Table I. Sulfur–Oxygen Stretching Frequencies for Some Organomercuric Sulfinates, $RHg(SO_2R')^a$

R	R′	Mp, °C dec	$\nu(SO_2)$, cm^{-1}	
Ph	p-$MeC_6H_4{}^b$	103–104	1051 (s)	843 (vs)
p-MeC_6H_4	Ph^b	113–114	1051 (vs)	853 (vs)
p-MeC_6H_4	p-$MeC_6H_4{}^b$	176	1054 (s)	852 (s, br)
C_6F_5	Ph^b	165	1035 (m)	828 (vs)
$PhCH_2$	$PhCH_2{}^c$		1052 (s)	879 (s)
Et	Et^c		1156 (s, br)	1053 (s)

[a] In Nujol. [b] This work. [c] Reference 4.

ble I) of the compounds are similar to those of isomer A of phenylmercuric benzenesulfinate; hence we suggest all have polymeric or dimeric structures similar to IV. The possibility of preparing other isomers of these derivatives is still being investigated. Two other organomercuric sulfinates have been reported.[4] On the basis of the foregoing discussion, the infrared data (Table I) indicate that in the *solid state* $EtHg(SO_2Et)$ has a structure similar to I and $PhCH_2Hg(SO_2CH_2Ph)$ has a structure similar to IV. The nmr spectra of these compounds in deuteriochloroform (and liquid sulfur dioxide) have been interpreted as indicating the presence of S-sulfinato complexes in these solvents.[4] Thus the benzyl compound may give linkage isomers, *viz*., O-sulfinate in the solid state and S-sulfinate in deuteriochloroform.

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G. B. Deacon, P. W. Felder
Chemistry Department, Monash University
Clayton, Victoria, Australia

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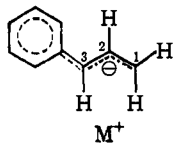
Resonance-Stabilized Carbanions. II.[1] Rotational Barriers in Phenylallyl Alkali Metal Salts

Sir:

We wish to report that the temperature-dependent nmr spectra of phenylallyllithium, -sodium, and -potassium (Ia–c) are remarkably informative as to their geometry and ionic character and provide accurate activation energies (in Ia) for the barriers to rotation around both the C_{1-2} and phenyl-C_3 bonds.



Ia, M = Li
b, M = Na
c, M = K

The spectrum of the lithium compound, in combination with its pentadeuteriophenyl analog,[2] in THF-d_8 at 5° (Figure 1a,b) is readily interpreted on a first-order basis as noted on the spectra.[3] The downfield shift of the central proton (δ_c in Figure 1b) and the upfield location of the p-phenyl protons (δ_p in Figure 1a) clearly indicate the *trans* geometry about C_{2-3} and the predominantly ionic nature of the compound, respectively.[1,4] At 5°, rotation about the C_{1-2} partial double bond is slow or absent,[5] as demonstrated by the multiplicity and coupling constants of the *cis* (H_b), *trans* (H_a), and central (H_c) protons in Figure 1b. Raising the temperature leads to interchange of the methylene protons H_a and H_b with the resulting spectral alterations documented in Figure 2. At 90°, rapid rotation about C_{1-2} collapses the methylene multiplet to a doublet and, since $J_{cd} \cong (J_{ac} + J_{bc})/2$, the octet assigned to H_c now approximates an AX_3 quartet.

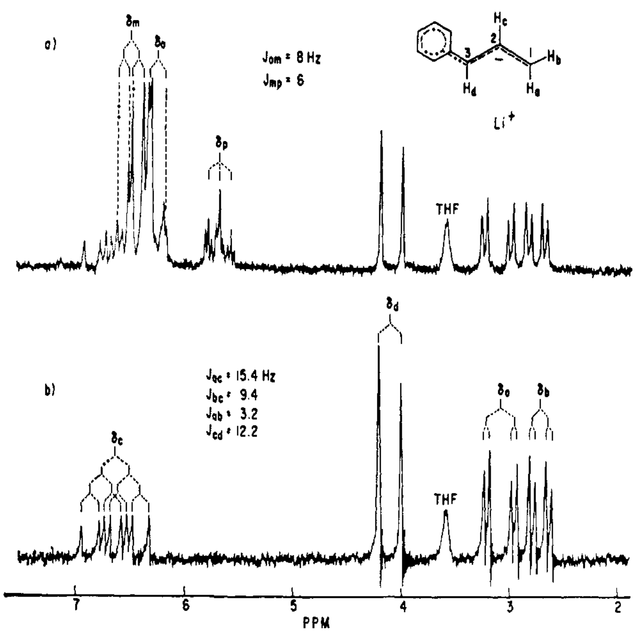


Figure 1. Nmr spectra, 60 MHz, at 5° in THF-d_8 of (a) phenylallyllithium and (b) pentadeuteriophenylallyllithium.

Comparison of exchange-broadened spectra of H_a and H_b with computer-generated curves[6] gave rates of rotation about the C_{1-2} bond. An Arrhenius plot of the data yielded the activation parameters $\Delta H^{\ddagger} = 19.8 \pm 0.3$ kcal/mole and $\Delta S^{\ddagger} = 8.5 \pm 1.0$ eu at 25°.

The phenyl rotation was investigated in a similar manner using 3,5-dideuteriophenylallyllithium to facilitate interpretation. At 5° the *ortho* and *para* ring protons are 2:1 singlets, respectively (Figure 3a). Upon cooling, the decrease in rotation about the phenyl-C_3 bond causes the *ortho* singlet to broaden, then split into two bands 27 Hz apart at −58° (Figure 3b). The Arrhenius plot

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(1) Part I: H. H. Freedman, V. R. Sandel, and B. P. Thill, *J. Am. Chem. Soc.*, **89**, 1762 (1967).

(2) Prepared, using vacuum techniques, by treatment of 3-phenylpropene with excess n-butyllithium in hexane containing a small amount of THF. The solid was washed with hexane, filtered, dried, and dissolved in THF.

(3) The vinyl parameters shown in Figure 1b were obtained by use of Bothner-By and Castellano's LAOCOON II computer program for iterative least-squares fitting of spectral data. The constants obtained differed little from the first-order analysis.

(4) V. R. Sandel and H. H. Freedman, *J. Am. Chem. Soc.*, **85**, 2328 (1963).

(5) Rotation about C_{2-3} is not readily detected due to the low concentration of the less thermodynamically stable *cis* isomer of I.

(6) The program used, EXCH 10, was written and kindly supplied by G. M. Whitesides. The H_a and H_b part of the spectrum was approximated as two overlapping AB quartets (G. M. Whitesides and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4878 (1965)).

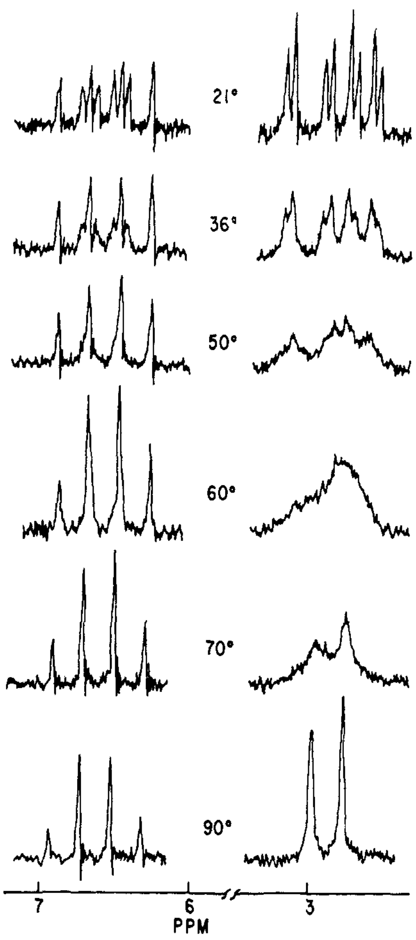


Figure 2. Temperature dependence of H_a–H_b and H_c protons (see Figure 1) of pentadeuteriophenylallyllithium in THF-d_8.

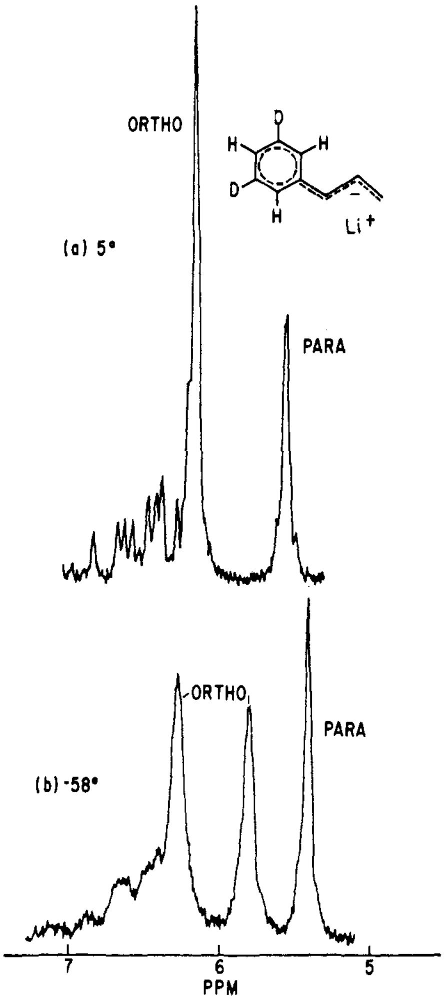


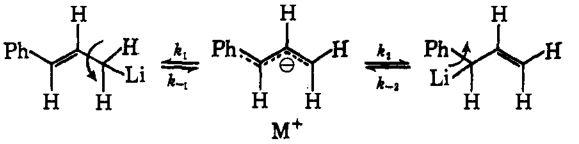
Figure 3. Spectra of aromatic region of 3,5-dideuteriophenylallyllithium in THF-d_8 showing the *ortho* protons (a) as a singlet at 5°, and (b) as two nonequivalent singlets at −58°.

yielded: $\Delta H^{\ddagger} = 13.9 \pm 0.5$ kcal/mole and $\Delta S^{\ddagger} = 7.6 \pm 1.7$ eu.

The spectra of phenylallylsodium (Ib) and potassium (Ic) in THF[7] are closely similar in form to that of Ia. They differ, however, in two important aspects: the chemical shift of the *para*-phenyl proton in Ic is upfield from that of Ia,b and the coalescence temperatures of Ib,c are considerably higher than that of Ia, as shown in Table I. Finally, we note that in the less basic solvent, ether, the lithium and sodium spectra exhibit downfield shifts for the *para* protons and lower rotational barriers, both effects reflecting a decrease in ionic character.

The ratio of the C_{1-2} to the phenyl–C_3 barrier in Ia (19.8:13.9 = 1.4) is in good agreement with that predicted from Hückel MO π-bond orders (0.775:0.516 = 1.50), and this raises the provocative possibility that the experimentally determined barriers in these and similar anions will directly correlate with theoretically derived parameters.

For the above premise to be valid, one must exclude the alternative possibility that rotation occurs *via* nmr-undetectable, finite concentrations of covalent organometallic species (eq 1) and that, therefore, the barriers reflect only k_1 and k_2, the rates of collapse of the ion pair to the covalent species. Such an explanation has been utilized by Bates[8] for the temperature-dependent pentadienyllithiums and implied by others[9,10] for similar systems. Superficially, eq 1 can rationalize the data



(1)

M = Li, Na, or K

of Table I, but we prefer the equally satisfactory alterna-

Table I. Nmr Chemical Shift and Kinetic Data for Ia–c

Metal	Solvent	δ_p, ppm	Methylene T_c,[a] °C	Methylene $\Delta G^{\ddagger}(T)$, kcal/mole	Phenyl T_c,[a] °C	Phenyl $\Delta G^{\ddagger}$ (−15°), kcal/mole
Li	THF	5.70	60	17.0 (55°)	−31	11.9
Li	Ether	6.12	25	15.7 (55°)	−77	10.3
Na	THF	5.70	>95	>17.8 (95°)	−15	12.9
Na	Ether	6.02			−38	11.7
K	THF	5.63	>115	>20.1 (115°)	−15	12.9

[a] Coalescence temperature.

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(7) Prepared from 3-phenylpropene and amylsodium and phenylpotassium, respectively.

(8) R. B. Bates, D. W. Grosselink, and J. A. Kaczynski, *Tetrahedron Letters*, 205 (1967).

(9) E. Grovenstein, S. Chondra, C. E. Collum, and W. E. Davis, Jr., *J. Am. Chem. Soc.*, **88**, 1275 (1966).

(10) D. Seyferth and T. F. Jula, *J. Organometal. Chem.* (Amsterdam), **8**, 13 (1967).

tive involving a single, solvent- and cation-dependent, partially delocalized structure for Ia-c.[11] It is hoped that studies now in progress will eventually supply a definitive answer.

[11] Two previously described (and possibly equivalent) hypotheses can be mentioned: (a) that we are dealing with "contact ion pairs" as postulated for the alkali metal salts of fluorene (T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307 (1966)) or (b) a Lewis acid type of anion-cation interaction as suggested for 1,1-diphenyl-*n*-hexyllithium (R. Waack, M. A. Doran, and P. E. Stevenson, *ibid.*, **88**, 2109 (1966)).

V. R. Sandel, S. V. McKinley, H. H. Freedman
Eastern Research Laboratory, The Dow Chemical Company
Wayland, Massachusetts 01778

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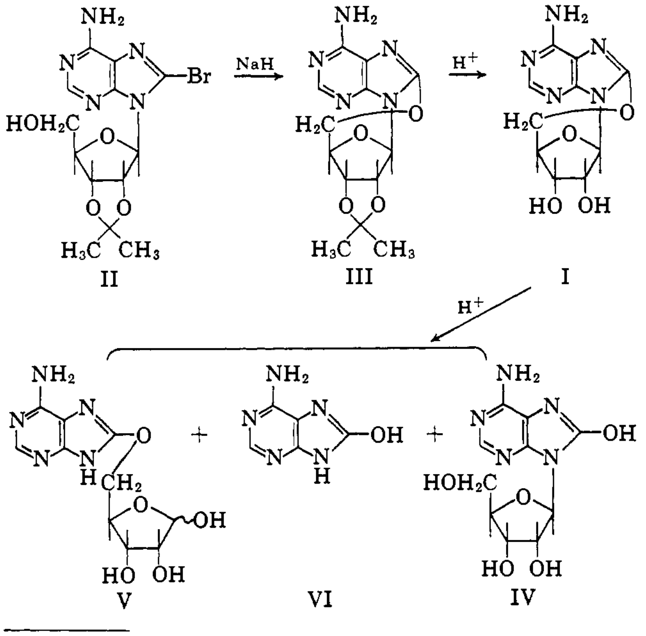
A Novel Method for the Synthesis of Cyclonucleosides. Synthesis of 8,5′-O-Anhydro-8-oxyadenosine

Sir:

In recent years knowledge about purine nucleosides has extensively accumulated.[1-6] These cyclonucleosides have O- or S-anhydro linkages between C_8 of the purine and $C_{2'}$ or $C_{3'}$ of the sugar moiety, except for a guanosine cyclonucleoside[2] having a 8,5′-S-anhydro linkage. All of these cyclonucleosides were synthesized *via* intermediates having aryl- or alkylsulfonyl groups on the sugar hydroxyl by back-side attack of oxy or thiol group on the base moieties. However, adenine cyclonucleosides having the 8,5′-O-anhydro linkage could not be synthesized because of the rapid cyclization of 5′-sulfonylated adensosine to the N_3 position to give N_3,5′-cyclonucleoside salts.[7]



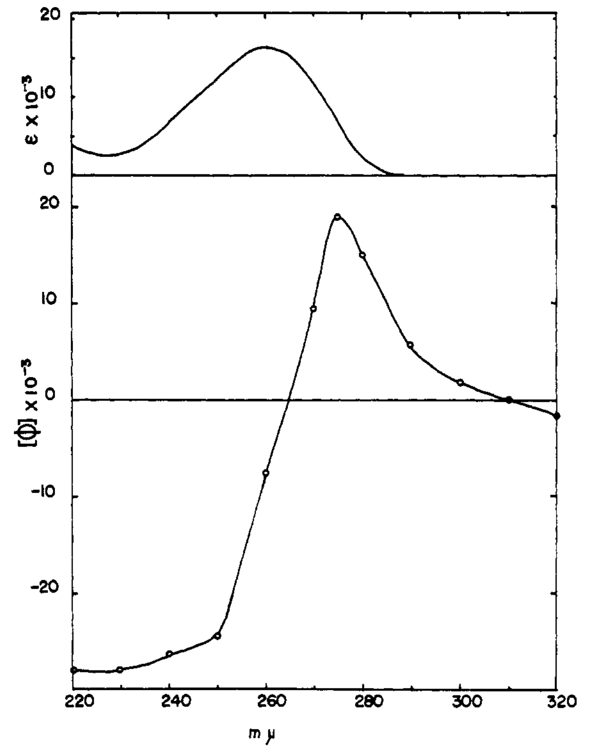


Figure 1. Optical rotatory dispersion curve of 8,5′-anhydro-8-oxyadenosine, 0.870 optical density unit/ml at 20°, 1-cm light path, using a Jasco Model ORD/UV-5 spectrophotometer.

We wish to report a new method for the cyclization of halogenated purine nucleoside and the synthesis of 8,5′-anhydro-8-oxyadenosine (I) by this method.

To a solution of 2′,3′-O-isopropylidene-8-bromoadenosine (II) dissolved in anhydrous dioxane was added portionwise 2 equiv of sodium hydride. The reaction mixture was kept at room temperature for 12 hr. The usual work-up and recrystallization from ethanol gave 8,5′-anhydro-2′,3′-O-isopropylideneadenosine (III), mp 226–226.5°,[8] in a yield of 80%. The structure of III was supported by ultraviolet absorption ($\lambda_{max}^{0.05N\,HCl}$ 260 mμ (ϵ 15,400), λ_{max}^{EtOH} 259 mμ (ϵ 15,100), $\lambda_{max}^{0.05N\,NaOH}$ 259 mμ (ϵ 14,900)), infrared absorption (ν_{max}^{KBr} 3360 (6-NH_2), 1040–1090 (sugar C-O-C), 1110–1155 cm^{-1} (isopropylidene)), and elemental analyses. Paper chromatography gave R_f(A)[9] 0.45, R_f(C) 0.83, R_f(D) 0.85 for compound III.

When compound III was heated in 1 *N* sulfuric acid at 60° for 3 hr to remove the isopropylidene group, 8,5′-anhydro-8-oxyadenosine (I) was obtained together with 8-oxyadenosine (IV)[10] and the starting material. Compound I, mp 209–210°, showed ultraviolet absorption properties ($\lambda_{max}^{0.1N\,HCl}$ 260 mμ (ϵ 15,000), $\lambda_{max}^{H_2O}$ 260.5 mμ (ϵ 16,200), $\lambda_{max}^{0.1N\,NaOH}$ 261 mμ (ϵ 16,400)) which were similar to those reported for 8-methoxyadenosine[12] and values in

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[1] M. Ikehara and H. Tada, *J. Am. Chem. Soc.*, **85**, 2344 (1963); **87**, 606 (1965).

[2] M. Ikehara, H. Tada, and K. Muneyama, *Chem. Pharm. Bull.* (Tokyo), **13**, 639 (1965).

[3] M. Ikehara, H. Tada, K. Muneyama, and M. Kaneko, *J. Am. Chem. Soc.*, **88**, 3165 (1966).

[4] M. Ikehara and H. Tada, *Chem. Pharm. Bull.* (Tokyo), **15**, 94 (1967).

[5] M. Ikehara and K. Muneyama, *J. Org. Chem.*, **32**, 3039 (1967).

[6] M. Ikehara and M. Kaneko, *Chem. Pharm. Bull.* (Tokyo), **15**, 126 (1967).

[7] V. M. Clark, A. R. Todd, and J. Zussman, *J. Chem. Soc.*, 2959 (1951).

[8] All crystalline compounds reported in this communication gave elemental analyses in satisfactory agreement with the theoretical values.

[9] R_f(A) stands for the R_f value obtained in solvent A. Solvents used were: A, water, adjusted to pH 10; B, 1-butanol-water, 86:14; C, 2-propanol-concentrated ammonia-water, 7:1:2; D, 1-butanol-acetic acid-water, 5:2:3.

[10] Identical with an authentic sample synthesized from 8-bromoadenosine by the acetic acid-sodium acetate procedure[11] (unpublished experiment by M. Kaneko).

[11] M. Ikehara, H. Tada, and K. Muneyama, *Chem. Pharm. Bull.* (Tokyo), **13**, 1140 (1965).

[12] R. E. Holmes and R. K. Robins, *J. Am. Chem. Soc.*, **87**, 1772 (1965).