

Failure in earlier experiments to achieve catalytic hydrogenation of olefinic compounds with other metal ions and complexes (*e.g.*, Cu^{II}, Ag^I and Hg^{II}) which activate hydrogen homogeneously in solution¹ is attributable to two factors, (a) failure of the catalyst to activate the olefinic substrate as well as the hydrogen molecule and (b) the tendencies of these catalysts to undergo reduction themselves in preference to hydrogenation of the olefin. In the present system, complex formation between Ru^{II} and the olefinic compound apparently activates the latter, while stabilizing Ru^{II} itself against reduction (or disproportionation), and thus contributes to fulfillment of the requirements associated with both these factors.

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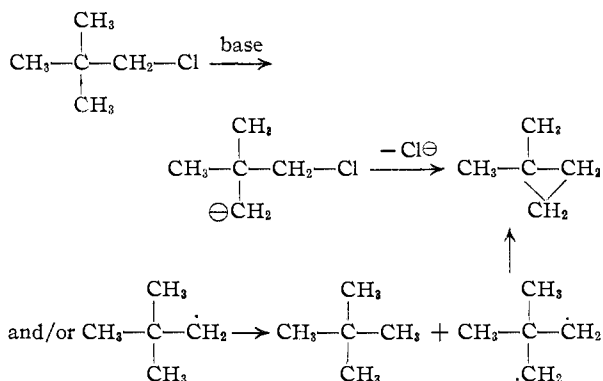
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CARBENE INTERMEDIATE IN THE WURTZ REACTION. α -ELIMINATION OF HYDROGEN CHLORIDE FROM NEOPENTYL CHLORIDE

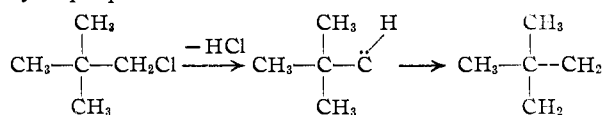
Sir:

The conversions of neopentyl chloride by (a) sodium metal¹ to 1,1-dimethylcyclopropane and neopentane, and (b) sodium *n*-propyl² to 1,1-dimethylcyclopropane were explained in the early 1940's by Whitmore and co-workers by assuming a carbanion intermediate which undergoes cyclic self-alkylation, or a diradical intermediate in the case of sodium reactions.



The recent observations³ that bases convert alkyl halides to carbenes and that carbenes cyclize readily to cyclopropanes⁴ by insertion at C₃ suggested an alternative mechanism for the conversions of neopentyl chloride to dimethylcyclopropane. If neopentyl chloride undergoes α -elimination of H and Cl to produce *t*-butylcarbene, this intermedi-

ate might be expected to cyclize to 1,1-dimethylcyclopropane.



The carbene mechanistic scheme is readily distinguished from the earlier proposals through a study of 1,1-dideuterio-neopentyl chloride, (CH₃)₃CCD₂Cl, since the older mechanisms predict a di-deuterio- and the carbene mechanism a mono-deuterio-dimethylcyclopropane.

1,1-Dideuterio-neopentyl alcohol was prepared by lithium aluminum deuteride reduction of trimethylacetic acid (72% based on LiAlD₄). The alcohol was converted to the neopentoxyltriethylsilane and then to neopentyl chloride (37%) with thionyl chloride by the method of Sommer, *et al.*⁵ Proton magnetic resonance spectra (40 Mc.) of the neat alcohol and chloride showed no protium on the α -carbons, using the undeuterated alcohol and chloride to determine the δ 's of the methylene groups.

The original observations of Whitmore, *et al.*, were confirmed, neopentyl chloride and sodium yielding neopentane (70%) and 1,1-dimethylcyclopropane (26%) (separated by gas chromatography and identified by gas phase infrared spectra of the pure substance). Under similar conditions 1,1-dideuterio-neopentyl chloride is converted to neopentane (63%) and 1,1-dimethylcyclopropane (35%). Since neither infrared nor proton resonance spectroscopies yielded readily interpretable results, mass spectral cracking patterns were employed for isotopic analysis.⁶

Neopentane yields no parent peak, but instead yields a mass 57 peak (C₄H₉⁺) by methyl cleavage. The labeled neopentane yielded peaks at 57, 58, 59, 60 and 61, with relative intensities 48.2, 7.7, 63.9, 100 and 4.3. By correcting for natural abundance C₁₃ and assuming there is no isotope effect in methyl and hydrogen cleavages, the calculated composition is 58.6% tri-, 36.8% di-, 1.9% mono-deuterio-neopentanes, and 2.8% undeuterated neopentane.

Unlabeled 1,1-dimethylcyclopropane yields peaks of mass 71, 70, 69 and 68, with relative intensities 5.9:100:7.3:0. The labeled 1,1-dimethylcyclopropane yields peaks of mass 72, 71, 70 and 69, with relative intensities 6.3:100:6.8:1.6. By correcting for natural abundance C₁₃ and assuming no isotope effect in the cracking pattern, this mixture is calculated to be 0.3% C₅H₁₀D₂, 97.8% C₅H₁₁D and 1.8% C₅H₁₂.

The carbene mechanism with intermediate (CH₃)₃C- $\ddot{\text{C}}$ -D, is strongly indicated by the conversion of 1,1-dideuterio-neopentyl chloride to monodeuterio-1,1-dimethylcyclopropane.

The 38% yield of (CH₃)₃CCD₃ is 58.6% of the total yield of neopentane. It is reasonable to suppose that the 23% conversion to (CH₃)₃CCD₂H

(5) L. H. Sommer, H. D. Blankman and P. S. Miller, *ibid.*, **76**, 803 (1954).

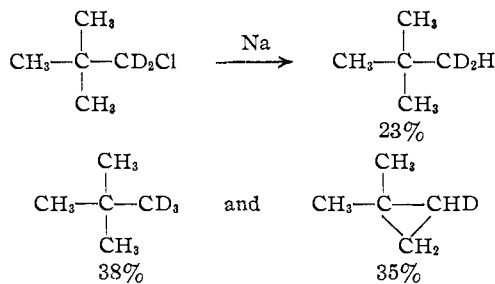
(6) We wish to thank Professor F. W. Lampe and Dr. Thomas Acelz (Humble Oil and Refining Company) for obtaining the cracking patterns of the reaction products.

(1) F. C. Whitmore, A. H. Popkin, H. I. Bernstein and J. P. Wilkins, *J. Am. Chem. Soc.*, **63**, 124 (1941).

(2) F. C. Whitmore and H. D. Zook, *ibid.*, **64**, 1783 (1942).

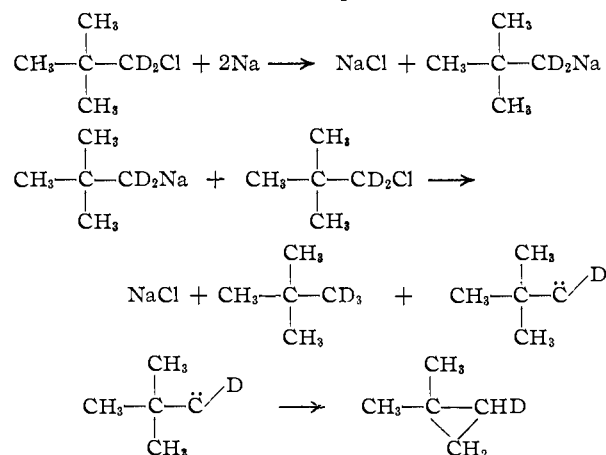
(3) L. Friedman and J. G. Berger, *ibid.*, **82**, 5758 (1960); G. L. Closs, presented before the Organic Section of the American Chemical Society, September 1960, p. 9; P. W. Kirmse, *Angew. Chem.*, **72**, 716 (1960); L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 492 (1961).

(4) L. Friedman and H. Shechter, *ibid.*, **81**, 5512 (1959).



is not related to the above reaction, but represents conversion of neopentyl sodium or other intermediates, such as neopentyl radical, by reaction with moisture or the solvent.

A reasonable mechanism consonant with the close correspondence of yields of trideuterio-neopentane and monodeuterio-dimethylcyclopropane involves an α -elimination step.



(7) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research and to the Office of Ordnance Research, Contract No. DA-36-061-ORD-607.

DEPARTMENT OF CHEMISTRY PHILIP S. SKELL⁷
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THE ENTROPIES OF ASSOCIATION OF IONS

Sir:

It is the opinion of some workers that the entropy changes accompanying the association of ions in aqueous solution, ΔS , are reasonably well understood¹ The changes usually are related to physical properties of the ions taking part or to their entropies of hydration, ΔS_{hyd} . George,² in an analysis of a large number of data, recognized two types of behavior:

(1) For many ion pairs having one ion in common, ΔS^0 conformed to the empirical equation $\Delta S^0 = -\Delta S_{\text{hyd}} + C$, where C was a constant for each common ion. It was suggested that in these cases there was a loss of water of hydration and possible complex formation.

(2) Reactions for which ΔS^0 was independent of ΔS_{hyd} . This was attributed to the formation of true ion pairs and was illustrated by data for

(1) R. J. P. Williams, *Ann. Reports Chem. Soc.*, **56**, 87 (1959).
(2) J. H. B. George, *J. Am. Chem. Soc.*, **81**, 5530 (1959).

bivalent metal sulfates. Unfortunately, George used the figures of Singh³ for calcium, strontium, barium and lead sulfates and these are not association entropies at all but refer to entropy changes, ΔS^1 , for the reaction $\text{MSO}_4(\text{solid}) \rightleftharpoons \text{M}^{2+} + \text{SO}_4^{2-}$. Indeed it would be difficult to recognize ion association in solutions of salts as sparingly soluble as barium sulfate. Where comparison is possible, for calcium sulfate, $\Delta S^1 = 26.3 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$ whereas $\Delta S^0 = 16.1 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.⁴ Furthermore, $-\Delta S_{\text{hyd}}(\text{Mg}^{2+})$ used by George, $71 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$, differs from the calculated value $63.7 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$.⁵

More data now are available for bivalent metal sulfates and these are given in the table together with $\Delta S_{\text{hyd}}(\text{M}^{2+})$ and calculated values of $\Delta S_{\text{hyd}}(\text{MSO}_4)$.

TABLE I

ENTROPIES OF ASSOCIATION AND OF HYDRATION

Reaction	ΔS^0 (cal./deg. mole)	$-\Delta S_{\text{hyd}}$ (M^{2+}) (cal./deg. mole)	$-\Delta S_{\text{hyd}}$ (MSO_4) (cal./deg. mole)	Ref.
$\text{Mg}^{2+} + \text{SO}_4^{2-}$	26.2	63.7	66	6
$\text{Ca}^{2+} + \text{SO}_4^{2-}$	16.1	50.2	62.5	4
$\text{Mn}^{2+} + \text{SO}_4^{2-}$	22.6	61.5	63	7
$\text{Co}^{2+} + \text{SO}_4^{2-}$	16.6	65	71	7
$\text{Ni}^{2+} + \text{SO}_4^{2-}$	21.7	66.5	67	7
$\text{Zn}^{2+} + \text{SO}_4^{2-}$	24.4	64	67	6

It is apparent immediately that ΔS^0 is not independent of $\Delta S_{\text{hyd}}(\text{M}^{2+})$ and the second class of behavior suggested by George² cannot be substantiated.

(3) D. Singh, *J. Sci. Research Benares Hindu Univ.*, **6**, 131 (1955).

(4) R. P. Bell and J. H. B. George, *Trans. Faraday Soc.*, **49**, 619 (1953).

(5) G. H. Nancollas, *J. Chem. Soc.*, 744 (1956).

(6) V. S. K. Nair and G. H. Nancollas, *ibid.*, 3706 (1958).

(7) V. S. K. Nair and G. H. Nancollas, *ibid.*, 3934 (1959).

DEPARTMENT OF CHEMISTRY

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RARE EARTH STANNATES, $\text{R}_2\text{Sn}_2\text{O}_7$

Sir:

Polycrystalline stannates of general formula $\text{R}_2\text{Sn}_2\text{O}_7$, isostructural with pyrochlore, where $\text{R} = \text{Tb}, \text{Dy}, \text{Ho}, \text{Tm}, \text{Lu}$, have been prepared by solid state reaction from intimate mixtures of R_2O_3 and SnO_2 . The details of preparation are the same as given in a recent publication.¹ Tb_2O_3 was prepared by heating the commercial oxide mixture in hydrogen at 680° for 2 hours and cooling to room temperature in hydrogen.

X-Ray diffraction investigations were made on powder samples with filtered copper radiation using both film and Geiger diffractometer techniques. Experimental lattice constants, determined as before,¹ are compared with calculated lattice constants in Table I. The latter were obtained from linear equations¹ using the rare earth radii of Templeton and Dauben.² All of the lanthanide stannates now have been prepared

(1) C. G. Whinfrey, D. W. Eckart and A. Tauber, *J. Am. Chem. Soc.*, **82**, 2695 (1960).

(2) D. H. Templeton and C. H. Dauben, *ibid.*, **76**, 5237 (1954).