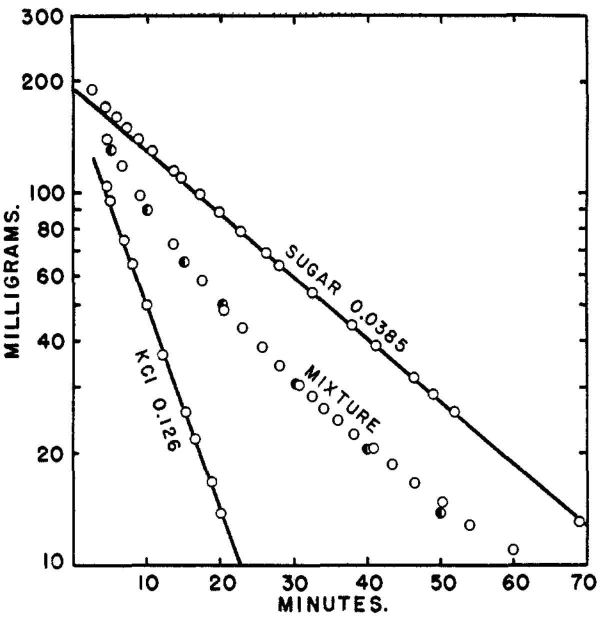

Fig. 1.—Diffusion of sugar and KCl, solutions of equal density, and equal volume mixture of the two solutions used, plate G-10: O, observed; ◐, calculated.

weight-average molecular weights of 54,000 and 8,600 as measured by light scattering. The polymer concentration was 75 g./liter.

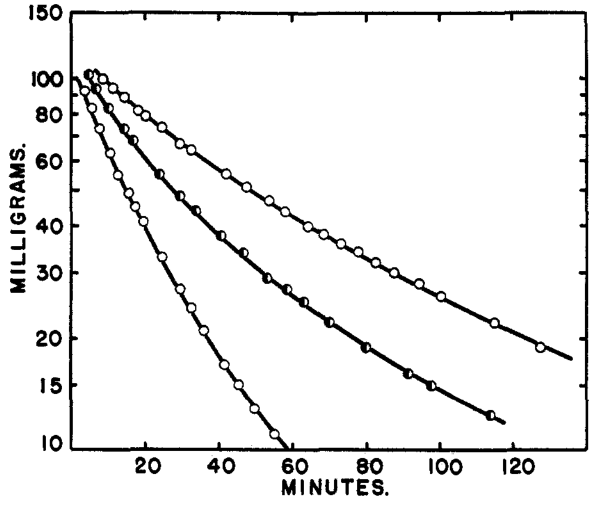

Fig. 2.—Diffusion of polyvinyl acetates (O) and mixtures of the two (◐), Plate G-015.

Measurements with really high molecular weight synthetic polymers are handicapped by the high viscosity of solutions at concentrations giving adequate density differences. The weight of solution clinging to the plate is relatively large and not easily swabbed off so as to get a clean-cut start.

It is not possible to derive any reasonable kind of average diffusion coefficient from the data for a given polymer–solvent system without making some assumption for a distribution function. It is evident that mixtures of materials having different diffusion coefficients will not give straight lines upon plotting ln ($W_t - W_\infty$) *vs.* *t*. However, if the difference between the diffusion coefficients of a binary mixture is sufficiently great, the curve obtained will, after a long period of time, approach the straight line associated with the slower moving material.

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The Reaction of Grignard Reagents with α,β-Olefinic Acids

BY JOHN H. WOTIZ, JOSEPH S. MATTHEWS AND HAROLD GREENFIELD

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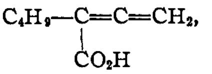
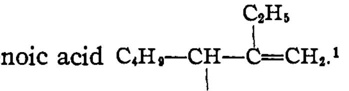
Recent work in our laboratory has shown that the ethylmagnesium bromide addition product to the allenic acid, 1,2-heptadiene-3-carboxylic acid,

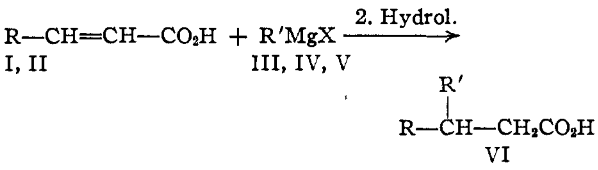


$\underset{\displaystyle CO_2H}{C_4H_9—C}=C=CH_2$, yields upon hydrolysis 2-butyl-3-ethyl-3-butenoic acid



$C_4H_9—\underset{\displaystyle CO_2H}{CH}—\overset{\displaystyle C_2H_5}{C}=CH_2$.[1] The reported over-all yield was 85%. The purpose of the present study was to establish whether some α,β-olefinic acids, and (or) their halomagnesium salts, also add Grignard reagents producing a new branch at the β-carbon atom. So far as we know, such reactions of Grignard reagents have not been recorded. However, the conjugate addition of Grignard reagents to α,β-unsaturated carbonyl compounds is well known. Other conjugate additions have also been reported.[2]

We have used crotonic (I), and cinnamic acid (II) and treated them with 2.5 moles of ethyl-(III), *t*-butyl-(IV), or phenylmagnesium halide (V).



$$\underset{\text{I, II}}{R—CH=CH—CO_2H} + \underset{\text{III, IV, V}}{R'MgX} \xrightarrow{\text{2. Hydrol.}} \underset{\text{VI}}{R—\overset{\displaystyle R'}{CH}—CH_2CO_2H}$$

With the exception of the reaction of I with IV, the yields of the acid VI were at least 40%. The remaining product consisted of a high boiling acidic portion, probably formed by self-condensation of the olefinic acid, and a neutral fraction probably formed by the addition of the Grignard reagent to the carboxy group. In the reaction of I and II with IV, 50 and 13%, respectively, of the starting acid was recovered. In the other cases none of the olefinic acid was recovered. Because of the ready availability of starting materials, simplicity of reaction, and relatively good yields, we consider such reactions to be of general use for the synthesis of many β branched acids.

Experimental

In the following experiments 21.5 g. (0.25 *M*) of crotonic acid (I) in 100 ml. of dry ether was added with good stirring to 0.62 mole of the Grignard in about 100 ml. of ether, at a rate to maintain refluxing. Stirring was continued for an hour at room temperature and the product was poured into a mixture of ether, ice and hydrochloric acid. Experiments where inverse hydrolysis was used gave significantly lower yields of VI. The ether layer was extracted with 10% sodium carbonate and the aqueous layer acidified with 6 *N*

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[1] J. H. Wotiz and J. S. Matthews, THIS JOURNAL, **74**, 2559 (1952).

[2] F. S. Prout, *ibid.*, **74**, 5915 (1952), and references therein.

hydrochloric acid. The liberated organic acids were usually redissolved in ether and purified. The experiments using cinnamic acid (II) used 14.8 g. (0.10 *M*) of II and 0.25 mole of the Grignard reagent.

3-Methylpentanoic acid (I + III) was formed in 40% yield (11.6 g.); b.p. 112–113° at 37 mm., $n^{25}D$ 1.4139, neut. equiv., 116 (calcd. for $C_6H_{12}O_2$: neut. equiv., 116); amide, m.p. 123–124° (petroleum ether) (lit.[3a] m.p. 125°); no depression of m.p. when mixed with an authentic sample.[3b] There were 7.3 g. of a higher boiling acidic fraction and 2.5 g. of a neutral product.

3-Phenylbutyric acid (I + V) was formed in 40% yield (16.3 g.); b.p. 122° at 2 mm., m.p. 35–36° (petroleum ether) (lit.[4] m.p. 37–38°), neut. equiv., 164 (calcd. for $C_{10}H_{12}O_2$: neut. equiv., 164). Amide, m.p. 105–106 (water) (lit.[4] 105–106°). Anilide m.p. 136–137° (ethanol-water) (lit.[4] 136–137°). There were 4.1 g. of a higher boiling acidic fraction and 16.0 g. of a neutral product.

3,4,4-Trimethylpentanoic acid (I + IV) was formed in 3% yield (1.2 g.); b.p. 88–92° at 3 mm. (lit.[5] 97–98° at 4 mm.), $n^{25}D$ 1.4348 (lit.[5] $n^{21}D$ 1.4320), neut. equiv., 142 (calcd. for $C_8H_{16}O_2$: neut. equiv., 144); amide, m.p. 166–167° (ethanol–water) (lit.[5] 166–167°). In this reaction 10.7 g. (50%) of I was recovered, b.p. 105–107° at 40 mm., m.p. 69–70° (no depression of melting point when mixed with a sample of authentic crotonic acid). There were 8.9 g. of a higher boiling acidic fraction and 2.7 g. of a neutral fraction.

3-Phenylpentanoic acid (II + III) was formed in 42% yield (7.5 g.); b.p. 135° at 3 mm., m.p. 60–61° (petroleum ether) (lit.[6] 58°), neut. equiv., 179 (calcd. for $C_{11}H_{14}O_2$: neut. equiv., 178); benzylamine salt, m.p. 111–112° (ethyl acetate) (lit.[6] 96.5°). Calcd. for $C_{18}H_{23}NO_2$: C, 75.7; H, 8.1. Found[7]: C, 75.2; H, 8.0. The higher boiling acidic fraction weighed 5.0 g. and the neutral fraction 2.6 g.

β-*t*-Butylhydrocinnamic Acid (II + IV).—In this reaction the acidic portion was distilled, collecting 11.3 g. of a product boiling up to 142° at 2 mm. There was 4.4 g. of a residue. The distillate was analyzed spectroscopically (ultraviolet and infrared absorption[8]). It consisted of 2.0 g. (13% recovery) of II and 9.3 g. (45% yield) of the *t*-butylhydrocinnamic acid. The distillate was crystallized several times from an ethanol–water mixture until a constant melting point of 115–116° (4.1 g.) was reached (lit.[9] 114–116°). Its neutral equivalent was 207 (calcd. for $C_{13}H_{18}O_2$: 206). The neutral fraction in this experiment was 1.9 g.

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[3] (a) I. Heilbron, "Dictionary of Organic Compounds," Vol. 2, Oxford University Press, New York, 1946, p. 829. (b) Prepared from the acid which was synthesized by the malonic ester synthesis.

[4] L. F. Eykman, *Chem. Weekblad*, **5**, 655; *Chem. Abstr.*, **3**, 779 (1909).

[5] M. S. Newman and R. Rosher, *J. Org. Chem.*, **9**, 224 (1944).

[6] T. W. Campbell and W. G. Young, THIS JOURNAL, **71**, 296 (1949).

[7] Microanalyses by G. Stragand of the Microanalytical Laboratory of the University of Pittsburgh.

[8] We wish to thank Dr. R. A. Friedel of U. S. Bureau of Mines, Bruceton, Pa., for these analyses.

[9] C. F. Koelsch, THIS JOURNAL, **65**, 1640 (1943).

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Crystalline 2,4-Dinitrophenylhydrazones of D-Fructose

BY LAWRENCE M. WHITE AND GERALDINE E. SECOR

RECEIVED AUGUST 4, 1953

Attempts in this Laboratory to synthesize D-fructose 2,4-dinitrophenylhydrazone by methods used for the formation of the 2,4-dinitrophenylhydrazones of certain aldose sugars[1–3] yielded an orange-colored mass that behaved somewhat like a thixotropic gel. The mass, probably cryptocrystalline, could not be purified easily and no conditions were found that gave recognizable crystals from ethanol. No synthesis of a crystalline D-fructose 2,4-dinitrophenylhydrazone has been reported

The authors have found that D-fructose and 2,4-dinitrophenylhydrazine react rapidly in cold or hot dioxane containing favorable amounts of water and acid to form very small needles of the dioxane solvate of D-fructose 2,4-dinitrophenylhydrazone. Conditions favoring a slower reaction produce trichitic crystals or long needles usually growing in spherulitic clusters and sheaves. Although the corresponding pyridine solvate can be made in small yield by the reaction of D-fructose and 2,4-dinitrophenylhydrazine in pyridine, it is most easily prepared from the dioxane solvate by a simple crystallization procedure.

The solvates are soluble in cold or hot pyridine; slightly soluble in cold or hot 95% ethanol, acetone, water, dioxane and ethyl acetate; and insoluble in cold or hot ethyl ether, chloroform, benzene and petroleum ether (b.p. 64–70°).

Free fructose can be regenerated from the solvated hydrazones and, under certain conditions, the dioxane and pyridine can be removed quantitatively from the molecule.

The optical, X-ray and crystallographic properties and the analytical applications of these compounds will be reported elsewhere.

Experimental

Reagents.—Reagent grade dioxane was passed through chromatographic grade activated alumina.[4,5] Immediately before use, the dioxane was made to contain 3% water and 0.3% hydrochloric acid (sp. gr. 1.19).

Reagent grade 2,4-dinitrophenylhydrazine was recrystallized from ethyl acetate before use.[5]

Reagent grade D-fructose was used without further purification.

D-Fructose 2,4-Dinitrophenylhydrazone Dioxane Solvate.—A mixture of 1 g. of D-fructose, 1 g. of 2,4-dinitrophenylhydrazine and 50 ml. of acidified, aqueous dioxane was agitated vigorously at room temperature. After 3 to 5 minutes, fine chrome yellow needles began to form. The needles were filtered under nitrogen,[6] washed with reagent grade dioxane and ethyl ether, and dried to constant weight at room temperature *in vacuo;* yield 1.85 g. (82%), m.p. (cor.) 176–178° dec., $[\alpha]^{26}D$ −35.4° (*c* 1, pyridine).

Anal. Calcd. for $C_{12}H_{16}N_4O_9 \cdot C_4H_8O_2$: C, 42.86; H, 5.40; N, 12.50. Found: C, 42.9; H, 5.47; N, 12.3.

D-Fructose 2,4-Dinitrophenylhydrazone Pyridine Solvate.—D-Fructose 2,4-dinitrophenylhydrazone dioxane solvate (1.83 g.) was dissolved in 25 ml. of pyridine at room temperature and 25 ml. of 95% ethanol was added. Large, yellow, blade-like crystals grew slowly. The product was filtered under nitrogen[6] and dried to constant weight at room temperature *in vacuo;* yield 1.43 g. (79.9%), m.p. (cor.) 173–175° dec., $[\alpha]^{25}D$ −34.7 (initial and final) (*c* 1, pyridine).

Anal. Calcd. for $C_{12}H_{16}N_4O_9 \cdot C_5H_5N$: C, 46.47; H, 4.82; N, 15.94. Found: C, 46.5; H, 4.85; N, 15.7.

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[1] E. Glaser and N. Zuckermann, *Z. physiol. Chem.*, **167**, 37 (1927).

[2] E. A. Lloyd and D. G. Doherty, THIS JOURNAL, **74**, 4214 (1952).

[3] J. A. Dominguez, *ibid.*, **73**, 849 (1951).

[4] W. Dasler and C. D. Bauer, *Ind. Eng. Chem., Anal. Ed.*, **18**, 52 (1946).

[5] Unpurified reagent and practical grades of dioxane adjusted to the proper water and acid contents, and unrecrystallized reagent grade 2,4-dinitrophenylhydrazine were used successfully in unreported experiments.

[6] Since the crystals are readily oxidized when wet, they must be kept from contact with air until they are dry; thereafter they are reasonably stable to air and light. This precaution was used only when preparing samples for analysis.