

Furthermore, the fact that a number of different fractions is isolated argues against simple ring formation in this reaction. A preliminary infrared examination of the different fractions also supports the thesis that there are species with different molecular weights present. In general the spectra are similar, but there are differences in the PO_2 absorption bands that are suggestive. The PO_2 absorption bands for the dimer and for diphenylphosphinic acid in the region $1100\text{--}1230\text{ cm}^{-1}$ are fairly sharp, whereas in the various products described here there appear to be several overlapping absorptions lying above and below the location of the corresponding PO_2 absorption in the dimer and in diphenylphosphinic acid. This suggests the presence of a mixture of different polymeric species with the PO_2 absorption band shifted to various positions depending on its environment. Preliminary confirmation for such a sensitivity is afforded by the observation of a frequency shift for this absorption maximum when the acetylacetonate group in the dimer is replaced by another chelating ligand.

Thermogravimetric analysis gives a temperature of $296\text{--}300^\circ$ for initial weight loss for the insoluble fraction and 336° for initial weight loss of a fraction soluble in benzene. Since chromium(III) acetylacetonate has been found to start decomposing at an appreciable rate at 250° ,¹⁴ it is most likely that the weakest spot in the structure is at the acetylacetonate group.

Acknowledgment.—We are indebted to the Office of Naval Research for partial support of these studies, to our Analytical Department for the analyses, to Dr. A. J. Saraceno for assistance with the interpretation of the infrared spectra, and to Dr. J. R. Soulen for the thermogravimetric studies.

(14) J. Von Hoene, R. G. Charles, and W. M. Hickam, *J. Phys. Chem.*, **62**, 1098–1101 (1958).

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CONDENSATIONS AT THE GAMMA POSITION OF BETA-KETOALDEHYDES. A NEW METHOD OF ANGULAR METHYLATION¹

Sir:

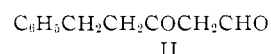
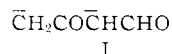
We wish to report that alkylations and other condensations have been directly effected at the gamma position of certain β -ketoaldehydes (hydroxymethylene ketones) through intermediate dianions. This is a novel mode of reaction of β -ketoaldehydes, although similar condensations at the terminal methyl group of acetylacetone and of other β -diketones previously have been accomplished through their dicarbanions.² The experimental procedure employed with β -diketones² was altered for β -ketoaldehydes, which are more reactive. The latter compounds were handled as their alkali metal salts or copper chelates.

Sodio formylacetone was prepared from acetone and ethyl formate in the usual manner³ and added

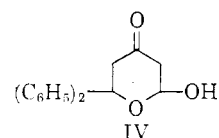
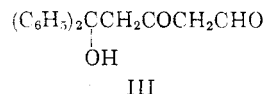
(1) Supported by the National Science Foundation (NSF-G14527).

(2) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

to a molecular equivalent of potassium amide in liquid ammonia. The resulting olive green dicarbanion I was treated with a molecular equivalent of benzyl chloride. After evaporation of the ammonia, alkylation product II was isolated in 80% yield as the copper chelate, m.p. $176\text{--}178^\circ$. This product was identified by comparison with an authentic sample of the chelate of II (lit. m.p. 176°) prepared by the method of Joshi, *et al.*⁴



Similarly, dicarbanion I was condensed with benzophenone to give hydroxy- β -ketoaldehyde III, which was isolated as its copper chelate (blue needles), m.p. $177\text{--}178^\circ$, in 67% yield. *Anal.* Calcd. for $\text{C}_{34}\text{H}_{30}\text{O}_6\text{Cu}$: C, 68.27; H, 5.06; Cu, 10.62. Found: C, 68.17; H, 5.10; Cu, 10.79. Treatment of this chelate with acid afforded a white crystalline product, m.p. $123\text{--}124^\circ$, infrared peaks (KBr): $2.98\text{ }\mu$ (OH), $5.85\text{ }\mu$ (non-conjugated ketone). *Anal.* Calcd. for $\text{C}_{17}\text{H}_{16}\text{O}_3$: C, 76.10; H, 6.01. Found: C, 76.00; H, 6.00. The product failed to give a positive enol test with ethanolic ferric chloride. It is tentatively assigned the hemiacetal structure IV.



Interestingly, the present method of alkylation furnished a new procedure for introducing an angular methyl group into 1-decalone at the 9-position. Sodio 2-formyl-1-decalone (V) was prepared in the usual manner⁵ and added to a molecular equivalent of potassium amide in liquid ammonia. The resulting dicarbanion was treated with methyl iodide to give a mixture of the isomers of VII, which was isolated in about 60% yield as the copper chelate, m.p. $171\text{--}175^\circ$. After two recrystallizations from ethanol the chelate melted $183\text{--}185^\circ$. *Anal.* Calcd. for $\text{C}_{24}\text{H}_{34}\text{O}_4\text{Cu}$: C, 64.05; H, 7.61; Cu, 14.12. Found: C, 63.85; H, 7.45; Cu, 13.88. Treatment of the crude chelate with acid and removal of the formyl group by alkali, afforded 9-methyl-1-decalone (VIII) in 85% yield. Vapor phase chromatography on a Ucon Polar column indicated that VIII was a 56:44 mixture of the *trans* and *cis* isomers. The isomers also were separated and identified by their relative rates of semicarbazone formation, *trans* isomer m.p. $218.5\text{--}219^\circ$ (lit. m.p. $219\text{--}220^\circ$) *cis* isomer m.p. $225\text{--}226^\circ$ (lit. m.p. $226\text{--}227^\circ$).⁶

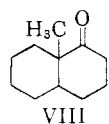
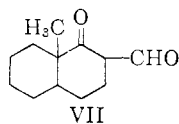
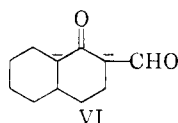
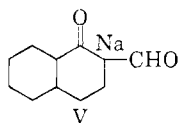
This direct method of introducing an angular methyl group appears more convenient than those involving the intermediate preparation from V of

(3) W. S. Johnson, E. Woroch and F. J. Mathews, *ibid.*, **69**, 566 (1947).

(4) S. N. Joshi, R. Kaushal and S. S. Deshapande, *J. Ind. Chem. Soc.*, **18**, 479 (1941).

(5) W. S. Johnson and H. Posvic, *J. Am. Chem. Soc.*, **69**, 1361 (1947).

(6) W. S. Johnson, *ibid.*, **65**, 1317 (1943).



the 2-methylanilinomethylene⁷ or the 2-isopropoxymethylene⁵ derivative of decalone.

Further studies are in progress on the reactions of the dicarbanions of formylacetone, formyldecalone and other β -ketoaldehydes.

(7) A. J. Birch and R. Robinson, *J. Chem. Soc.*, 501 (1944).

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RECEIVED MARCH 26, 1962

CARBONIUM ION SALTS. IV. TETRAIODOBORATES¹

Sir:

The literature on complexes of boron iodide is sparse. The single reference to iodoborate formation—a remarkably terse communication by Waddington²—gives no details of preparation or characterization, and the ammonia adduct reported by Besson³ has been shown^{4,5} not to exist. We wish to report that the method used for the preparation of tropenium chloroborate⁶ and bromoborate⁷ has yielded tropenium iodoborate, and to present evidence for the existence of triphenylcarbonium iodoborate.

Boron iodide reacts rapidly and smoothly with cycloheptatriene in dry methylene chloride (glove box; dry, O₂ free N₂ atmosphere) to give 60.6% tropenium iodoborate as a precipitate of brilliant yellow single crystals, m.p. 223°, ultraviolet spectrum (96% sulfuric acid)⁸: λ_{\max} 268 (sh), 274 (4330), 280 m μ ; (water)⁹: λ_{\max} 275 (4380), 280 (sh). *Anal.* Calcd. for C₇H₇BI₄: C₇H₇⁺, 14.9; B, 1.77; I, 83.28. Found⁷: C₇H₇⁺, 14.8; B, 1.65; I, 83.32. The iodoborate is stable in a dry atmosphere and does not seem light sensitive; however, it is hygroscopic and darkens with liberation of hydrogen iodide on exposure to moist air. The compound is not decolorized by ice-cold water, in which it is sparingly soluble, and dissolves smoothly on warming to room temperature to give water-white solutions of tropenium ion, boric acid, and hydriodic acid. It is decomposed instantly by

acetone to give scarlet tropenium iodide, m.p. 127°.^{8,10} On attempted sublimation (85°, 0.2 mm.) the iodoborate decomposed slowly; a mixture of tropenium iodide and triiodide collected on the cold finger.

Reaction of boron iodide with triphenylmethyl iodide in methylene chloride (conditions as above, then precipitation with cyclohexane) gave dark, viciously hygroscopic, light sensitive crystals for which satisfactory analyses could not be obtained. The formation of triphenylcarbonium iodoborate in the methylene chloride solution is inferred from the following: (1) Addition of cycloheptatriene to a boron iodide–triphenylmethyl iodide solution in methylene chloride gives an instantaneous precipitate of 57% tropenium iodoborate of high purity and 95% triphenylmethane is isolated from the reaction solution. This rapid hydride exchange shows^{6,7,8,11} the existence of an ionic triphenylcarbonium salt; the iodoborate ion is the most probable anionic species.¹² (2) B¹¹ n.m.r. spectra¹³ of boron iodide–triphenylmethyl iodide solutions in methylene chloride show a single resonance at $\delta = +112.2$ (relative to (C₂H₅)₂O·BF₃=O) compared to a value of $\delta = +5.5$ for boron iodide. Triphenylcarbonium chloroborate ($\delta = -4.5$) and bromoborate ($\delta = +23.9$) in methylene chloride show similar shifts to higher field relative to the halides (BCl₃, $\delta = -45.6$; BBr₃, $\delta = -40.1$)¹⁴ as do alkali metal haloborates in nitrobenzene.¹⁵ The theoretical predictions of Landesman and Williams¹⁵ that tetrahedral iodoborate ion should show a chemical shift greater than $\delta = +100$ (higher than any other known boron compound) are in agreement with the value observed for presumed triphenylcarbonium iodoborate.

(10) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957).

(11) D. L. Pearson, Ph. D. Thesis, University of Washington, 1955; *Dissertation Abstr.*, **15**, 978 (1955).

(12) Under these conditions triphenylmethyl iodide and cycloheptatriene give a precipitate of only 1.5% tropenium triiodide in 24 hours.

(13) We are indebted to Dr. Robert E. Williams and the National Engineering Science Company, Pasadena, California, for determination of the B¹¹ chemical shifts of the haloborates.

(14) T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(15) H. Landesman and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 2663 (1961).

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RECEIVED FEBRUARY 17, 1962

FORMATION OF BIS-(METHYLTHIO)-METHYLENE FROM METHYL ORTHOTHIOFORMATE AND POTASSIUM AMIDE

Sir:

Earlier work has provided evidence that a number of trisubstituted methanes, upon treatment with base, undergo α -elimination reactions yielding derivatives of methylene as reaction intermediates.¹ There is evidence that the α -dehydrohalogenations

(1) (a) J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950); J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954); (b) W. v. E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954); (c) S. M. McElvain and P. L. Weyna, *ibid.*, **81**, 2579 (1959); J. Hine, R. J. Roscup and D. C. Duffey, *ibid.*, **82**, 6120 (1960); (e) J. Hine and J. J. Porter, *ibid.*, **82**, 6178 (1960).

(1) Supported by the Petroleum Research Fund.

(2) T. C. Waddington and J. A. White, *Proc. Chem. Soc.*, 315 (1960).

(3) A. Besson, *Compt. rend.*, **114**, 542 (1892).

(4) A. Joannis, *ibid.*, **135**, 1106 (1902).

(5) W. J. McDowell and C. W. Keenan, *J. Am. Chem. Soc.*, **78**, 2069 (1956).

(6) K. M. Harmon, A. B. Harmon and F. E. Cummings, *ibid.*, **83**, 3912 (1961).

(7) K. M. Harmon and A. B. Harmon, *ibid.*, **83**, 865 (1961).

(8) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *ibid.*, **79**, 4557 (1957), report λ_{\max} 268 (sh), 273.5 (4350), 280 m μ for tropenium ion in this solvent.

(9) W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954), report λ_{\max} 275 (4350), 280 m μ (sh) for tropenium ion in this solvent.