

suggested the experiment described here—measurement of $\Delta\bar{H}_s$ of sodium tetraphenylboride in aqueous *t*-butyl alcohol mixtures—since this should magnify the effect and cause it to come at a higher water content than in aqueous ethanol.

In Figure 1, it is seen that $\Delta\bar{H}_s$ for several salts do indeed give sharp endothermic maxima at about 0.96 mole fraction of water (the corresponding maxima in aqueous ethanol appeared at about 0.85 mole fraction of water and were uniformly smaller).¹⁰ Again, the size of the peak is roughly related to the size of the ions, although in both solvent systems there is a distinct difference between sodium tetraphenylboride and tetraphenylarsonium chloride, suggesting that the sign of the charge on a large ion is important. We also find similar behavior for nonelectrolytes, although large molecules, such as tetraphenylmethane, are too insoluble for accurate study at present. All of the heat measurements were made at $25 \pm 1^\circ$ with a special solution calorimeter, which will presently be described in detail.¹⁰ These results imply that the main effect of adding the solute to highly aqueous alcohol solutions is to reorganize the solvent structure in the neighborhood of the solute particles. It would be very difficult to explain the effect of size and charge (or lack of charge) in terms of solvation by coordination or solvent sorting. We will present a simple phenomenological interpretation of such behavior soon,¹⁰ including its application to solvent effects on activation parameters. The present case is presented here as a dramatic example of the unexpected behavior of cosolvents in highly aqueous systems and to encourage the use of *t*-butyl alcohol rather than ethanol in future studies of aqueous alcohol systems. There is every reason to believe³ that aqueous solutions of glycols and polyols will give much smaller effects, although the miscibility problem will be greatly reduced.

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Dicyanocarbene

Sir:

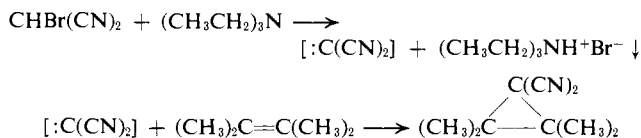
We wish to report the preparation of dicyanocarbene with evidence for its existence as an intermediate. In an earlier reference to the possible formation of dicyanocarbene, Cairns and co-workers proposed that dicyanocarbene may be an intermediate in the preparation of tetracyanoethylene from dibromomalononitrile and copper powder in boiling benzene.^{1,2} However, they were unable to obtain direct evidence for the existence of dicyanocarbene as an intermediate having failed to obtain the expected 7,7-dicyanobicyclo[4.1.0]heptane by trapping dicyanocarbene with cyclohexene.

We have prepared dicyanocarbene from bromomalononitrile by the abstraction of hydrogen bromide with triethylamine. The dicyanocarbene was trapped with

(1) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick, W. J. Middleton, R. M. Scribner, C. W. Theobald, and H. E. Winberg, *J. Am. Chem. Soc.*, **80**, 2775 (1958).

(2) NOTE ADDED IN PROOF. E. Ciganek has recently reported the generation of dicyanocarbene from dicyanodiazomethane in the preparation of 7,7-dicyanonorcaradienes: E. Ciganek, *ibid.*, **87**, 652 (1965).

2,3-dimethyl-2-butene (tetramethylethylene), employed as the solvent in the reaction, to produce the expected 1,1-dicyanotetramethylcyclopropane. The proposed reaction sequence is



In a typical reaction, 10.0 g. (0.069 mole) of bromomalononitrile dissolved in 600 ml. of tetramethylethylene and 7.7 g. (0.076 mole) of triethylamine in 660 ml. of tetramethylethylene were added simultaneously (12 hr.) to 4.8 l. of tetramethylethylene with stirring at -8° in a nitrogen atmosphere. The triethylamine hydrogen bromide salt which precipitated during the reaction was removed by filtration and the tetramethylethylene was stripped off at 50 mm. in a rotary vacuum evaporator leaving a yellow oil. The 1,1-dicyanotetramethylcyclopropane was recovered, by fractional distillation (57° at 0.04 mm.), as a colorless oil which solidified and was recrystallized from ligroin to yield 2.5 g. (24%) of white needles melting at $51.5\text{--}52.0^\circ$. The n.m.r. spectrum of the product in carbon tetrachloride shows only a single sharp peak due to the 12 equivalent methyl hydrogens (τ 8.62 p.p.m.); the infrared spectrum of the product in carbon tetrachloride has a strong single peak due to the nitrile groups (2265 cm.^{-1}).

Anal. Calcd. for $\text{C}_9\text{H}_{12}\text{N}_2$ (148.23): C, 72.92; H, 8.18; N, 18.90. Found: C, 72.84; H, 8.33; N, 18.71.

The triethylamine hydrogen bromide salt was washed with acetone and recrystallized from ethanol to give white needles melting at $247\text{--}248^\circ$. Decomposition of the salt with sodium hydroxide released the triethylamine which formed a yellow picrate melting at $170\text{--}172^\circ$.

We are continuing to study the reactions of dicyanocarbene in a number of different systems and will report our findings in future papers.

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A New Type of Bis Arene-Metal Complex

Sir:

Bis arene-metal complexes so far known contain a single atom between the sandwich arenes.¹ We wish to report an example of a new type of bis arene-metal complex in which two metal atoms are contained between the two arene rings.

The new complex has the formula $[\text{PdAl}_2\text{Cl}_7(\text{C}_6\text{H}_6)]_2$ (I) and has been obtained by allowing AlCl_3 , Al, and

(1) See, e.g., H. Zeiss, "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, pp. 380-425.