TABLE I

EFFECTS OF LITHIUM PERCHLORATE ON IONIZATION OF I

Solvent	Temp., °C.	10^5k^0 sec.$^{-1}$	b	Av. fit % of k
AcOH[2b]	50.0	11.9	12.2[a]	0.6
50% AcOH–Ac_2O	50.0	6.43	13.1[b]	1.0
Me_2SO	75.0	18.2	0.0[c]	
$HCONMe_2$	75.0	4.96	1.4[c]	0.3
Ac_2O	75.0	3.41	47.1[b]	2.6
12.5% AcOH–Dioxane	75.1	1.22	462[d]	2.3
Me_2CO	75.1	0.857	47.0[c]	0.5
n-$C_7H_{15}COOH$	75.0	0.434	461[b,e]	1.6
EtOAc	75.0	0.113	553[b]	5.6
THF[f]	75.0	0.0847	482[c]	3.1
Et_2O	50.0	0.0006[g]	$2.98^{b,h} \times 10^5$	1.3

[a–d] ($LiClO_4$) range: [a] 0–0.06 M; [b] 0–0.10 M; [c] 0–0.05 M; [d] 0–0.07 M. [e] Equation 2; c = 1184. [f] Tetrahydrofuran. [g] 0.005 at 75°. [h] Equation 2; $c = 2.65 \times 10^6$.

competing ionization of the organic substrate and make it predominant.[3]

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[3] S. Smith, J. Gall and D. Darwish, unpublished work.

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RARE EARTH METAL–METAL HALIDE SYSTEMS. THE PREPARATION OF NEODYMIUM(II) HALIDES

Sir:

It has been suggested previously that the apparent solution of a number of metals in their molten halides is a result of the formation of a slightly stable, lower halide.[1] Although the subhalide is frequently stable only in dilute solution, in some systems the amount of reduction is sufficient to exceed the normal salt–lower salt eutectic composition so that the latter can be obtained as a stable solid.[2] These metal–metal halide studies are presently being extended to the rare earth systems, where knowledge of the reduction characteristics under these conditions has been limited to the Ce–$CeCl_3$ system. Here the reduction limit recently has been reported to be about 9 mole % Ce ($CeCl_{2.73}$) in a solution in equilibrium with liquid Ce and solid $CeCl_3$ at 777°,[3] in contrast to an earlier value of 32%.[4] Although evidence for an oxidation state lower than three for neodymium in aqueous solution has been doubtful,[5,6] and in liquid ammonia, inconclusive,[7] reduction of the molten trichloride and triiodide by metal has been found to yield the corresponding neodymium (II) halide. With praseodymium, reduction only in solution is observed with the chloride, while a new phase is obtained with the iodide.

The chlorides and iodides were prepared from the metals[8] and their reactions with metal studied in tantalum containers both by cooling curves and by analysis of salt phases in equilibrium with excess metal. The essentials of the phase diagram results are given in Table I. These salts were also equilibrated at higher temperatures with excess metal, quenched, and analyzed. For $PrCl_3$, X/M values for 6 runs at 978° averaged 2.34 ± 0.03; for $NdCl_3$, 6 at 950°, 2.00 ± 0.04; for NdI_3, 2 at 970°, 1.99 ± 0.05; incomplete separation of metal may make the X/M ratios somewhat low. Although phase equilibrium studies with PrI_3 are at present incomplete, powder patterns of the product from reaction with excess metal at >740° show a new phase and little PrI_3 to be present. The bronze product has an I/Pr ratio less than 2.6 and does not appear to be the diiodide.

TABLE I

System	Eutectic		Reduction limit		
	X/M	T, °C.	X/M	T, °C.	Solid phase
Pr–$PrCl_3$	2.50 ± 0.04	644 ± 5	2.50 ± 0.04	644 ± 5	Pr, $PrCl_3$
Nd–$NdCl_3$	2.56 ± .01	640 ± 3	2.01 ± 0.03	844 ± 2	$NdCl_2$
Nd–NdI_3	2.12 ± .02	492 ± 2	(2.0)	560 ± 5	NdI_2

The dark green $NdCl_2$ has been further identified from powder pattern data as isomorphous with the orthorhombic $PbCl_2$ structure reported for $SmCl_2$ and $EuCl_2$ by Döll and Klemm,[9] with lattice constants of 4.51, 7.58 and 9.07 A. ($SmCl_2$: 4.49, 7.53, 9.97 A.). Such a comparison has not yet been made for the dark purple NdI_2. Phase diagram and X-ray data for the $NdCl_3$–$NdCl_2$ system also show the existence of an intermediate phase near $NdCl_{2.3}$ in composition, melting probably incongruently near 703°.

Contribution No. 793. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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[1] J. D. Corbett, S. v. Winbush and F. C. Albers, THIS JOURNAL, **79**, 3020 (1957).

[2] J. D. Corbett and A. Hershaft, *ibid.*, **80**, 1530 (1958).

[3] G. Mellors and S. Senderoff, *J. Phys. Chem.*, **63**, 1110 (1959).

[4] D. Cubicciotti, THIS JOURNAL, **71**, 4119 (1949).

[5] C. Estee and G. Glocker, *ibid.*, **70**, 1344 (1948).

[6] H. Laitinen and E. Blodgett, *ibid.*, **71**, 2260 (1949).

[7] P. S. Gentile, Ph.D. Thesis, University of Texas, Austin, Texas, 1955.

[8] We are indebted to Drs. F. H. Spedding and A. H. Daane for the generous supply of pure metal and the benefit of their experience in experimental techniques.

[9] W. Döll and W. Klemm, *Z. anorg. allgem. Chem.*, **241**, 246 (1939).

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CARBENOID AND CATIONOID DECOMPOSITION OF DIAZO HYDROCARBONS DERIVED FROM TOSYLHYDRAZONES

Sir:

Tosylhydrazones (p-toluenesulfonylhydrazones) of aromatic aldehydes and ketones react with sodium in ethylene glycol to give aryldiazoalkanes; tosylhydrazones of benzyl methyl ketone (equation 1) and cyclohexanone yield olefins and nitrogen.[1]

$$C_6H_5CH_2C(CH_3){=}NNHO_2SC_7H_7 + NaOCH_2CH_2OH \longrightarrow C_6H_5CH{=}CHCH_3 + N_2 + NaO_2SC_7H_7 + HOCH_2CH_2OH \quad (1)$$

Carbon-skeleton rearrangements occur in decomposition of pinacolone and camphor tosylhydrazones[1] to give 2,3-dimethyl-2-butene and camphene.[2]

An investigation has now been made of reactions of arylsulfonylhydrazones with bases in protonic and aprotic solvents. The experimental condi-

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[1] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

[2] See also R. Hirschmann, E. S. Snoddy, Jr., C. F. Hiskey and N. L. Wender, THIS JOURNAL, **76**, 4013 (1954) and G. H. Phillips, D. A. H. Taylor and L. J. Wyman, *J. Chem. Soc.*, 1739 (1954).

tions result in a simple method for generating diazo compounds *in situ* and studying their decomposition by cationoid and carbenoid processes. Reaction of camphor tosylhydrazone and sodium methoxide in diethylene glycol at 140–180° thus gives camphene (55%) and tricyclene (45%) in near-quantitative yield; decomposition of the hydrazone by sodium methoxide in diethyl Carbitol gives the hydrocarbons (~100% yield) in proportions > 49:1.[3] The effects of solvents on such processes are also indicated by reaction of 2-methylpropanal tosylhydrazone and sodium methoxide in diethylene glycol to give 2-methylpropene (65%), *cis*-2-butene (4%), *trans*-2-butene (8%), 1-butene (10%), and methylcyclopropane (12%) in 30% yield, whereas in diethyl Carbitol or hexadecane, 2-methylpropene (62, 64%) and methylcyclopropane (37, 36%) are formed in 80 and 78% yields.[4]

The initial reaction of 2-methylpropanal tosylhydrazone (and other tosylhydrazones) is formation of its salt and methanol; thermal decomposition of this salt in diethyl Carbitol or hexadecane gave 2-methylpropene (61, 62%) and methylcyclopropane (39–37%) in composition essentially identical with that from the hydrazone and sodium methoxide in aprotic solvents. It is suggested that salts of tosylhydrazones decompose to diazo compounds; the diazo compounds undergo (1) proton transfer from donor solvents and cationic decomposition of the Wagner–Meerwein type involving hydrogen and carbon-skeleton rearrangement and (2) carbenic decomposition in aprotic solvents to give olefins by hydrogen migration and *cyclopropanes by intramolecular insertion*. Additional evidence for the carbenic processes is derived from the observations that diazo compounds are detectable in the aprotic reaction products and that thermal decomposition of 1-diazo-2-methylpropane yields 2-methylpropene (67%) and methylcyclopropane (33%).

The carbenoid decomposition of other tosylhydrazones in sodium methoxide-diethyl Carbitol has been investigated.[5] The hydrocarbons and their per cent. compositions as obtained from these tosylhydrazones are: (1) propanal; propene (90%), cyclopropane (10%); (2) butanal; 1-butene (92%), methylcyclopropane (4.6%), *trans*-2-butene (2.3%), *cis*-2-butene (1.2%); (3) 2,2-dimethylpropanal; 1,1-dimethylcyclopropane (92%), 2-methyl-2-butene (7%), 2-methyl-1-butene (1%); (4) 2-butanone; *trans*-2-butene (67%), *cis*-2-butene (28%), 1-butene (5%), methylcyclopropane (0.5%); and (5) 3,3-dimethyl-2-butanone[6] (pinacolone); 3,3-dimethyl-1-butene (52%), 1,1,2-trimethylcyclopropane (47%). It is concluded that (1) rearrangements in carbenoid decomposition of diazo compounds involving hydrogen migration[7a] occur more readily than do carbon-skeleton rearrangements, (2) carbenoid decomposition of diazo compounds results in extensive intramolecular cyclization to give cyclopropanes,[7b] and (3) the secondary carbenes presumably formed as reaction intermediates are more selective in their decomposition than are their primary analogs.

We wish to acknowledge the assistance of Drs. R. R. Hopkins and I. J. Oita, Whiting Research Laboratories, Standard Oil Company (Ind.).

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(3) For related reactions see H. Meerwein and K. v. Emster, *Chem. Ber.*, **53**, 1815 (1920); W. Hückel and F. Nerdel, *Ann.*, **528**, 57 (1957).

(4) The yields of hydrocarbons from proton-donor solvents are considerably smaller than that in aprotic solvents.

(5) Cationic decomposition is not totally suppressed in these systems because methanol is formed.

(6) Decomposition in diethylene glycol gave 3,3-dimethyl-1-butene (16%), 2,3-dimethyl-2-butene (16%), 2,3-dimethyl-1-butene (56%), 1,1,2-trimethylcyclopropane (11%). The fact that the decomposition of tosylhydrazones of 2-methylpropanal and 3,3-dimethyl-2-butanone in diethylene glycol yields cyclopropanes indicates that carbenoid decomposition occurs competitively with cationoid processes.

(7) (a) F. O. Rice and A. L. Glasebrook, THIS JOURNAL, **56**, 741 (1934) report that diazoethane decomposes to ethylene and nitrogen. (b) For related reactions of methylene see W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

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RECEIVED AUGUST 21, 1959

ISOLATION OF CYTIDINE-5'-MONOPHOSPHO-N-ACETYLNEURAMINIC ACID[1]

Sir:

In conjunction with studies[2,3,4] on the metabolism and structure of the sialic acids, we have now isolated a new nucleotide, cytidine-5'-monophospho-N-acetylneuraminic acid, from *Escherichia coli* K-235, an organism which produces a polymer of NAN.[5,6]

The nucleotides from sonically disrupted cells were fractionated on Dowex-1,Cl^- resin using LiCl as eluting agent. A nucleotide, giving characteristic color reactions for sialic acid, was eluted slightly behind C5P, but before other nucleoside monophosphates. Paper chromatography of the material in this peak yielded two major components, C5P and C5P-NAN (R_{NAN} 0.36 and 0.61, respectively); free NAN was not detected.[7]

After elution from the paper, the C5P-NAN yielded these analyses (molar ratios): NAN, 0.97; cytidine, 1.00; organic phosphate, 1.01. The isolated C5P-NAN represented 6% of the total nucleotide adsorbed by the ion-exchange resin. Evidence that C5P-NAN was a single substance,[7] not a mixture of C5P and NAN, was obtained by paper chromatography in three solvent systems, paper electrophoresis at *p*H 5.0 and 7.7, and complete resistance to attack by NANaldolase[2] and rattlesnake venom 5'-nucleotidase. The ultraviolet-absorbing material on the paper chromato-

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(1) The Rackham Arthritis Research Unit is supported by a grant from the Horace H. Rackham School of Graduate Studies of The University of Michigan. This investigation was aided by a grant from the American Cancer Society and one from the National Institutes of Health (A-512).

(2) D. G. Comb and S. Roseman, THIS JOURNAL, **80**, 497 (1958).

(3) D. G. Comb and S. Roseman, *Biochim. et Biophys. Acta*, **29**, 653 (1958).

(4) S. Roseman and D. G. Comb, THIS JOURNAL, **80**, 3166 (1958); C. T. Spivak and S. Roseman, *ibid.*, **81**, 2403 (1959).

(5) G. T. Barry and W. F. Goebel, *Nature*, **179**, 206 (1957); G. T. Barry, *J. Exp. Med.*, **107**, 507 (1958).

(6) These abbreviations are used: NAN, N-acetylneuraminic acid; C5P, cytidine-5'-monophosphate; C5P-NAN, cytidine-5'-monophospho-N-acetylneuraminic acid; NANaldolase, N-acetylneuraminic acid aldolase.

(7) When stored in the dry state at −16°, C5P-NAN decomposed to NAN and C5P to the extent of 5 to 10% per day. Fresh samples of C5P-NAN exhibited trace spots of C5P and NAN on the chromatograms; these became more apparent each day the samples were stored.