rapid and step 2 rate-controlling. Figure 2 shows the initial rate, k_2ab, plotted against this calculated Schiff base concentration. The straight line obtained indicates second-order kinetics involving the Schiff base and nitromethane concentrations, consistent with a mechanism in which the Schiff base or its conjugate acid is an intermediate.

As we stated earlier,[3] the existence of a Schiff base intermediate does not preclude catalysis by secondary and tertiary amines. Preliminary experiments led to the isolation of nitrostyrene when piperidine and triethylamine were substituted for *n*-butylamine. A 74% yield was obtained with *N*-butylacetamide, in analogy with the efficiency of acetamide as catalyst for condensations in acetic acid.[8] It is quite possible that piperonylidene *n*-butylamine was formed under these conditions.[9]

EXPERIMENTAL

Materials. Glacial acetic acid, reagent grade, was dried by adding either acetic anhydride or benzene and fractionating. The water content was found by Karl Fisher titration to be 0.03%. Other reagents were as previously described.[4]

Formation of piperonylidene *n*-butylamine in acetic acid was demonstrated by its preparation in 74% yield.

Kinetic studies. Piperonal (about 0.2 g.) was weighed into a volumetric flask and dissolved in acetic acid. Nitromethane, *n*-butylamine, and water were added with calibrated pipets before dilution to 50 ml. This solution was then divided into 5-ml. samples which were sealed in 12 mm. diameter Pyrex ampoules and immersed for the desired time in a polyethylene glycol bath at 100.4 ± 0.3°. The ampoules were removed at intervals, cooled, and opened, and the contents transferred quantitatively into a solution of 2,4-dinitrophenylhydrazine for gravimetric determination of the aldehyde.[3]

Equilibrium studies. A solution of *n*-butylamine, water, and piperonylidene *n*-butylamine or piperonal was prepared in a drybox and placed in the thermostat. Equilibrium was reached within a minute or two. A sample was withdrawn after 30 min. and pipetted into methanolic hydrochloric acid for spectrophotometric determination of the Schiff base conjugate acid.[4] The rather small temperature coefficient of K probably rendered any shift of equilibrium, due to cooling of the sample during transfer, unimportant in this work. Since this sample was the only volume measured at 100°, the resulting Schiff base concentration was multiplied by 1.08, the ratio d_{25}/d_{100} for acetic acid. Thus, the concentrations given in this paper refer to solutions at 25°. While K would be independent of concentration units, the rate constant, k_2, must be multiplied by 1.08 for conversion to l/mole min. at the reaction temperature.

The spectrum of the methanol dilution of the reaction mixture showed only the peaks of piperonal and Schiff base in concentrations equal in sum to the stoichiometric piperonal concentration.

COBB CHEMICAL LABORATORY
UNIVERSITY OF VIRGINIA
CHARLOTTESVILLE, VA.

---

(8) A. C. Cope, *J. Am. Chem. Soc.*, **59**, 2327 (1937).

(9) R. N. Castle, *J. Am. Pharm. Assoc.*, **40**, 162 (1951), reports the formation of Schiff bases from aldehydes and sulfonamides in acetic acid.

New Synthesis of Dimethylaminodimethylborane

C. E. ERICKSON AND F. C. GUNDERLOY, JR.[1]

Received February 19, 1959

In the course of preparing dimethylaminomethylchloroborane, $(CH_3)_2NB(CH_3)Cl$,[2] moderate amounts of dimethylaminodimethylborane, $(CH_3)_2NB(CH_3)_2$, were required. Previous syntheses of the latter compound[3-5] were conducted in vacuum trains, under conditions not easily attained in ordinary laboratory equipment.

We have found that $(CH_3)_2NB(CH_3)_2$ may be prepared in high yield and in reasonable quantity by the action of methyl Grignard reagent on dimethylaminodichloroborane, $(CH_3)_2NBCl_2$. This is the first direct application of a Grignard reagent to the synthesis of an aminodialkylborane. Similar applications to the synthesis of *B*-alkylborazines (*i.e.*, *B*-alkylborazoles) have recently been discussed.[6-8]

We believe that this reaction represents a general method for the synthesis of dialkyl (and, presumably, diaryl) boron compounds that have been prepared up to now only by more indirect or cumbersome methods. The dimethylamino group may be regarded as a blocking group and can subsequently be replaced if desired. For example, hydrolysis yields a dialkylhydroxyborane (i.e., borinic acid).

EXPERIMENTAL

The reaction is carried out in a three-neck flask, fitted with a dropping funnel and stirrer, and protected with a dry nitrogen atmosphere. Dimethylaminodichloroborane, diluted with 10 to 20 volumes of ether, is placed in the flask, which is then immersed in an ice bath. The theoretical amount of methyl Grignard reagent in ether is added dropwise over a 3-hr. period, after which the bath is removed. The stirring is continued until the solution and suspended magnesium salts have warmed to room temperature. The ether and the product are then distilled from the flask at reduced pressure, trapping them in a reservoir at Dry Ice temperature. The residual magnesium salts are heated briefly to insure complete separation of product. Subsequent fractional distillation of the ether solution yields a small forerun and a main fraction of $(CH_3)_2NB(CH_3)_2$, boiling at 63-65° at atmospheric pressure. The product of an early run was found to contain 16.2%N (theory, 16.5%) by a Kjeldahl procedure. The chlorine content was nil. Methanol gave an adduct, melting at 49-51° (lit. 51-53°).[4]

---

(1) Present address: Esso Research and Engineering Co., Linden, N. J.

(2) To be published subsequently.

(3) E. Wiberg, *Naturwiss.*, **35**, 182 and 212 (1948).

(4) G. E. Coates, *J. Chem. Soc.*, 3481 (1950).

(5) T. E. Steinberg, M.S. Thesis, University of Southern California (1947).

(6) L. F. Hohnstedt and D. T. Haworth, Abstracts of Papers, 132nd ACS Meeting, 8S (1957).

(7) G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, *J. Am. Chem. Soc.*, **80**, 4515 (1958).

(8) S. J. Groszos and S. F. Stafiej, *J. Am. Chem. Soc.*, **80**, 1357 (1958).

Three runs gave yields of 49–61% of isolated, pure product in amounts up to 5.5 g. When product in the forerun and still residue was included, the yield was 69–71%. One run that gave a yield of only 20% was carried out with the flask initially immersed in a Dry Ice bath. When this was done the Grignard reagent did not react until after all of it had been added and the flask was warmed to near room temperature. A large amount of trimethylborane was formed, resulting in a low yield of the desired product. When the reaction was conducted at 0°, an excess of Grignard reagent was avoided, and yields were very good. Dimethylaminodibromoborane reacted equally well.

Dimethylaminodiethylborane was also prepared[9] in 58% yield of distilled, pure product from dimethylaminodibromoborane and an ethyl Grignard reagent.

Acknowledgement. The authors gratefully acknowledge a Frederick Gardner Cottrell Grant awarded by the Research Corp. in support of this research.

School of Chemistry
Rutgers, The State University
New Brunswick, N. J.

---

(9) By K. E. Kalantar.

Some Reactions of Methyl 2,4,6-Heptatrienoate

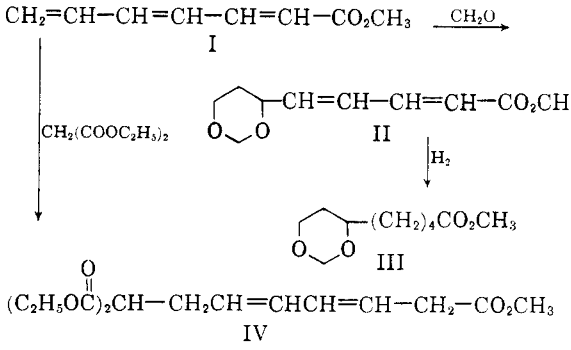
D. S. Acker and B. C. Anderson

Received February 20, 1959

Previous work[1,2] with long conjugated systems has indicated that most reactions yield mixtures of products which are quite difficult to separate. However, we have found that methyl 2,4,6-heptatrienoate[2] (I) reacts with surprising selectivity with formaldehyde in an acid-catalyzed reaction and with diethyl malonate in a base-catalyzed reaction. The products in each case result from attack of the reactive species on the terminal portion of the long conjugated system. There have been few, if any, examples in the literature of this type of selective reaction.

Condensation of methyl 2,4,6-heptatrienoate (I) with formaldehyde in dioxane-sulfuric acid gave methyl 6,8-methylenedioxy-2,4-octadienoate (II) in 35% yield. The structure of II was determined by its ultraviolet spectrum and by hydrogenation to methyl 6,8-methylenedioxyoctanoate (III), a known compound.[3]

The saturated ester III was obtained from I in 48% over-all yield when the ester II was hydrogenated without purification. The identity of III was further established by its conversion to lipoic acid by a series of known reactions.[3,4]



The base-catalyzed (Michael) addition of diethyl malonate to Compound I occurred predominantly in a 1,8-manner as shown by conversion of methyl 2,4,6-heptatrienoate through the intermediate diolefinic triester (IV) to azelaic acid in 62% yield. The high yield of azelaic acid is remarkable in view of the number of possible side reactions.

EXPERIMENTAL

Azelaic acid. A solution of 0.6 g. of sodium in 6 ml. of absolute methanol was diluted with 10 ml. of dry ether and then mixed with a solution of 20 g. (0.145 mole) of freshly distilled methyl 2,4,6-heptatrienoate in 75 ml. of diethyl malonate. The resulting solution was heated under reflux on a steam bath for 21 hr. and then diluted with 400 ml. of ether. This was washed with 12 ml. of 2*N* hydrochloric acid and two 10-ml. portions of water. The ethereal solution was dried over anhydrous magnesium sulfate, and all material volatile at 0.2 mm. at steam bath temperature was removed. The residual oil was dissolved in 100 ml. of absolute ethanol and hydrogenated in a low pressure apparatus over 10% Pd on carbon. The hydrogen absorption was rapid and stopped sharply. The catalyst was removed and the mother liquor diluted with 200 ml. of 95% ethyl alcohol before 40 g. of potassium hydroxide was added. This mixture was heated under reflux for 2 hr. Water (300 ml.) was then added and the apparatus was arranged for distillation. After all of the alcohol and 100 ml. of water had distilled, the mixture was cooled and carefully treated with 200 ml. of concentrated hydrochloric acid. After refluxing 40 hours, the solution was evaporated to dryness and extracted with ether. The ether was concentrated to give 16.0 g. of crude azelaic acid, m.p. 97–103°. This was recrystallized from water with 85% recovery to give good quality azelaic acid, m.p. 104–106°, which did not depress the melting point of an authentic sample. Infrared comparison confirmed its identity. The ether solution was evaporated to dryness to give an oil which upon distillation yielded (after recrystallization) 0.92 g. of azelaic acid, m.p. 103–107° (total yield 16.92 g., 62%) and 3.5 g. of material distilling at 100–125° (0.2 mm.) which was not identified.

Methyl 6,8-methylenedioxy-2,4-octadienoate (II). A mixture of 55 g. of purified dioxane, 8.0 g. of 96% sulfuric acid, and 6.0 g. (0.20 mole) of paraformaldehyde was stirred briefly and cooled to 0°. Methyl 2,4,6-heptatrienoate, 13.8 g. (0.10 mole), was added slowly, and the mixture was stirred at room temperature for 40 hr. The reaction mixture was cooled in an ice bath and diluted with 300 ml. of ice water. The organic layer was separated, and the water was extracted with three 150-ml. portions of ether. The organic layer and

---

(1) J. L. Charlish, W. H. Davies, and J. D. Rose, *J. Chem. Soc.*, 232 (1948).

(2) T. L. Cairns, V. A. Engelhardt, H. L. Jackson, G. H. Kalb, and J. C. Sauer, *J. Am. Chem. Soc.*, **74**, 5636 (1952).

(3) R. P. Linstead, E. A. Braude, and K. R. H. Wooldridge, *J. Chem. Soc.*, 3074 (1956).

(4) D. S. Acker and W. J. Wayne, *J. Am. Chem. Soc.*, **79**, 6483 (1957).