starting materials. Some of the thiols used in this work were gifts of the following companies: Pitt Consol

Chemical, Air Reduction Chemical, Evans Chemetics, Inc., and E. I. du Pont de Nemours.

Electronic Spectra of Organolithium Compounds

BY RICHARD WAACK AND MARY A. DORAN

The absorption maxima in the ultraviolet and visible spectra of 16 organolithium compounds in THF solution and molar absorption coefficients are reported. A convenient technique is described for measuring the spectra of these oxygen- and moisture-sensitive systems that is not restricted by vacuum operations. These data are discussed in light of the previous literature on the spectra of carbanions and with reference to the concepts expressed by molecular orbital theory.

A study of electronic absorption spectra and their interpretation in terms of the molecular orbital theory is proving a fruitful approach to an understanding of electronic structure. Of equal importance are the extremely useful analytical applications of electronic spectra. It is with these objectives that we initiated a study of the ultraviolet and visible spectra of organolithium compounds. In this first part of these studies, we report spectral data for 16 organolithium compounds.

Experimental

The extreme sensitivity of organolithium compounds to oxygen and moisture necessitates the use of a closed absorption cell, yet it is an advantage to be able to add reagents to the cell at will without the restrictions of break seals or other vacuum operations. The absorption cell apparatus used in these studies consists of a 0.2-cm. quartz absorption cell sealed to a side arm of a round bottom flask, as shown in Fig. 1. The apparatus was connected to a high vacuum system for alternate degassing and flushing with argon. Access to the flask was through a second side arm closed by a rubber syringe cap. The organolithium compounds were handled via a Hamilton gas-tight syringe,[1] protected by an argon atmosphere. A slight positive argon pressure was maintained when piercing the rubber cap. A removable quartz spacer sealed into the side arm permitted us to decrease the cell path length to 0.015 cm. Spectra were measured with a Cary model 14 recording spectrophotometer. The extinction coefficients were determined by a difference technique, in which after a base absorption curve for the species being measured was established, an additional amount of organolithium compound was added, and the resulting difference in optical density used to calculate the extinction coefficient.[2] Concentrations of the organolithium compounds were determined by titration of total alkali. Each experiment was completed by the addition of a few drops of ethanol, resulting in complete loss of the long wave length absorption. In some cases the spectrum of the hydrocarbon was measurable.

The tetrahydrofuran (THF) solvent was purified by distillation from lithium aluminum hydride under an argon atmosphere. So treated, it was optically transparent to ~215 mμ. The organolithium compounds were obtained as follows: n-Butyllithium was obtained from Foote Mineral Corp. and Lithium Corp. of America in hydrocarbon solution. sec-Butyllithium and t-butyllithium in hydrocarbon solution were obtained from Lithium Corp. of America. Ethyllithium in benzene solution was supplied by Orgmet, Hampstead, N. H. Phenyllithium which we prepared[3] from lithium metal and bromobenzene in ether, from chlorobenzene in THF,[4] from diphenylmercury in THF or in ether[5] gave identical results to phenyllithium in ether solution obtained from Anderson Chemical Co. and Lithium Corp. of America. Vinyllithium and allyllithium were prepared

in n-hexane from the corresponding tetrasubstituted tin compounds via transmetalation with n-butyllithium.[6] The insoluble organolithium was twice washed with hexane before dissolving it in THF. Benzyllithium was prepared from tribenzyltin chloride and phenyllithium in ether,[3,7] chilling the reaction after 2 hours to precipitate the tetraphenyltin and filtering, and from dibenzylmercury and lithium metal[5] in THF, shaking for 3–4 hours. α-Methylbenzyllithium and methylallyllithium were prepared from the corresponding triphenyltin compounds[8] via transmetalation with phenyllithium in ether in the previous manner.[3] 1-Phenyl-2-propenyllithium was prepared by metalating allylbenzene with n-butyllithium in THF solution. The spectrum of terminated [EtOH] 1-phenyl-2-propenyl-lithium solution shows >85% conversion of the allylbenzene to β-methylstyrene, in agreement with previous findings.[9] Triphenylmethyllithium was prepared in THF from freshly recrystallized[10] triphenylmethyl chloride and metallic lithium at 0°, filtering after stirring for 4 hours. The two substituted diphenylmethyllithium species were produced via the reaction of the appropriate organolithium compound and 1,1-diphenylethylene. Polystyryllithium and poly-α-methylstyryllithium were formed by adding n-butyllithium to the respective monomer in THF solution. The concentration of the latter monomer was well below its equilibrium value.[11] Thus, the initiation product 1-methyl-1-phenyl-n-hexyllithium should predominate. The olefins were vacuum distilled from CaH$_2$.

Several of the organolithium compounds were carbonated to the corresponding acids or ketones. Phenyllithium gave benzoic acid in 87% yield; benzyllithium gave phenylacetic acid in 65% yield; vinyllithium gave only a poor yield of acrylic acid, but on carbonation of its reaction product with 1,1-diphenylethylene a 68% yield of 2,2-diphenyl-4-pentenoic acid was recovered; hydrolysis of vinyllithium gave ethylene quantitatively, identified by mass spectroscopy.

Allyllithium was characterized by its reaction with styrene and near infrared analysis of the polymer showing a single vinyl group per polymer chain. The recovery of tetraphenyltin was 95–100% in the preparations of benzyllithium, α-methylbenzyllithium and methylallyllithium. The recovery of mercury was 95–100% in the preparation of phenyllithium and benzyllithium from the corresponding mercury compounds.

Results

The wave lengths of the absorption maxima of the major bands we observe in the spectrum of each organolithium compound and the molar extinction coefficients are reported in Table I. Prior literature data are summarized in the right-hand column of Table I.

Some of the organolithium compounds were prepared in solvents other than THF. In such cases the other solvents were present in 5–10% concentration. We feel these solvent mixtures do not differ appreciably from THF in their ability to solvate the carbanions.[11a] This is

(1) Obtained from Hamilton Co., Inc., Whittier, Calif. These were found to be much more effective for handling the organolithium compounds than the usual ground glass syringes, which were used in the early phase of this work.

(2) The extinction coefficients given in Table I are reproducible within the limits ±10% from one experiment to the next or between different preparations of organolithium compounds. However, in view of the sensitivity of these compounds to impurities, we feel it is better to consider these extinction coefficients as "best estimates" (minimum values) and not as final values.

(3) These preparations will be described in detail in a subsequent publication.

(4) H. Gilman and T. S. Soddy, J. Org. Chem., 22, 565 (1957).

(5) G. Wittig, F. J. Meyer and G. Lange, Liebigs Ann., 517, 167 (1951).

(6) D. Seyferth and M. A. Weiner, J. Am. Chem. Soc., 83, 3583 (1961).

(7) H. Gilman and S. D. Rosenberg, J. Org. Chem., 24, 2063 (1959).

(8) Kindly supplied to us by Dr. F. C. Leavitt and Miss Priscilla A. Carney of this Laboratory.

(9) T. W. Campbell and W. G. Young, J. Am. Chem. Soc., 69, 688 (1947).

(10) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 846.

(11) H. W. McCormick, J. Polymer Sci., 25, 488 (1957).

(11a) For convenience we use the term carbanion or anion in referring to organolithium compounds. This is not meant to imply that the organolithium compounds are completely ionized. Although the true nature of organolithium compounds in solution is not known, they are believed to exist as ion pairs or aggregates of ion pairs.

TABLE I
ELECTRONIC ABSORPTION SPECTRA OF ORGANO-ALKALI METAL COMPOUNDS

	A. Organolithium compounds in tetrahydrofuran solution			B. Literature data
Organolithium compound	Principal absorption λ_{max}, mμ	log ϵ (λ)	Color of solution	Alkali metal; λ_{max} (log $\epsilon\lambda$); solvent; ref.
Ethyllithium[a]	Incr. end. abs., no max.	1.7 (300)	Pale straw	
n-Butyllithium[b]	Incr. end. abs., no max.	1.5 (300)	Pale straw	
s-Butyllithium	c		Yellow	
t-Butyllithium[b]	d	..	Orange-yellow	
Allyllithium	315	3.66	Yellow	Na; 375 (3.5); THF[12] 310–320[h]
Methylallyllithium[e,f]	291	3.79	Green-yellow	
Benzyllithium	330	3.98	Yellow	{Na; 510 (3.3); THF[12] 330–350[h] Na; 355 (4.08); THF[13]
α-Methylbenzyllithium[e]	333	4.08	Brown-yellow	
Polystyryllithium[g]	335	4.00	Red	{Li; 340 (4.08); THF[14] Na; 343 (4.06); THF[14,15] Na; 340 (....); THF[18]
Poly-α-methylstyryllithium (1-methyl-1-phenyl-n-hexyllithium)	340	..	Red	{K[i]; 338 (4.26); THF[18] Na[j]; 350 (....); THF[16]
Phenyllithium	292	2.88[l]	Pink	
	268	2.99	Yellow	
	261	3.02		
Vinyllithium	280 (sh)	2.71[l]	Light yellow	
1-Phenyl-2-propenyllithium	395	4.38	Red	K; 420 (4.18); liq. NH₃[17]
1,1-Diphenyl-n-hexyllithium	496	4.26	Deep red	{Li; 425 (4.28); benzene[18] ....; 434[k] (4.34); Et₂O[19] K; 440[k] (4.6); liq. NH₃[17]
	315	3.5		
1,1-Diphenyl-3-butenyllithium[m]	495	..	Deep red	{Na; 475 (4.18); Et₂O[19] 410 (3.87)
Triphenylmethyllithium	500	4.27	Brilliant red	{Na; 478 (....); Et₂O[20] 393 (....)
	425	3.97		{K; 495 (4.40); liq. NH₃[17]

[a] Solvent is ~5% benzene in THF. [b] Solvent is ~5% n-hexane in THF. [c] sec-Butyllithium, which is supplied in commercial heptane, shows an absorption maximum at 325 mμ in THF, which results from the reaction of s-C₄H₉Li with olefin impurities; e.g., allylic H⁺ abstraction, in the heptane and is promoted by the good solvating property of THF; s-C₄H₉Li reacts readily with THF. [d] t-Butyllithium reacts rapidly with THF causing the solution to quickly lose color. We were unable to obtain a reliable spectrum. [e] Solvent is ~10% diethyl ether in THF. [f] An equilibrium mixture of α- and γ-methylallyl-Li. [g] From the reaction of excess styrene monomer with butyllithium. The extinction coefficient was based on complete utilization of the added BuLi. [h] Read from graph of spectrum, reported to be caused by impurities. [i] Cumylpotassium. [j] Disodium α-methylstyrene tetramer. [k] Diphenylmethyl. [l] Not corrected for end absorption. [m] Spectrum measured in 1-cm. path length cell, not recorded below 350 mμ.

substantiated by the identity of the spectrum of phenyllithium or of benzyllithium with and without small amounts of ether present.

Alkyllithium.—The normal alkyllithium compounds, as one might expect, have no discrete bands and show only increasing end absorption. The sec-butyllithium (and presumably the tert-butyllithium; see footnotes Table I) also do not have absorption maxima in the near ultraviolet. The possibility of near ultraviolet absorption by sec- and tert-butyllithium compounds was suggested by a recent report of absorption maximum ~295 mμ for sec- and tert-alkylcarbonium ions.[21] This has recently been questioned, however.[22] Primary carbonium ions, like the n-alkyllithiums, have no absorption maxima in the near ultraviolet.[21]

Conjugated Organolithiums.—Our observation of the absorption maximum of allyllithium is in agreement with a theoretical estimate of 326 mμ for the absorption of allylcarbanion.[12] The spectrum of allylsodium is reported[12] to contain two absorption maxima, a short wave length band comparable to our finding for allyllithium and a longer wave length band not evident in the spectrum of allyllithium. This longer wave length absorption could be caused by a decomposition product,

as suggested below for Kuwata's[12] findings for the spectrum of benzylsodium.

There is good agreement between the spectrum of benzyllithium, α-methylbenzyllithium, polystyryllithium and poly-α-methylstyryllithium. This leaves little doubt that in the anionic polymerization of styrene and similar monomers the propagating species is the substituted benzyl anion, as has been pointed out by others.[13] Calculation of the transition energy for the benzyl anion by both molecular orbital method and free electron model predicts it to have an absorption maximum at 328 mμ,[23] in agreement with our findings. Another theoretical estimate of 462 mμ for the benzyl ion absorption appears high in view of our data.[24] A report of 510 mμ for the absorption maximum of benzylsodium is too high compared to our findings, but a shorter wave length absorption reported by these authors[12] to be an impurity is in agreement with our findings for benzyllithium and with that of others for the sodium analog.[13] Their reported long wave length absorption[12] was perhaps caused by aging of the benzylsodium solution as shown by Levy, et al.,[13] who find a new band appearing at 485 mμ in aging benzylsodium solution. Our experience with benzyllithium is similar, but not identical, in that on aging three days at room temperature a new weaker band at 545 mμ appears in the spectrum, while the typical strong band shifts to 322 mμ. In the shorter time of 24 hours, we found the spectrum of benzyllithium and α-methylbenzyllithium to show no change. A similar time-dependent transformation has been reported for the spectrum of polystyrylsodium.[16,25] We find that the spectrum of poly-

(12) K. Kuwata, Bull. Chem. Soc. Japan, 33, 1091 (1960).
(13) R. Asami, M. Levy and M. Szwarc, J. Chem. Soc., 361 (1962).
(14) D. J. Worsfold and S. Bywater, Can. J. Chem., 38, 1891 (1960).
(15) D. J. Worsfold and S. Bywater, J. Chem. Soc., 5234 (1960).
(16) M. Szwarc, M. Levy, D. J. Worsfold and S. Bywater, Polymer, 1, 515 (1961).
(17) V. Astaf'ev and A. I. Shatenshtein, Optics and Spectroscopy (English Ed.), 6, 410 (1959).
(18) A. G. Evan and D. B. George, Proc. Chem. Soc., 144 (1960).
(19) S. F. Mason, Quart. Rev., 15, 336 (1961).
(20) L. C. Anderson, J. Am. Chem. Soc., 57, 1673 (1935).
(21) J. Rosenbaum and M. C. R. Symons, Mol. Phys., 3, 205 (1960).
(22) N. C. Deno, et al., J. Am. Chem. Soc., 84, 2016 (1962).

(23) W. Bingel, Z. Naturforsch., 10A, 476 (1955).
(24) H. C. Longuet-Higgins and J. A. Pople, Proc. Phys. Soc. (London), A68, 591 (1955).

styryllithium shows an analogous change. This type of transformation is particularly facile when vinyllithium or phenyllithium are used to initiate the styrene polymerization, although as above we find the product shows different absorption. For example, with vinyllithium-initiated styrene, overnight standing results in a new strong band at 415 mμ and weaker absorption at 565 mμ.

The small differences between the absorption of allyllithium and benzyllithium suggest a similar chromophoric behavior of a vinyl substituent and a phenyl substituent in conjugation with the anionic center. A second phenyl group on the α-carbon of benzyllithium, forming diphenylmethyllithium (I), results in an appreciable red shift in the absorption. By comparison, the absorption of 1-phenyl-2-propenyllithium (II) is only red shifted ~one-third as much, relative to benzyllithium. This is in contrast to the behavior of the potassium salts in liquid ammonia solution where λ_{max} of II was found to be only ~5% less than λ_{max} of I.[17] A third phenyl substituent has only a small effect on the position of the longest wave length absorption, although the shorter wave length band is shifted considerably to the red. The explanation may be that only two of the phenyls may participate in conjugation (at a given instant) to form the chromophore responsible for the absorption. The third phenyl acts as a cross-conjugated electron donor. The absorption maxima previously reported for diphenylmethyl anion (I) in diethyl ether[19] or 1,1-diphenyl-n-hexyllithium (III) in benzene[18] are at appreciably shorter wave lengths that we find in THF solution. Our measurements of 1,1-diphenyl-n-hexyllithium in ether or benzene solution, however, are identical with these previous values. The differences are caused by a solvent-induced shift of the absorption maximum.[26] Apparently the alkyl substituent on II has little effect on the spectrum. This is further illustrated by the similarity of the absorption of 1,1-diphenyl-3-butenyllithium to that of I and II. A solvent effect is also found in the spectrum of triphenylmethyl anion as illustrated by comparing our data in THF with the previous observations in diethyl ether.[19,20]

Methyl Substitution.—Methyl or alkyl substitution of a conjugated molecule usually causes a small bathochromic shift in the conjugation bands.[27] Such red shifts are evident in the spectrum of benzyllithium (λ_{max} 330 mμ) on α-methyl substitution; e.g., α-methylbenzyllithium (λ_{max} 333 mμ). Dialkyl substitution, e.g., 1-methyl-1-phenyl-n-hexyllithium (λ_{max} 340 mμ), causes a further red shift in absorption maximum. In contrast, a terminal methyl on the allyl carbanion results in a hypsochromic shift in absorption maximum. This appears to be a case where methyl substitution decreases the importance of resonance structures, since the two resonance forms of methylallyllithium are not expected to be of equal energy. On the other hand, α-methyl substitution on the benzyl carbanion would be expected to favor resonance by making structures with the charge on the ring more equal in energy to the primary resonance form. We are exploring these ideas by examining the spectra of other methyl-substituted allyl and benzyl carbanions. The similarity of the extinction coefficients of allyl and methylallyl is noteworthy.

sp^2 Organolithium Compounds.—The spectra of phenyllithium and vinyllithium are similar in appearance. Both spectra occur superimposed on increasing end absorption. The phenyllithium spectrum has a
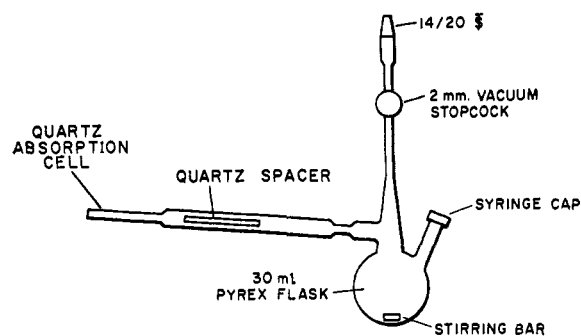

Fig. 1.—Apparatus for electronic spectral measurements in inert atmosphere.

well defined maximum, having in addition to the principal band two sharp bands in the usual phenyl region. We have established that these two bands are not benzene absorption resulting from hydrolysis of phenyllithium, as their extinction is much too high and the ratio of absorption at 261 to 292 mμ is approximately constant for different methods of preparing the phenyllithium. The vinyllithium absorption is only a shoulder superimposed on the end absorption. The absorption observed for these species, e.g., phenyllithium, is at rather long wave length for a carbanion having no charge delocalization. This can be rationalized, however, by comparing phenyl carbanion to its isoelectronic pyridine. The negative charge of the phenyl anion will lower the effective electronegativity of the negatively charged carbon, and also lower somewhat the effective electronegativity of the adjacent carbons. Thus, the π-electrons and the lone pair electrons of the phenyl anion are more shielded from the positively charged molecular frame than in neutral benzene or pyridine.[28] Usually n → π^* transitions are of lower energy. Pyridine has both non-bonding electrons and π-electrons. Its light absorption is due to an n → π^* transition (~286 mμ in vapor) or π → π^* (~261 mμ in vapor).[29] Presumably the phenyllithium absorption is due to a similar transition, but it is displaced to longer wave length because the positive potential field acting on the electrons is reduced.[30,31] A similar absorption in vinyllithium is perhaps comparable to the absorption of the isoelectronic >C=N—system, (λ_{max} ~230 mμ for alkyl substituted)[32] again presumably shifted to longer wave length owing to the reduction of the π-electron potential field by the negatively charged carbon.

Gegenion Effect.—Comparing our results with the literature values for the sodium derivatives, a small bathochromic shift in the spectrum of the polystyryl anion of 5–8 mμ is apparent with increasing size of the gegenion from lithium to sodium. A similar small red shift, of 10 mμ, is evident in the spectrum of poly-α-methylstyryl anion with a change in the gegenion from

(25) G. Spach, M. Levy and M. Szwarc, J. Chem. Soc., 355 (1962).

(26) R. Waack and M. A. Doran, J. Phys. Chem., **67**, 148 (1963).

(27) F. A. Matsen, "Chemical Application of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, p. 696.

(28) Because they experience a lower potential field the π-electrons of the phenyl anion are less firmly bound (i.e., the π-electron bonding orbitals are raised relative to the antibonding orbitals) and should be more easily excited to a higher electronic state. The lone pair electrons (consider a completely ionized phenyllithium) are also more loosely bound than in the isoelectronic pyridine, since the negatively charged carbon has a much diminished effective electronegativity.

(29) H. P. Stephenson, J. Chem. Phys., **22**, 1077 (1954).

(30) Bathochromic shifts in the spectrum of fluorobenzene, relative to benzene, has been attributed to this same effect of negative charge migration into the ring. However, the effect is small, ~2 mμ; see H. Sponer, J. Chem. Phys., **22**, 234 (1954). Bathochromic shifts in the spectra of other halobenzenes are also attributed to mesomeric release of electrons by the halogen; see W. F. Forbes, Can. J. Chem., **39**, 2295 (1961). The bathochromic effect of increased negative charge in the ring is also illustrated by the spectral red shift between phenol and phenoxide ion.[31]

(31) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 289.

(32) L. Ferguson, Chem. Rev., **43**, 408 (1948).

lithium to sodium. Kuwata[12] found a small bathochromic shift in absorption maximum as the ionization potential of the alkali metal gegenion decreases, suggesting to him that the anion and gegenion behave as partners in an intramolecular charge transfer spectra. In a somewhat different system, the alkali metal benzophenone ketyl,[33] an increase in the size of the gegenion was found to result in a 25–35 mμ bathochromic shift in absorption maximum. These authors attribute the linear correlation found between the frequency of the absorption maximum and the radius of the gegenion to a decrease in the perturbation of the energy levels of the anion by the cationic field as the cation size increases. In another system, the alkali metal aromatic hydrocarbon radical-anions, the spectrum is reported to show no change between a lithium and sodium gegenion, but ~5 mμ bathochromic shift occurs with potassium.[34] Thus, the behavior to be expected is that increasing size of the gegenion usually causes a small bathochromic shift in absorption maximum.

Discussion

In every organolithium derivative studied, the absorption is at considerably longer wave length than it is in the corresponding hydrocarbon. This is generally believed to be the result of increased electron delocalization in the ion,[35] but the fractional negative charge on the ion is also expected to be a contributing factor. In the majority of these organolithium compounds electron delocalization via π- or σ-electrons (via hyperconjugation as discussed for sec-alkyl ions) is an important factor in their electronic structure. The extent of such conjugation is more restricted in the corresponding hydrocarbon. Resonance usually causes a lowering of the potential energy of both the ground and excited states, with respect to the non-delocalized (or less delocalized) system. The contribution of resonance is, in most instances, greater in the excited state than in the ground state; thus the energy of the former is lowered more by resonance than that of the latter. Also, electron delocalization in an odd alternant hydrocarbon[36] creates a new non-bonding zero energy π-orbital which is midway between the highest bonding and lowest antibonding orbitals of the even alternant component parts.[24] Consequently, the transition energy for odd alternant ions is predicted to be roughly half that of the lowest energy transition in the corresponding hydrocarbon.[37] An additional effect (perhaps most important when delocalization is not possible) is the reduction of the effective electronegativity of the carbon atom skeleton of the organolithium species by virtue of its partial negative charge. This causes the π-electrons to

be less firmly bound, hence more easily excited. For these reasons, the first electronic transition of the anion should occur, as observed, at appreciably longer wave length than the lowest energy transition in the corresponding hydrocarbon.

Both the Hückel and self-consistent field molecular orbital treatments predict (to a first approximation) that the transition energy for the long wave length absorption of the anion and cation, of an even or odd alternant hydrocarbon, should be similar in energy.[38] This prediction by molecular orbital theory results from the antibonding π-orbitals in such molecules being a mirror image of the bonding orbitals. The odd alternant molecule has a central zero energy non-bonding orbital. Because the difference in charge will doubtless alter the effective electronegativity of the carbon atoms and so change the molecular potential field,[39] experimentally, the absorption of the anion and cation would not be expected to be identical, but should be similar. A good example supporting this prediction is the almost identical absorption reported for the cation and anion derived from the reaction of 1,1-diphenylethylene with strong acid (λ_{max} 425 mμ in H_2SO_4) or strong base (butyllithium in benzene λ_{max} 425 mμ).[18] We find, however, in THF this same anion has λ_{max} 495 mμ, which shows solvent effects can be important in making such comparisons. Other comparisons have been illustrated recently.[19,40] Comparing our carbanion data with that for the spectra of carbonium ions shows striking agreement between methylallyl carbonium ion,[41] λ_{max} 290 mμ H_2SO_4, and crotyllithium λ_{max} 291 mμ. The agreement is not as good between the allyl cation,[41] λ_{max} 273 mμ H_2SO_4, and allyllithium, λ_{max} 315 mμ. The absorption reported for the benzyl cation,[42] λ_{max} 470 mμ H_2SO_4, is not at all near that of benzyllithium, λ_{max} 330 mμ, but is more like the absorption observed for aged solutions of benzylsodium,[13] λ_{max} 485 mμ. Progressive methyl substitution of benzyl causes the absorption of the corresponding anions and cations to become more similar, e.g., α-methylbenzyl cation,[42] λ_{max} 435 mμ H_2SO_4, compared to α-methylbenzyllithium, λ_{max} 333 mμ, and α,α-dimethylbenzyl cation, λ_{max} 390 mμ H_2SO_4, compared to 1-phenyl1-methylhexyllithium, λ_{max} 340 mμ. Good correspondence between spectra of positive and negative radicals-ions of alternant hydrocarbons has also been reported.[43] This prediction of MO theory, of a correspondence between electronic spectra of organic cations and anions, is supported by experimental data. It is not, however, without exception. Also solvation is found to have a pronounced effect on the relative positions of the absorption of cations and anions. Thus, it is still questionable if the observed agreement is real or fortuitous.

(33) H. V. Carter, B. J. McClelland and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960).

(34) E. DeBoer and S. I. Weissman, *Rec. trav. chim*, **76**, 824 (1957).

(35) E. A. Braude, "Chemistry of Carbon Compounds," E. H. Rodd, Ed., Elsevier Publ. Co., New York, 1951, p. 91.

(36) R. Daudel, R. Lefevre and C. Moser, "Quant. Chem., Methods and Applications," Interscience Publ., New York, N. Y., 1959, p. 57.

(37) M. J. S. Dewar, Chemical Society Special Publ. No. 4, 1956, p. 78.

(38) D. P. Craig, Chemical Society Ann. Rept., 1958, p. 173.

(39) A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron*, **5**, 149 (1959).

(40) R. Grinter and S. F. Mason, *Proc. Chem. Soc.*, 386 (1961).

(41) J. Rosenbaum and M. C. R. Symons, *J. Chem. Soc.*, 1 (1961).

(42) J. A. Grace and M. C. R. Symons, *ibid.*, 958 (1959).

(43) W. I. Haibersberg, G. J. Hoijtink, E. L. Mackor and W. P. Weijland, *ibid.*, 3049 (1959).