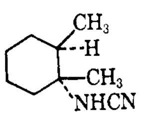
bonds stereospecifically, irrespective of light wavelength employed in its generation. In addition the gas chromatographs displayed by the three photolysis mixtures (reactions 1–3) were found to be virtually superimposable on one another and also qualitatively identical with that afforded by the mixture of amines formed from thermolysis of N_3CN in the same hydrocarbon (reaction 4). This suggests a close similarity between NCN produced thermally and that generated photolytically. It is also interesting to note that the proportion of products from insertion of NCN into tertiary C–H bonds appears to be consistently greater in the thermal than in the photochemical reaction. This is not unexpected, since input energy considerations require that photolysis produce a "hotter" NCN than thermolysis.



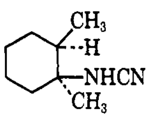


Table I. Stereochemistry of the Insertion of Cyanonitrene into the Tertiary C–H Bonds of *cis*- and *trans*-1,2-Dimethylcyclohexane

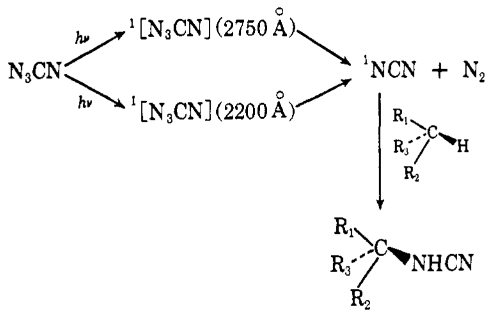
Reaction	Conditions for decomposition of N_3CN^a	Hydrocarbon	% *cis*-RNHCN (**1**)^b	% *trans*-RNHCN (**2**)^b
1	*hν*, λ >2120 Å	*cis*	41	<0.5
2	*hν*, λ >2580 Å	*cis*	39	<0.5
3	*hν*, λ >2800 Å	*cis*	34	<0.5
4	Δ, 50°	*cis*	44	<0.5
5	*hν*, λ >2800 Å	74% *cis* 26% *trans*	29	7
6[2]	Δ, 43.5°	74% *cis* 26% *trans*	52	10

[a] Photolyses were carried out at ~15°. [b] Proportion in total product mixture.

Translating the stereochemical results in terms of electronic multiplicity of generated NCN we conclude that *photolysis of cyanogen azide with light ranging from 2100 to ~3000 Å produces exclusively singlet NCN, and consequently that both the 2200- and the 2750-Å bands in the spectrum of N_3CN arise from singlet–singlet transitions.* Our conclusions, though in contradiction with previous suggestions[7,9] based on spectroscopic work, are clearly in keeping with theory. Insofar as the photolysis of N_3CN described here can be compared to that carried out in a solid nitrogen matrix, we offer the following tentative explanation to account for the discrepancy between the two sets of results. Irradiation through quartz very probably generates highly vibrationally excited singlet NCN. In a rigid matrix vibrational relaxation of this species to a level from which isoenergetic crossing to the $^3\Sigma_g^-$ potential surface could occur is undoubtedly a relatively slow process. Therefore the employed[7] delay times of 30–200 μsec between flash and analysis lamp are adequate for observation of the initially formed $^1\Delta_g$ state.[11] On the other hand photolysis of N_3CN through Pyrex would probably produce $^1\Delta_g$ NCN in a low vibrational level from which isoenergetic crossing to the $^3\Sigma_g^-$ state ought to occur rapidly. Hence, it is not inconceivable that under these latter conditions the lifetime of the $^1\Delta_g$ state will be reduced to a value below the minimum delay time employed (30 μsec) so that singlet NCN may escape detection altogether and its decay product $^3\Sigma_g^-$ NCN may erroneously be characterized as a primary fragment. The situation in our chemical experiments is quite different in that here insertion of initially produced singlet NCN into tertiary C–H bonds occurs more rapidly than decay to the $^3\Sigma_g^-$ ground state.[2]

Our findings are summarized in Scheme I.

Scheme I



Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation under Grant GP 6618.

---

[11] A lifetime of ~500 μsec has been estimated for $^1\Delta_g$ NCN, generated by irradiation of N_3CN through quartz.[7]

A. G. Anastassiou, J. N. Shepelavy
Department of Chemistry, Syracuse University
Syracuse, New York 13210

Received October 13, 1967

Linkage Isomerism in Phenylmercuric Benzenesulfinate

Sir:

Recently there has been considerable interest in complexes of metals with sulfinate ions,[1–10] and especially in the structures of sulfinato complexes formed by sulfur dioxide insertion into metal–carbon bonds.[1,3,4,7,8]

---

(1) J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, **86**, 5051 (1964); **88**, 4862 (1966); F. A. Hartman and A. Wojcicki, *ibid.*, **88**, 844 (1966); F. A. Hartman, P. J. Pollick, R. L. Downs, and A. Wojcicki, *ibid.*, **89**, 2493 (1967).

(2) G. E. Coates and R. N. Mukherjee, *J. Chem. Soc.*, 1295 (1964).

(3) A. Wojcicki and J. P. Bibler, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 36M.

(4) J. P. Bibler, Ph.D. Thesis, Ohio State University, 1965; University Microfilms, 66-6231.

(5) B. Chiswell and L. M. Venanzi, *J. Chem. Soc., Sect. A*, 1246 (1966).

(6) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 180 (1966).

(7) F. Huber and F. J. Padberg, *Z. Anorg. Allgem. Chem.*, **351**, 1 (1967).

(8) R. Gelius, *ibid.*, **349**, 22 (1967).

(9) G. B. Deacon, *Australian J. Chem.*, **20**, 1367 (1967).

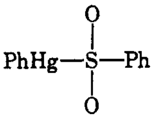
(10) D. A. Langs and C. R. Hare, *Chem. Commun.*, 853 (1967).

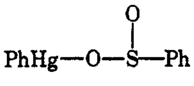
Complexes with metal–sulfur bonding[1,3–6,9] (analogous to sulfones) and with metal–oxygen bonding[2,7,8,10] (analogous to sulfinate esters) are known and are readily distinguished by their infrared spectra,[1,2,5–7,9] but no case of linkage isomerism has yet been reported. We now report the preparation of linkage isomers of phenylmercuric benzenesulfinate.

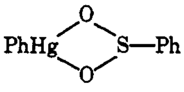
Phenylmercuric benzenesulfinate has been prepared by the reaction of diphenylmercury with liquid sulfur dioxide.[3,4] We have obtained the compound by this route and also from the reaction of mercuric benzenesulfinate[9] with diphenylmercury in chloroform. Crys-

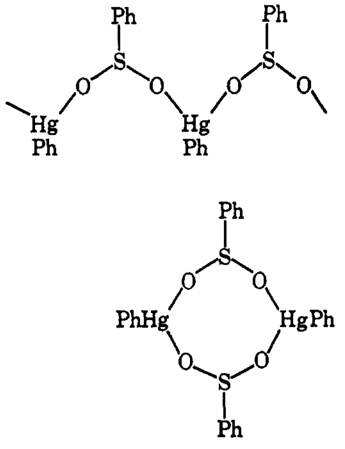
$$Hg(SO_2Ph)_2 + Ph_2Hg \longrightarrow 2PhHg(SO_2Ph)$$

tallization of the product of either reaction from chloroform–pentane gives crystals of what is now designated isomer A,[11] mp 110–111° dec (lit.[4] mp 105°) [sulfur–oxygen stretching frequencies, 1048 (vs), 838 (vs, br) cm^{-1} in Nujol (lit.[4] 1050, 840 cm^{-1})]. If a solution of this isomer in acetone is cooled to $-23°$, crystals of isomer B,[11] mp 119° dec [sulfur–oxygen stretching frequencies, 1175 (vs, br), 1049 (vs, br) cm^{-1} in Nujol] are deposited.[12]


I


II

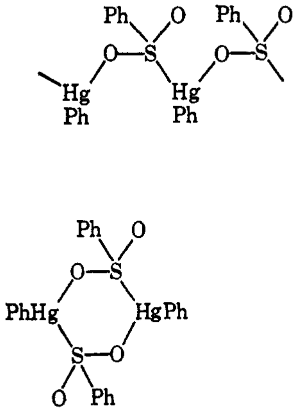

III


IV

polymeric

or

dimeric


V

The reverse isomerization can be carried out by evaporating a solution of B in chloroform to dryness, when A is obtained. The two isomers are readily distinguished by their sulfur–oxygen stretching frequencies (above) and their X-ray powder diffraction patterns. Comparison of the latter with the powder patterns for diphenylmercury and mercuric benzenesulfinate shows that neither isomer is an equimolar mixture of these compounds.

For the two isomers, there are several possible structures (I–V) involving different ways of linking the sulfinate ligands to mercury. The sulfur–oxygen stretching frequencies of isomer B are within the ranges for the corresponding frequencies of S-sulfinato complexes (*ca.* 1250–1150 and *ca.* 1100–1030 cm^{-1}),[1,4–6,9] and accordingly it is considered to have structure I. The frequencies of isomer A are well outside these ranges but are nearer to the sulfur–oxygen stretching frequencies of O-sulfinato complexes [for the few known examples, $\nu(SO_2)$ absorptions are in the region 1050–900 cm^{-1}],[13] and it is likely that A has one of the structures II–IV. These alternatives are not distinguishable by infrared spectroscopy (see examples cited[13]). Structure V, which may be regarded as midway between the extreme cases of S coordination (I) and O coordination (II), is tentatively discarded for isomer A, since it is considered[2] that structures of this type should have one sulfur–oxygen stretching frequency above 1100 cm^{-1}. Isomer A gives approximately monomeric molecular weights in chloroform.[14] The infrared spectrum of A in this solvent shows sulfur–oxygen stretching frequencies [1034, 1018 (vs, br), and 981 (vs, br) cm^{-1}] indicative of an O-sulfinato complex, but the values differ markedly from those for the crystalline isomer. Clearly, A in chloroform must have one of the monomeric O-sulfinate structures II or III. Thus, the polymeric or dimeric structure IV is likely for A in the solid state. The situation parallels that for many carboxylato complexes, which are dimeric or polymeric in the solid state but monomeric or only slightly associated in solution.[15]

A number of other arylmercuric arenesulfinates have been prepared[11] by reaction of mercuric benzenesulfinate or *p*-toluenesulfinate[9] with diarylmercurials. The sulfur–oxygen stretching frequencies (Ta-

(11) Satisfactory analyses (C, H, S) were obtained for all compounds;

(12) Successful conversions were achieved using solutions of isomer A ($\geq \sim 0.08$ *M*) in Analar grade acetone, the first crystals being deposited after *ca.* 30 min at $-23°$. With more dilute solutions, crystallization was slower, and solutions $\leq \sim 0.05$ *M* gave mixtures of the two isomers. Impure samples of A also gave mixtures of the isomers, but further crystallizations from acetone at $-23°$ gave pure B.

(13) Values for $Cu(H_2O)_4(p\text{-}MeC_6H_4SO_2)_2$, which has unidentate O-sulfinate ligands,[10] are 998 and 938 cm^{-1} (this work), and frequencies[2,7] for compounds with bridging O-sulfinate groups are in the region 1050–900 cm^{-1}, *e.g.*, $[Me_2Ga(SO_2Ph)]_2$, 1005 and 941 cm^{-1}.

(14) Calcd for $C_{12}H_{10}HgO_2S$: mol wt, 419. Found (by osmometry): mol wt, 456 (concn 1.04% w/v). A similar value has been reported.[4]

(15) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964); T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *ibid.*, 3632 (1965); M. J. Janssen, J. G. A. Luijten, and G. J. M. van der Kerk, *Rec. Trav. Chim.*, **82**, 90 (1963); G. B. Deacon and P. W. Felder, *Australian J. Chem.*, **20**, 1587 (1967).

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.

Acknowledgment. This work was supported by a grant from the Australian Research Grants Committee and by the award of a Commonwealth Scholarship (to P. W. F.).

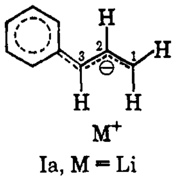
G. B. Deacon, P. W. Felder
Chemistry Department, Monash University
Clayton, Victoria, Australia

Received November 9, 1967

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.

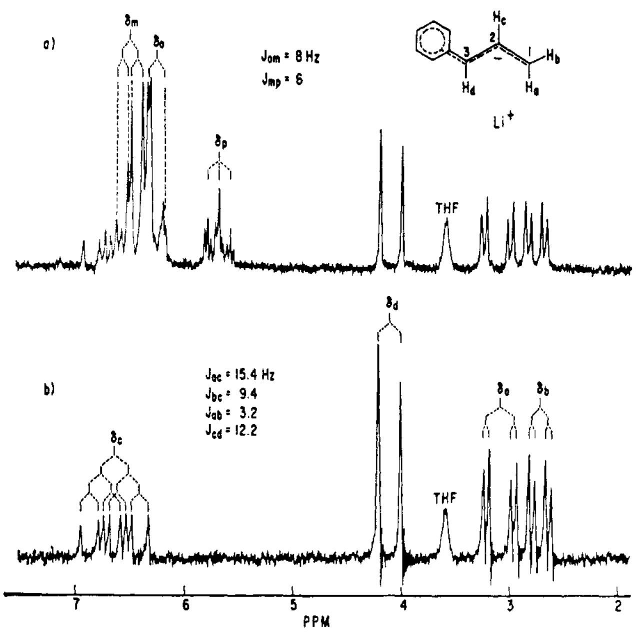


Figure 1. Nmr spectra, 60 MHz, at 5° in THF-d_8 of (a) phenylallyllithium and (b) pentadeuteriophenylallyllithium.

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

---

(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)).