton n.m.r. spectra for the CH_2–CH_2 groups of the AA′BB′ type,[2,3] but if inversion occurs at the α carbon at a rate which is rapid on the n.m.r. time scale, then the spectra are of the simple A_2B_2 type. In general, the AA′BB′ spectrum presented by these compounds when the configurations are stable may be relatively easily analyzed, a particular advantage is the symmetry of the spectrum, which permits a complete analysis even if the A (or B) part is hidden under the solvent resonances. The procedure used for obtaining rate constants for inversion of configuration from line shapes was the same as before.[2b]



$$\begin{array}{ccccccc} & & CH_3 & & H^{(B)} & & H^{(A)} \\ & & | & & | & & | \\ CH_3 & — & C & — & C & — & C — X \\ & & | & & | & & | \\ & & CH_3 & & H^{(B')} & & H^{(A')} \end{array}$$

I, X = Li, Mg, Zn, Al, and Hg

Results and Discussion

The proton resonance spectra at 60 Mc.p.s. of ether solutions of neohexyllithium (−18°), dineohexylmagnesium (30°), dineohexylzinc (30°), trineohexylaluminum (30°), and dineohexylmercury (30°) show typical AA′BB′ patterns for the methylene resonances (Figures 1–5). For the first four compounds, the β-methylene signals are partly obscured by the methyl peaks of ether, while with dineohexylmercury, the α-methylene signal is partially hidden. Reducing the temperature to −35° does not introduce any observable changes in these spectra.

The analysis of the spectra was carried out in the usual way[4]; the notation for the couplings in I being $K = J_{AA'} + J_{BB'}$, $L = J_{AB} - J_{AB'}$, $M = J_{AA'} - J_{BB'}$, $N = J_{AB} + J_{AB'}$. Six transitions of the AA′ (or BB′) part of the AA′BB′ system are independent of *K*; two of them immediately give *N* and, in combination with their symmetrical counterparts in BB′, the chemical shift. The remaining four, together with their counterparts in BB′, give *L*, *M*, and the chemical shift, thus providing a check on the assignments. The final values of the spectral parameters were chosen on the basis of comparisons with theoretical spectra, plotted by a computer for several values of *K*. The results are summarized in Table I, along with values of the

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[1] Supported in part by the National Science Foundation and the Office of Naval Research.

[2] (a) G. M. Whitesides, F. Kaplan, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 2167 (1963); (b) G. M. Whitesides, M. Witanowski, and J. D. Roberts, *ibid.*, **87**, 2854 (1965).

[3] The spectra closely approximate AA′XX′ when the chemical shift difference is large.

[4] See, for example, K. B. Wiberg and B. J. Nist, "Interpretation of N.M.R. Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, pp. 309–317.