

atom, could also be involved. Exner and Steiner¹¹ have reported sufficient data to suggest that the potassium *tert*-butoxide formed from reference alcohol 4 could be about half associated and that the methoxide salt would be more so. Likewise, we find strong indications of ion pairing from effects of cation variation on ΔH_D^{DMSO} in our system. We are thus unable at this time to describe the respective roles of counterion and solvent in determining what we have referred to grossly as solvation energies.

In the course of a systematic extension of this structure-reactivity study of about 20 alcohols, we have found that ΔH_D^{DMSO} correlates rather well with Taft's σ^* aliphatic substituent constants. The deprotonation reaction becomes progressively less exothermic as the aliphatic bulk of ROH is developed in conformity with previous studies of alcohol acidities in solution¹¹ but contrary to results in the gas phase. This has the important implication that in this series of compounds the correlation of ΔH_D^{DMSO} with σ^* is determined primarily by changes in solvation energy rather than changes in the gas-phase potential energies of ROH or RO⁻.

Tri-*tert*-butylcarbinol was prepared by the method of Bartlett and Lefferts¹² and di-*tert*-butylcarbinol by LiAlH₄ reduction of di-*tert*-butyl ketone. Neopentyl alcohol was commercial material (Aldrich).

All three solid alcohols were triply sublimed to give melting points in agreement with literature values and provided spectra, both pmr and ir, supporting their structures. Evidence that clean deprotonation occurred was obtained from pmr spectra of the alkoxide solutions which were identical with those of the alcohols in every way save for the absence of an OH peak.¹³

Completeness of deprotonation is suggested, but not proved, by the reported pK_a 's¹⁴ (28.3–29.2) in this medium whose H_- is about 33. Also, it was shown routinely that the observed heats of deprotonation in the working range of 10⁻³ to 10⁻² M were independent of alcohol concentration. Thus complications from homoconjugate ion (ROH ··· OR⁻) formation¹¹ are unlikely.

In this connection the very high solvation energy of hydroxide ion and the very low gas phase acidity of water are intriguing. We have noted elsewhere² the low basicity of water and the implied high solvation energy of H₃O⁺ into aqueous media. In view of the very low basicity and acidity of separated water molecules in the gas phase,¹⁵ the high autoprotolysis constant of liquid water implies a remarkable ability of this extraordinary medium to solvate its lyonium and lyate ions. This fact, so essential to biophysical processes, is illustrated here with great force.

(11) See J. H. Exner and E. C. Steiner, *J. Amer. Chem. Soc.*, **96**, 1782 (1974), for discussion and key references.

(12) P. D. Bartlett and E. B. Lefferts, *J. Amer. Chem. Soc.*, **77**, 2804 (1955). Yields were considerably improved by use of tetramethylethylenediamine to complex the lithium ion.

(13) In preliminary discussions of these data we erroneously reported that the large exothermic reaction of tri-*tert*-butylcarbinol was due to deprotonation. This conclusion was based on superimposable pmr spectra of reactants and products but is controverted by a recovery experiment from high dilution. The details of this reaction will be presented in a subsequent report. Alcohols 5 and 6 were completely recoverable.

(14) C. D. Ritchie in "Solute-Solvent Interactions," Marcel Dekker, New York, N. Y., 1969.

(15) C. D. Ritchie and R. E. Uschold, *J. Amer. Chem. Soc.*, **89**, 1721 (1967), have deduced that water is both a very weak acid and base in DMSO.

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(16) Alfred P. Sloan Fellow, 1973–1975.

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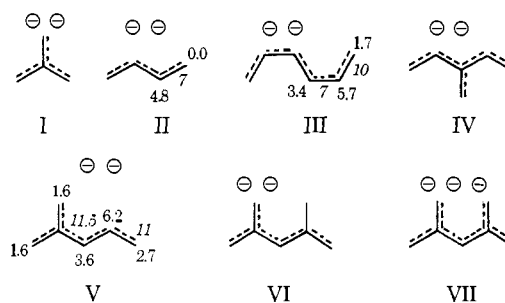
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Allylic Di- and Trimetalation of Some Simple Alkenes and Dienes¹

Sir:

Dimetalation of isobutylene gives the Y-shaped dianion I (possibly aromatic²).³ 1,3,6-Cyclononatriene dimetalates to produce homocyclooctatetraene dianion (homoaromatic).⁴ To learn whether aromatic or homoaromatic stabilization is required for dimetalation of alkenes, we attempted the preparation of further dianions, including some linear acyclic ones which definitely lack aromaticity. We wish to report the preparation of four new dilithiated species II, III, V, and VI, and one trilithiated substance VII; though



depicted as anions for convenience, these substances may contain at least one covalent carbon-lithium bond.

Metalation was carried out using 2 equiv (three for the preparation of VII) of *n*-butyllithium in 2 equiv of tetramethylethylenediamine (TMEDA) under argon at 25° for 1–4 days. Higher proportions of TMEDA gave less dianion and more TMEDA cleavage products. Conjugated dienes were unsuitable precursors due to competing addition, but monoenes and unconjugated dienes were successfully used. II was prepared from 1-butene and (*Z*)- and (*E*)-2-butenes, showing that an

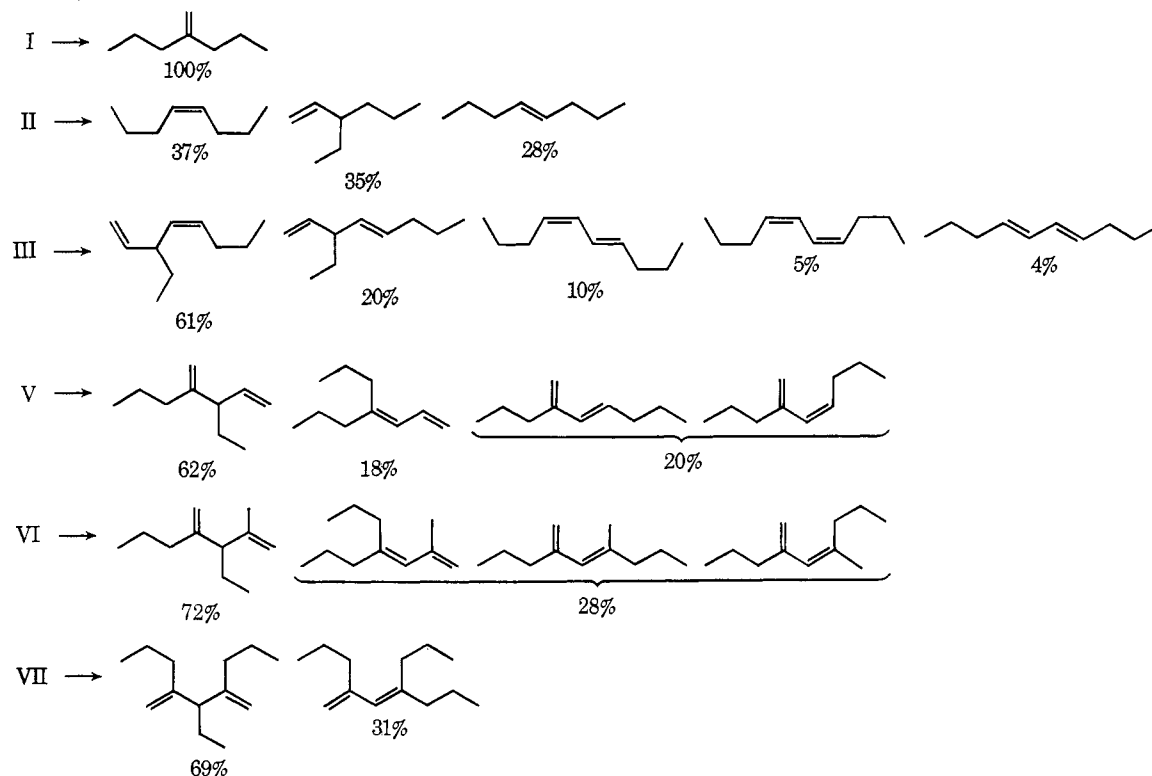
(1) Presented in part at the First Fall Organic Conference, American Chemical Society, N. Falmouth, Mass., Sept 30, 1973, Abstracts, p 35.

(2) P. Gund, *J. Chem. Educ.*, **49**, 100 (1972).

(3) J. Klein and A. Medlik, *J. Chem. Soc., Chem. Commun.*, 275 (1973).

(4) M. Barfield, R. B. Bates, W. A. Beavers, I. R. Blacksborg, S. Brenner, B. I. Mayall, and C. S. McCulloch, unpublished results.

Scheme I. Alkylation Products from Di- and Trianions



allyl anion bearing an alkyl substituent on carbon 1 can be metalated at that carbon.⁵ The preparation of III and V but not IV from the corresponding 1,4-dienes⁶ shows the feasibility of metalating pentadienyl anions⁷ containing alkyl substituents at positions 1 and 2 but not 3; in these cases, the second metalation is ~ 100 times slower than the first. Interestingly, III was formed more rapidly from 1,5-hexadiene ($\sim 100\%$ in 4 hr); the first metalation is slower in this case, so the second metalation, *i.e.*, of 1-allylallyl anion, must be very fast. VI and VII are di- and trimetalation products, respectively, of 2,4-dimethyl-1,4-pentadiene.⁶

Evidence for di- and trimetalation comes from nmr spectral observations and alkylation results. Obtaining the spectral parameters was complicated by overlap with solvent and monoanion absorptions and in some cases by low solubility of the higher metalation products, but, in the cases of II, III, and V, the pmr shifts (δ) and approximate coupling constants (hertz, italics) shown on the formulas could be deduced. Equivalence of the protons within a methylene group was observed in all three cases and is consistent with ionic structures rapidly equilibrating *via* covalent structures or with covalent structures rapidly equilibrating *via* ionic ones. The small value of J_{23} in III suggests the *Z,Z* shape as depicted, in agreement with a prediction of Hoffmann and Olofson.⁸ In contrast, V is apparently extended. The equivalence of protons in II prevents nmr determination of its geometry.

Alkylation results help show that these nmr signals are due to products of higher metalation. Table I

Table I. Alkylation and Energy Calculation Results for I-VII

	Alkylation product yields				Binding energy, au	Delocalization energy, β
	Total	Mono	Di	Tri		
I	37	14	86	0	-3.685	1.4
II	11	53	47	0	-3.626	1.2
III	95	5	95	0	-5.778	2.0
IV ^a	92	98	2 ^b	0	-5.694	1.8
V	94	4	96	0	-5.791	2.1
VI ^c	94	58	36	6		
VII ^{a,c}	91	47	35	18	-7.821	

^a At 50° for 3-7 days. ^b Products not identified. ^c Butyllithium: TMEDA = 1:1.5.

gives yield data from pouring reaction mixtures into excess ethyl bromide at -78° with gc, pmr, and mass spectrometric examination of the products. In the cases of III and V, solid (from the alkylation results, evidently dimetalation product) separated.⁹ The di- and trialkylation products (Scheme I) are clearly formed from alkenes metalated in the *allylic* positions; a previous result¹⁰ indicated the possibility of a second metalation in a vinyl position, but if such anions are formed in the present case, they equilibrate to allylic ones prior to quenching. Possibly some of the nine apparent polyalkylation products (none formed in over 0.5% yield) in the attempted preparation of IV result from vinyl metalation.

The absence of 3,4-diethyl-1,5-hexadiene among the diethylation products of III suggests that, as expected, the first alkylation of these dimetalation products proceeds at an end of the system to give the most stable

(5) The preparation of I³ involved metalation of an allyl anion with an alkyl substituent on carbon 2.

(6) Chemical Samples Co.

(7) R. B. Bates, D. W. Gosselink, and J. A. Kaczynski, *Tetrahedron Lett.*, 199 (1967).

(8) R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966).

(9) For alkylation, the solids were dissolved in THF; if quenching was not then carried out immediately, the yields of dialkylation products diminished with corresponding increases in monoalkylation products and THF cleavage products; *cf.* R. B. Bates, L. M. Kroposki, and D. E. Potter, *J. Org. Chem.*, **37**, 560 (1972).

(10) T. A. Antkowiak, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **12**, 393 (1971).

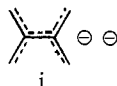
monoanion derivative, in this case 1-propylpentadienyllithium. For comparison purposes, 1-propylpentadienyllithium was generated⁷ from 1,4-octadiene⁶ and gave the same products obtained from III but in different yields: 45, 45, 5, and 5% (sum of last two products), respectively. Protonation of III gave exactly analogous products with protons instead of ethyl groups, in quite different yields:¹¹ 12, 9, 9, 56, and 14%, respectively. Interpretation of the dialkylation and diprotonation results on III may be complicated by the presence of more than one shape of III, the equilibration of these shapes during the first alkylation, formation of monoanions other than the predominant one, and equilibration of the various shapes of the monoanion before and during the second alkylation. Still, the finding that the predominant product from dialkylation has the *Z* configuration and that from diprotonation *Z,Z* seems to offer some support for the nmr evidence above that III has predominantly the *Z,Z* configuration as depicted.

In Table I are included the results of INDO-MO energy calculations for delocalized di- and trianions; there is some correlation between expected stability of the dianion and relative amounts of mono- and dialkylation.¹² In summary, the current findings support extra resonance stabilization for the "Y-aromatic" system I and the homoaromatic homocyclooctatetraene dianion but show that related but nonaromatic systems possessing less stabilization can still be prepared by allylic metalation. The structure and synthetic utility of these and related metalation products are being further investigated.

Acknowledgment. We thank Dr. E. R. Santee for a 300-MHz nmr spectrum which showed the relative amounts of the 3-ethyl-1,4-octadienes, and the National Science Foundation for financial support (Grants GU-1534 and GP-21115).

(11) Alkylation of pentadienyl anions has previously been observed to give a higher percentage of reaction at the central atom than protonation: R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *J. Amer. Chem. Soc.*, **95**, 926 (1973).

(12) III-V represent three of the four possible C₈H₈ dianions comprised of sp² hybridized carbons. The fourth, i (binding energy,



– 5.756 au; delocalization energy, 1.9β), is unfortunately inaccessible by dimetalation of an *unconjugated* diene.

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Structure of a σ -Carboranyl Complex of Platinum (II), 1-[(P-*n*-Pr₃)Pt^{II}(P-*n*-Pr₂CHCH₂CH₃)]-2-C₆H₅-1,2-

(σ -B₁₀C₂H₁₀). An Unusual Metal-Phosphine Bonding

Sir:

Recently it has been shown that coordination of carborane ligands to transition metal atoms may give

both π - and σ -bonded^{2,3} complexes. In the second case, besides the metal-carbon σ bond,² the metal-carborane coordination is also provided by a M···H-B bridge. On the other hand this kind of bonding may be interpreted in terms of a donation of electrons from a suitable hybrid orbital of the metal atom into an empty orbital delocalized on the C-B-H carborane atoms.² So far no structural evidence has been reported for a "pure" metal-carbon σ bond. Recently Bresadola, *et al.*,^{4,5} have synthesized and characterized a series of platinum(II) and palladium(II) complexes, containing tertiary phosphine and carborane or neo-carborane ligands, which they claim to be the first example of σ -bonded carboranyl complexes. Furthermore they reported that the complexes, obtained from Li-carborane derivatives and *trans*-Pt^{II}Cl₂(trialkylphosphine)₂, achieve four-coordination by internal metallation of one alkyl group of one-coordinated phosphine, involving the second carbon atom of the alkyl group.

In order to find an answer for both problems, we have performed the crystal structure determination of the reaction product between 1-lithium 2-phenyl-1,2-dicarbasododecaborane(12) and *trans*-dichlorobis(tri-*n*-propylphosphine)platinum(II). Details of the crystallographic results are as follows. The crystals were triclinic, with cell parameters $a = 11.77 \pm 0.01 \text{ \AA}$, $b = 10.20 \pm 0.01 \text{ \AA}$, $c = 15.84 \pm 0.01 \text{ \AA}$, $\alpha = 82.5 \pm 0.1^\circ$, $\beta = 95.2 \pm 0.1^\circ$, and $\gamma = 106.5 \pm 0.1^\circ$. Space group $P\bar{1}$ was determined from structure refinement. The density, $1.36 \pm 0.01 \text{ g/cm}^3$ as determined by flotation, is in agreement with the calculated value of 1.35 g/cm^3 with two formula units C₂₆H₅₆B₁₀P₂Pt in the unit cell.

Intensity data were collected by use of a Siemens automated diffractometer with Mo K α -filtered radiation and the θ - 2θ scan technique. Independent reflections (3407), up to $\theta = 25^\circ$, with $I > 3\sigma$, were corrected for Lorentz and polarization factors. Although the absorption coefficient is 42 cm^{-1} , no correction was applied because of the small size of the crystal used (nearly a cylinder of 0.2 mm diameter). The structure was determined by the heavy-atom method and refined to a present value of the conventional *R* index of 0.053, by block-diagonal matrix least-squares method with anisotropic temperature factors for the platinum and phosphorus atoms. No peak above 0.6 e/\AA^3 was detected on the final difference Fourier map.

The platinum(II) atom is coordinated by the carboranyl group through its 1-C atom, by one phosphine through its phosphorus atom, and by the other phosphine through the phosphorus and the first carbon atom of one *n*-propyl side group. The platinum and the four coordinated atoms are coplanar within $\pm 0.007 \text{ \AA}$. A sketch of the molecule is shown in Figure 1, together with some bond lengths of interest.

The structural results confirm (i) the "pure" σ bond between the carboranyl and the metal atom with a Pt-C bond length of $2.13 (1) \text{ \AA}$, the carboranyl atoms

(1) G. B. Dunks and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 7213 (1970), and references therein.

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(3) R. A. Love and R. Baw, *J. Amer. Chem. Soc.*, **94**, 8274 (1972).

(4) S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968).

(5) S. Bresadola, A. Frigo, B. Longato, and G. Rigatti, *Inorg. Chem.*, **12**, 788 (1973).