520 mμ.[1] When a chloroform solution of the orange-colored pigment is treated with concentrated hydrochloric acid and then with antimony trichloride, the solution exhibits the absorption spectrum characteristic of the gossypol–antimony trichloride reaction product. This observation indicates that the final reaction products of both pigments are the same and that concentrated hydrochloric acid converts the orange-colored pigment into gossypol.

The absorption spectra curves of chloroform extracts of some raw cottonseeds and cottonseed meals, as well as those of their reaction products with antimony trichloride, have maxima which indicate the presence of the orange-colored pigment.[2] The production of a characteristic gossypol reaction when such extracts are treated with concentrated hydrochloric acid prior to their reaction with antimony trichloride[2] confirms the presence of the orange-colored pigment in the seeds and meals. The occurrence of this pigment in high concentration in certain cottonseed meals may account, at least in part, for the frequently observed lack of correlation[3] of gossypol content with toxicity of these meals when the gossypol is determined as the dianilino compound.

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(2) Boatner, Caravella and Kyame, in press.

(3) Gallup, *Ind. Eng. Chem.*, **20**, 59–63 (1928).

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NEW ORLEANS, LOUISIANA RECEIVED FEBRUARY 16, 1944

The Preparation of Ethyl ε-Bromocaproate

BY GEORGE BOSWORTH BROWN AND C. W. H. PARTRIDGE

Ethyl ε-bromocaproate may be prepared conveniently and inexpensively from cyclohexanone. The crude mixed lactones of ε-hydroxycaproic acid, obtained by the procedure of Robinson and Smith,[1] may be treated directly with hydrobromic and sulfuric acids, thus obviating the losses involved in the use[2] of ethyl ε-hydroxycaproate as an intermediate.

The oxidation of 174 g. of cyclohexanone was carried out between 10 and 15° as described[1] in the preparation under the heading of ethyl 6-hydroxyhexoate using an oxidizing mixture prepared from 919 g. of potassium persulfate.

The 200 g. of crude lactones was then treated with a cooled mixture of 1 liter of 48% hydrobromic acid and 240 cc. of concentrated sulfuric acid. After standing for two hours at room temperature, this was heated for four hours on the steam cone, was cooled and poured into 2 liters of water. The organic layer was separated and the water solution was saturated with ammonium sulfate and was extracted four times with ether. The combined organic layer and extract were washed three times with saturated ammonium sulfate, and were dried and concentrated.

The 250 g. of crude bromo acid was esterified by refluxing for eight hours with 600 cc. of absolute alcohol and 15 cc. of sulfuric acid. After concentrating *in vacuo*, the residue was taken up in ether and was washed with water and with 5% sodium carbonate. The ether solution was dried over sodium sulfate and was distilled yielding 178 to 218 g. of the product distilling at 120–125° at 14 mm., $n^{21}\mathrm{D}$ 1.4566, d^{23}_{23} 1.241, MR_{D} 48.92 (calcd. 48.57). This represents an over-all yield from cyclohexanone of 45–55%. No evidence of the inhomogeneity noted once by Barger, Robinson and Smith[2] has been observed. The product has been used satisfactorily in the preparation of η-ketopelargonic acid.[2]

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(1) R. Robinson and L. H. Smith, *J. Chem. Soc.*, 371 (1937).

(2) G. Barger, R. Robinson and L. H. Smith, *ibid.*, 718 (1937).

DEPARTMENT OF BIOCHEMISTRY
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NEW YORK, N. Y. RECEIVED FEBRUARY 19, 1944

Polymerization of Undecylenic Acid in the Presence of Boron Fluoride

BY JOHN R. CANN[1] AND E. D. AMSTUTZ

It has been found that when undecylenic acid is treated with gaseous boron fluoride at room temperature much heat is evolved and the acid polymerizes to a dark heavy oily material. This polymer, after having been freed of catalyst, exhibits the characteristic properties of an acid and also those of an ester. Thus it shows some tendency to dissolve in dilute aqueous caustic and regenerates carboxyl groups on refluxing in alkaline solutions.

The loss in carboxyl function has been found to be directly related to the fall in iodine value which indicates that one of the processes of polymerization is the esterification of the carboxyl group by means of the unsaturated linkage. (It had been previously demonstrated that the same treatment of stearic acid did not cause decarboxylation.) Since the fall in iodine value was stoichiometrically greater than the loss of carboxyl function it appeared that some double bond polymerization also took place. The analytical data show that this is a reaction of secondary importance with esterification assuming the major role.

The oil resulting from saponification of the polymer gave a positive iodoform test which indicates the hydroxy acid produced had the methylcarbinol structure. This proves the orientation of at least part of the polymerization process.

This type of polymerization[2] of undecylenic

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(1) Raybestos-Manhattan Research Fellow in Chemistry 1942–1943. Present address, Frick Chemical Laboratory, Princeton, New Jersey.

(2) Unpublished results obtained in this Laboratory by Cann and by H. R. Nace indicate that this behavior is also shown by the fatty acids from drying oils and also by crotonic acid. The latter requires somewhat more strenuous conditions, however, due to its conjugated structure.

acid in the presence of boron fluoride was to be expected from the work of Nieuwland and his collaborators[3] who found that simple olefins condensed with phenols and carboxylic acids to produce phenolic ethers and esters, respectively.

Experimental

The polymeric material was usually prepared by passage of gaseous boron fluoride[4] into the sample to the point of saturation. Heat was immediately evolved and the temperature was allowed to rise to 70–80°. The color darkened to a deep chocolate brown and the viscosity increased markedly. The material was then allowed to cool to room temperature overnight and was taken up in ether. The ethereal solution was washed exhaustively with water and dried over anhydrous magnesium sulfate. Removal of the ether was accomplished by heating on a hot-plate and finally in vacuum for several hours. The residual oil was clear brown in color, and possessed the odor of coconuts.

Saponification of the polymer was carried out in the usual manner with alcoholic potassium hydroxide. The alcohol was evaporated, the residue acidified and extracted with ether. The ether solution was then dried over magnesium sulfate, filtered and evaporated. The residual oil was finally warmed and placed in high vacuum.

The iodoform test on the saponified polymer was carried out in the usual manner using methanol (negative blank) as solvent. The unrecrystallized iodoform melted at 116–119.2°; authentic specimen, m. p. 116–118.5°; mixed m. p. 121°.

Anal. Calcd. for $C_{10}H_{19}CO_2H$: acid no., 184.2; I_2 no., 184.2. Found: acid no., 196.9; I_2 no., 173.4. Calcd. for polymer: I_2 no., 358; sap. eq., 196.9. Found: I_2 no., 429.7; sap. eq.,[5] 196.7; acid no., 467.8. Calcd. for saponified polymer: acid no., 207.3; I_2 no., 452.5; acetyl value (g./OH), 510. Found: acid no., 249[6]; I_2 no., 467.4; acetyl no., 505.

Acknowledgment.—The authors express their appreciation to the Raybestos Division for financial support. To C. W. Simmons the authors are grateful for his interest.

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[3] Nieuwland, *et al.*, THIS JOURNAL, **54**, 3694 (1932); **56**, 2054, 2689 (1934).

[4] Samples of polymer prepared with boron fluoride etherate appeared to be identical with those upon which this report is based.

[5] Indicator used was Clearol Blue (see Fehnel and Amstutz, *Ind. Eng. Chem., Anal. Ed.*, **16**, 53 (1944).

[6] The acid number of the saponified polymer varied considerably and directly with the time and extent of heating during isolation. Reësterification occurred.

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p-(2,5-Dimethylpyrryl-1)-phenyl-magnesium Bromide and -Lithium

BY HENRY GILMAN AND GORDON J. O'DONNELL

In connection with studies on nitrogen heterocycles, directions have been developed for the preparation of *p*-(2,5-dimethylpyrryl-1)-phenylmagnesium bromide and the corresponding organo-lithium compound. The yields of the RM compounds are quite satisfactory, and directions are also given for the preparation of the precursory *p*-(2,5-dimethylpyrryl-1)-phenyl bromide in 90% yield.

Experimental

***p*-(2,5-Dimethylpyrryl-1)-phenyl Bromide.**—This compound was prepared in accordance with the general procedure of Hazelwood, Hughes, and Lions.[1] To a warm solution of 172 g. (1 mole) of *p*-bromoaniline in 114 g. (1 mole) of acetonylacetone was added one or two drops of concd. hydrochloric acid. On the addition of the hydrochloric acid, the solution assumed a dark red color, and a vigorous reaction set in immediately with droplets of water forming on the surface of the solution. After the initial reaction subsided, the mixture was refluxed for three hours under an air condenser. The reaction mixture was poured upon crushed ice, and the precipitate was filtered. The yield of product melting at 72–74° was 240 g. (96%). Recrystallization from ethanol gave 225 g. (90%) of compound melting at 74°.

Reaction of *p*-(2,5-Dimethylpyrryl-1)-phenyl Bromide with Magnesium and with Lithium.—The Grignard reagent was prepared by conventional procedures, and the yield by acid titration[2] was 76%. From a second preparation, starting with 0.08 mole of the RBr compound, the yield of crude *p*-(2,5-dimethylpyrryl-1)-benzoic acid was 78%, and purification from ethanol gave a 72% yield of pure acid melting at 195–196°. The reaction with magnesium proceeds slowly, and ordinary catalysts like iodine or some activated magnesium, or some methylmagnesium iodide are helpful. There is no significant color change in the solution when reaction takes place, but color test I is of diagnostic value when methylmagnesium iodide is not used as a catalyst.

The organolithium compound was prepared by adding a solution of 12.5 g. (0.05 mole) of *p*-(2,5-dimethylpyrryl-1)-phenyl bromide in 60 cc. of ether to a stirred suspension of 1 g. (0.14 g. atom) of finely divided lithium in 30 cc. of ether. Twenty cc. of the solution was added at once, after which addition the mixture was warmed until the reaction started. The remaining solution was then added at a rate to maintain gentle refluxing. Carbonation by dry-ice gave 8.6 g. (80%) of *p*-(2,5-dimethylpyrryl-1)-benzoic acid which melted at 196–197° after crystallization from dilute ethanol. Identification was completed by a mixed m. p. determination with a sample prepared[1] by the condensation of *p*-aminobenzoic acid with acetonylacetone.

The observation that the bromide reacts more promptly with lithium than with magnesium finds a parallel in the preparation of RMgX and RLi compounds, in high yields, from *p*-dimethylarsinophenyl bromide and *p*-di-*n*-propylarsinophenyl bromide.[3]

Acknowledgments.—The authors are grateful to C. G. Stuckwisch and L. Fullhart, Jr., for assistance.

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[1] Hazelwood, Hughes, and Lions, *J. Proc. Roy. Soc. N. S. Wales*, **71**, 92 (1937); [*C. A.*, **32**, 1695 (1938).]

[2] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

[3] Studies by L. Tolman and S. Avakian.

DEPARTMENT OF CHEMISTRY
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Double Invert Soaps: Symmetrical Di-morpholinium Salts

BY JOSEPH B. NIEDERL AND EDWARD J. KENNEY[1]

Since it appears that up to the present few symmetrical double invert soaps have been described in the literature, report is herewith given of such types of compounds. Thus methylene- and ben-

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[1] Abstracted from the thesis of Edward J. Kenney presented to the Graduate School of St. Peter's College, Jersey City, N. J., in partial fulfillment for the degree of Master of Science, May, 1944.