Figure 1. Reduced viscosity of Co(di-n-BP) in benzene as a function of concentration.
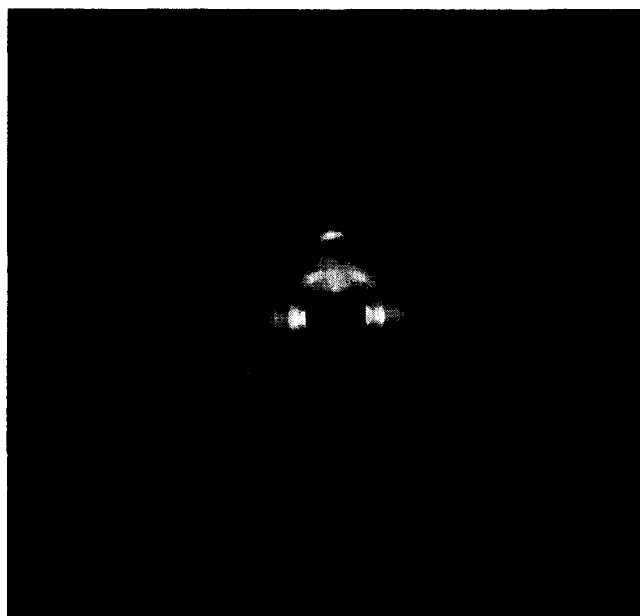

Figure 2. Fiber diagram of Zn(di-n-BP).

obtained as a crystalline powder isomorphous with the related Co compound.

Highly oriented fibers were drawn from the gel obtained by wetting the Zn(di-n-BP) powder with benzene. The fiber diagram, recorded with a cylindrical camera (diameter 57.3 mm.) using Cu Kα radiation, is shown in Figure 2. From this diagram a value of 9.90 Å. may be deduced for the identity period along the fiber axis which corresponds to the b axis of the twinned crystals of Co(di-n-BP). This indicates that the two polymers are isostructural and consist of molecular chains oriented along the b axis. The 9.90-Å. value for the b axis and a strong meridional reflection on the second layer of the fiber photograph strongly suggest that the structure repeats identically after two metal atoms along the chain. Assuming reasonable values of bond angles and bond lengths, a chain model with double phosphinate bridges between tetrahedrally coordinated metal atoms appears to be stereochemically feasible.

In conclusion these preliminary results give strong indication that cobalt(II) and zinc(II) di-n-butylphosphinates exist as linear chains in the solid state and in

solution, the metal atoms forming part of the repeating units of these chains through stable coordination linkages, as previously proposed[3,4] for the dimethyl, diphenyl, and methylphenyl derivatives. Further studies on this interesting class of inorganic polymers are in progress in our laboratory.

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Field-Dependent Conductance in Sodium–Liquid Ammonia Solutions

Sir:

We wish to report an unexpectedly large and complex influence of electrical field on the conductance of dilute solutions of sodium in liquid ammonia. At $-33°$ and concentrations from 3 to 7 × 10^{-3} M (well below the equivalent conductance minimum at 0.04 M), two distinctive effects are noted.[1] One is time dependent and may constitute a relaxation phenomenon. It is present under pulse conditions at the lowest fields we are currently able to observe experimentally,[1] 2.5 v./cm. On application of so small a field, the conductance increases within 1 μsec. to a value 2–3% larger than that observed on a commercial bridge at a field less than one-tenth as large and at audiofrequency, 0.2 v./cm. and 1592 c.p.s. After about 10 μsec. this time-dependent increase of conductance has diminished to near zero, and conductances comparable within 0.1% to the 0.2 v./cm.–1592 c.p.s. values are observed. It is not yet certain that we have conducted measurements at fields which are sufficiently low to assure constant conductance with changing field, nor has the frequency dependence of the conductance been further investigated, especially at the lower frequencies.

A second effect is even more striking. As the field is increased by factors of ten from the lowest value practical for measurement, the conductance, measured at a given time following the application of the pulse, increases abruptly and quickly reaches a near-limiting value. The effect is many times larger than observed in any previous electrolytic measurements, with the possible exception of studies on certain polyelectrolytes, and is larger than can be accounted for by change in dielectric constant or equivalent conductances of the conducting species using any currently accepted theory for the influence of high fields. The following figures are representative: field, 5 × 10^0 v./cm.; conductance quotient $\Delta\lambda/\lambda$ (measured at 0.2 v./cm. and 1592 c.p.s.), 2%; 5 × 10^1 v./cm., 5.2%; 5 × 10^2 v./cm., 8.5%; 5 × 10^3 v./cm., 9.8%; 8 × 10^3 v./cm., 9.9%. These latter measurements employ a constant product of oscilloscope sensitivity and applied pulse voltage. Under these circumstances the first-mentioned time-

(1) Since the bridge employed was designed for fields 10^3 larger than those evidently required in the present studies (see J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, **56**, 999 (1952)), practical limitations on pulse rise time, impedance level, and electrical noise level narrow the range of the present investigation. All of these limitations could be overcome in equipment designed specifically to study the newly observed phenomena.

dependent effect becomes relatively less important as the field is raised and disappears when fields of 5×10^2 v./cm. are reached. It must be regarded as field independent to a first approximation, or, as studies at the lowest fields show, as dependent on field to a very much smaller degree than is the conductance measured at longer pulse lengths, say 10 μsec., at higher fields.

Kraus' classic measurements[2] on dilute solutions of alkali metals in liquid ammonia were made in a cell with electrodes 0.7 mm. in diameter, the axes of which were separated by 1.5 mm., corresponding to a closest spacing of 0.8 mm., "by means of a bridge and telephone." If, as may reasonably be surmised, audio-voltages between 1 and 10 v. were employed, then the experimental conditions were very close to those under which we have found field-produced conductance increases of several per cent.

It is thus of compelling interest to examine in detail the frequency, field, and concentration dependence of the phenomena described above.

We have remarked somewhat similar phenomena in previous papers[3,4] under circumstances where the field was not known. The novel results reported here result from improved technical manipulation of the solutions[5] and are made possible by the construction of vacuum-tight conductance cells in which the field is as well known as in previous investigations of aqueous solutions.[1] The work is continuing.

(2) C A. Kraus, *J. Am. Chem. Soc.*, **43**, 749 (1921).
(3) G. Lepoutre, N. Segard, and A. Patterson, *Ann. Soc. Sci. Bruxelles*, **69**, 5 (1955)
(4) G. Lepoutre and A. Patterson, *Compt. rend.*, **240**, 1644 (1955).
(5) P. Schettler and A. Patterson, *J. Phys. Chem.*, **68**, 2870 (1964).

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Diazenes from Angeli's Salt

Sir:

We wish to report that the reaction of aliphatic secondary amines with nitrohydroxylamine (introduced as Angeli's salt, Na_2ONNO_2)[1] is an especially simple and convenient source of diazenes (1). Evidence for

$$>N\text{---}N \longleftrightarrow >\overset{+}{N}=\overset{-}{N}$$
$$1$$
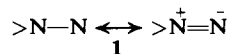
these short-lived species is provided by the marked parallelism between two sets of experiments, one involving base-catalyzed decomposition of arenesulfonyl derivatives of certain 1,1-dialkylhydrazines (a reaction known to proceed *via* diazenes)[2,3] and the other revealing the action of Angeli's salt on the corresponding secondary amines. Structure and reaction conditions wield great influence over the fate of a diazene, with the result that it may pursue any of a variety of characteristic reaction pathways. The experiments were chosen to exploit this ability, and thus to maximize the significance of parallel behavior in the two series.

(1) A. Angeli, *Chem. Zentr.*, **67**, I, 799 (1896); H. R. Hunt, Jr., J. R. Cox, Jr., and J. D. Ray, *Inorg. Chem.*, **1**, 938 (1962).
(2) *Cf.* D. M. Lemal, F. Menger, and E. Coats, *J. Am. Chem. Soc.*, **86**, 2395 (1964), and references contained therein.
(3) W. H. Urry and C. Ikoku, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 25C; R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, **64**, 174, 175 (1964).

Consider the "control" reactions (Chart I), the first of which has been reported previously. The diazene formed from 2 ($X = N(Na)SO_2C_6H_5$) by loss of sodium benzenesulfinate decomposes to bibenzyl and nitrogen, apparently because the transition state is stabilized by benzylic resonance.[4] Concerted fragmentation of the

Chart I

$$X = H \text{ or } N(Na)SO_2Ar$$
$$Y = O \text{ or } CH_2$$
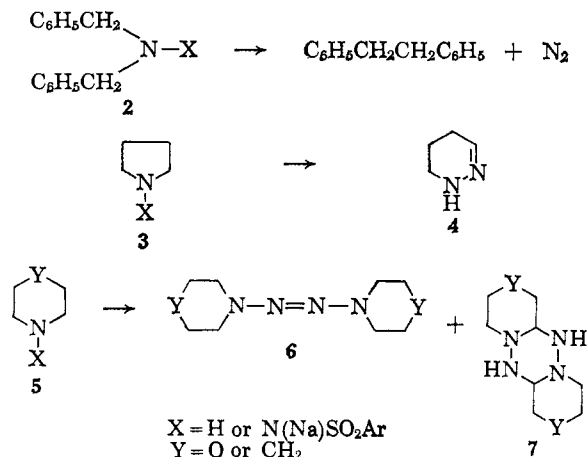
diazene derived from 3 ($X = N(Na)SO_2C_6H_5$) into ethylene and nitrogen occurs in aprotic solvents.[5,6] Interestingly, choice of a protic solvent such as water for the decomposition of 3 ($X = N(Na)SO_2\text{-}p\text{-}C_7H_7$) results in *complete suppression of gas evolution*. Ring expansion to 2,3,4,5-tetrahydropyridazine (4),[7] an example of the diazene–hydrazone rearrangement, is the dominant process (56% yield). The ability of hydroxylic solvents to catalyze tautomerization of a diazene to its 1,3-dipolar isomer, an intermediate in the rearrangement, has been discussed elsewhere.[2,8] Pyrolysis of the morpholine and piperidine derivatives 5 ($X = N(Na)SO_2Ar$) in diglyme gives the corresponding tetrazenes 6 and their decomposition products because no low-energy fragmentation pathway like that for the pyrrolidine derivative is possible. Again the switch to a hydroxylic solvent provides an opportunity for formation of the 1,3-dipolar tautomer of the diazene (8) isolated as its dimer 7.[9]

When dibenzylamine (2, X = H) reacted with Angeli's salt in aqueous dimethylformamide containing acetic acid, bibenzyl was produced in 70% yield (corrected for recovered amine). Addition of Angeli's salt (2 molar equiv.) to an aqueous solution of pyrrolidine (1 equiv.) and hydrochloric acid (2 equiv.) was accompanied by vigorous gas evolution due to decomposition of the salt; nevertheless, the tetrahydropyridazine 4 was formed in 68% yield. Morpholine and piperidine were each transformed by the action of Angeli's salt

(4) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 4427 (1957).
(5) D. M. Lemal, T. W. Rave, and S. D. McGregor, *ibid.*, **85**, 1944 (1963).
(6) Despite indications to the contrary, it is possible that decomposition of 2 and/or of 3 is totally concerted. Should this be true, merely an "incipient" diazene rather than a discrete diazene intermediate would be involved.
(7) Infrared, ultraviolet, and n.m.r. spectra of all new compounds were satisfactory, and correct carbon, hydrogen, and nitrogen analyses were obtained for all new compounds and/or their derivatives. Detailed evidence for all structures will be presented in a full paper.
(8) D. M. Lemal, C. D. Underbrink, and T. W. Rave, *Tetrahedron Letters*, No. 29, 1955 (1964).
(9) Yields of 7 from 5 (Y = CH₂, Ar = C₆H₅) were as high as 80%, those from 5 (Y = O, Ar = p-C₇H₇) were ~40%, and very little or no etrazene (6; Y = O, CH₂) was produced in typical runs.