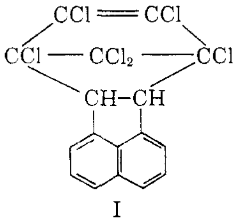
Accordingly, the addition of hexachlorocyclopentadiene to acenaphthylene was attempted and it was found that these interact readily in the cold to form the same adduct as is formed from acenaphthene but without tar production.

The adduct is a very stable substance, m.p. 192.5–194°, and unlike the naphthalene adducts[2] could not be cracked back to the components by pyrolysis under vacuum. Instead, it was distilled unchanged with slight decomposition at a low pressure.

The ultraviolet spectrum resembled that of a substituted acenaphthene, giving evidence that the five-membered ring only is attacked. The absorption peaks are given with ϵ values in parentheses: 225 (44,000), 268 (3710), 278 (6370), 288 (8020), 300 μ (5710). The corresponding figures for acenaphthene are: 227 (87760), 268 (3650), 279 (5780), 288 (6500), 300 μ (4150).

Structure I was thought to explain best the properties of the compound. The analytical values and the molecular weight are in agreement with this. The adduct undergoes nitration to give a mononitro derivative.



I

EXPERIMENTAL

Melting points are uncorrected and were taken on a Fisher-Johns block.

Addition to acenaphthylene. A mixture of 5 g. (0.033 mole) of acenaphthylene and 10 ml. (0.063 mole) of hexachlorocyclopentadiene was warmed for solution and then left to stand at room temperature. Deposition of crystals began in a few hours and, after 2 days, the paste of product was worked up. It was stirred with a mixture of equal volumes of ether and peteroleum ether (b.p. 30–60°) (35 ml.) and filtered. The material was washed three times with this solvent mixture and dried; yield 11.45 g. (best obtained), 81.8%. Without recrystallization, this melted at 190.5–193° and, when mixed with the purified material from acenaphthene, it melted 191.5–193.5°.

Addition to acenaphthene. A solution of 25.4 g. (0.165 mole) of acenaphthene in 80 ml. (0.5 mole) of hexachlorocyclopentadiene was heated by a bath of boiling pinene (155–156°) for 130 hr. During this time, the mixture darkened and slow evolution of hydrogen chloride occurred. After cooling, the contents formed a nearly solid black mass. This was warmed, mixed with a little benzene to promote fluidity, and then stirred with a mixture of equal volumes of ether and petroleum ether (b.p. 30–60°). Crystalline grains soon formed and the suspension was left overnight. The product was filtered and washed with the same solvent mixture. Concentration of the filtrates and washings afforded a little more product. Yield of crude dark material was 49.1 g., 70%.

The compound was recrystallized a number of times from benzene-hexane and from ether with use of Norit. A pure white product was finally obtained, m.p. 192.5–194°. It forms characteristic sandy grains from these solvents.

Anal. Calcd. for $C_{17}H_8Cl_6$: Cl 50.12. Mol. wt.: 425. Found Cl 50.0. Mol. wt.: (Rast) 415.

In an attempt to crack the compound, it was heated with a free flame in a small flask at a pressure of 1 mm. A very high boiling material slowly distilled leaving a black tar in the flask. The solid distillate was recrystallized from benzene–petroleum ether (b.p. 30–60°) and formed grains, m.p. 187–190°. When mixed with the purest sample of starting adduct, the melting point was 188–191°.

Nitration. A solution of 2 g. of the adduct in 100 ml. of boiling glacial acetic acid was treated with 5 ml. of sulfuric acid. Then 4 ml. of concd. nitric acid was added cautiously, in portions. The orange solution was kept at 100–115° for 20–25 min. It was then cooled to about 80° and 10 ml. of water added, with stirring and cooling. The product separated as a yellow crystalline powder which was filtered, washed, and dried; yield 2.1 g. (95%). The nitro compound was recrystallized from acetone-water and from benzene–petroleum ether (b.p. 30–60°). On heating it sintered at 195–200° with melting point at 230.5–233°.

Anal. Calcd. for $C_{17}H_7Cl_6NO_2$: N 2.98. Found: N 2.83.

Acknowledgments. The author is indebted to W. Morgan Padgett II, Dietrich Heinritz, and Mrs. Jane Clark for spectral measurements and interpretations and analytical determinations, to H. P. C. Lee for assistance, and to Dr. Julius Hyman for encouragement during the work.

HYMAN LABORATORIES, INC.
BERKELEY, CALIF.

Reaction of Isopropylzinc Iodide with Terebic Acid Chloride. A Suggested New Mode of Action of the Blaise Reagent

TAKESHI MATSUMOTO AND AKIRA SUZUKI

Received February 8, 1960

In the course of a study on the synthesis of a certain terpenoid compound, the authors became interested in the reaction of isopropylzinc iodide with terebic acid chloride. The reaction has been investigated by M. Matsui, *et al.*,[1] who by the reaction obtained pyrocin[2] (I), in 5% yield based on the acid chloride. They interpreted their unusual result by scheme A.

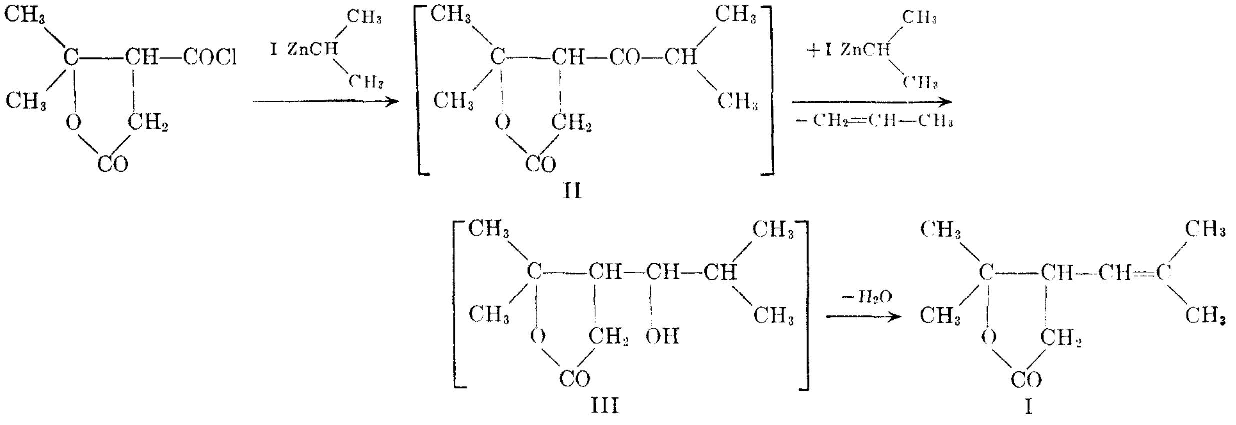
It is well known that a number of branched-chain Grignard reagents reduce carbonyl compounds to carbinols.[3] However, similar reduction by alkylzinc iodide seems never to have been described before the appearance of the above-cited work.[4] The present study was undertaken to ex-

---

(1) M. Matsui, T. Ohno, S. Kitamura, and M. Toyano, *Bull. Chem. Soc. Japan*, **25**, 210 (1952).

(2) Pyrocin was first isolated from the pyrolysate of pyrethrum flowers [M. Nagase and M. Matsui, *J. Agr. Chem. Soc. Japan*, **20**, 249 (1944)]. For structural studies, see S. H. Harper *et al.*, *J. Sci. Food Agr.*, **2**, 414 (1951).

(3) For a review, see M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall Inc., New York, 1954, pp. 147–165.



Scheme A

amine the property of the Blaise reagent as a reducing agent. This paper reports that the reagent possesses a fairly good reducing ability and that the above reaction does not proceed through a ketone (II).

In the original method,[1] the reaction was effected by condensing 0.25 mole of terebic acid chloride with the Blaise reagent prepared from 0.32 mole of isopropyl iodide. If the reaction follows the above presented scheme, at least two moles of the Blaise reagent should be used for one mole of the acid chloride. Simply by employing the molar ratio of 2:1 and by lengthening the reaction period as compared with the original method, a 49% yield of product I was easily obtained by distillation of the reaction mixture. In this case, as a by-product, a compound, m.p. 42.5-43.5°, was isolated from the higher boiling fraction by the countercurrent distribution method in 10% yield. The by-product possessed a molecular formula $C_{10}H_{16}O_4$ and exhibited infrared absorption bands at 1770 (γ-lactone) and 1720 cm.$^{-1}$ (C=O) and hence was formulated as isopropyl terebate. The validity of this conclusion was confirmed by comparison with an authentic sample. The ester seems to be formed as a result of air oxidation of the Blaise reagent. Thus a better yield of pyrocin may be obtained through complete exclusion of oxygen during the reaction. The presence of propylene in the gas evolved during the reaction was suggested by the reduction of the volume of the gas on treatment with concentrated sulfuric acid. It is therefore very probable that pyrocin is not formed as a result of complex side reactions and that the reaction path actually exists as stated above in the scheme A. However, the intermediate carbonyl compound (II) was not detected in the reaction mixture by dinitrophenylhydrazine, even when the starting materials were used in 1:1 molar ratio. In hope of proving the scheme A, preparation of the assumed ketone (II) was then attempted by the action of diisopropylcadmium upon terebic acid chloride in ether. The infrared spectrum of the reaction product however, revealed that an appreciable amount of isopropyl terebate was formed together with the desired ketone.[5] The presence of the ketone and of the ester was respectively confirmed by the isolation of dinitrophenylhydrazone and of the ester itself. However, as the separation of the two compounds was not so easy, the crude product was directly treated with isopropylzinc iodide. This treatment should afford pyrocin (I) and isopropyl terebate as a mixture, from which the two components may be separated by means of a combination of fractional distillation and countercurrent distribution. Contrary to expectation, the infrared spectrum of the reaction mixture, being almost identical with that of the starting material, strongly suggested that the material had been recovered unchanged. In fact the ketone (II) was isolated as dinitrophenylhydrazone. In the infrared spectrum of the reaction mixture no sign of the presence of pyrocin and its hypothetical precursor (III), which should exhibit an absorption band at 3300 cm.$^{-1}$ region, was indicated. The absence of pyrocin was confirmed by nuclear magnetic resonance absorption.[6] In Fig. 1 is depicted the NMR spectrum of the reaction mixture in carbon tetrachloride solution, taken on a Varian 40 MC machine.[7] The spectrum clearly demonstrates the absence of pyrocin[8] which should show two resonance lines due to one vinyl

---

[4] It was already known that diethylzinc reduces chloral to trichloroethanol. Gozarolli-Thurnlakh, *Ann.*, **210**, 63 (1881); **213**, 369 (1882); M. Delare, *Bull. soc. chim. France*, **48**, 784 (1887). Arylsulfonyl chlorides are reduced to sulfinic acids by mixed organozinc compounds. E. E. Blaise, *Bull. soc. chim. France*, 9 I (1911).

[5] Formation of the terebate may be due to air oxidation of diisopropylcadmium. Susceptibility of dialkylcadmium to oxidation was recently noted: A. G. Davies and J. E. Packer, *Chem. & Ind.*, **1958**, 1177. Ethyl terebate, which may be anticipated as a by-product [J. Cason and E. G. Reist, *J. Org. Chem.*, **23**, 1668 (1958) and previous papers of this series by J. Cason] was not detected by infrared spectrum. The ethyl ester shows characteristic absorption bands at 1162, 1038, and 1018 cm.$^{-1}$, while the mixture does not.

[6] Infrared spectrum alone does not provide a conclusive evidence for the absence of pyrocin, since its characteristic absorption band at 1665 cm.$^{-1}$ is weak.

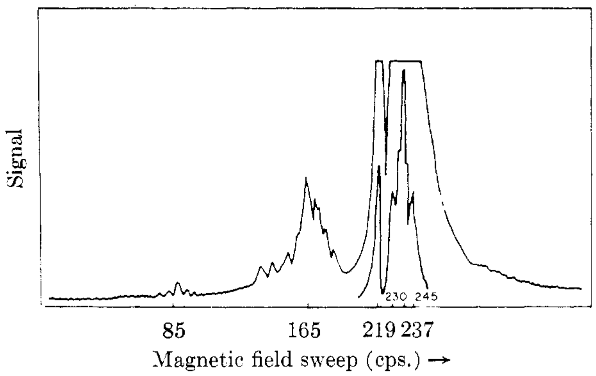
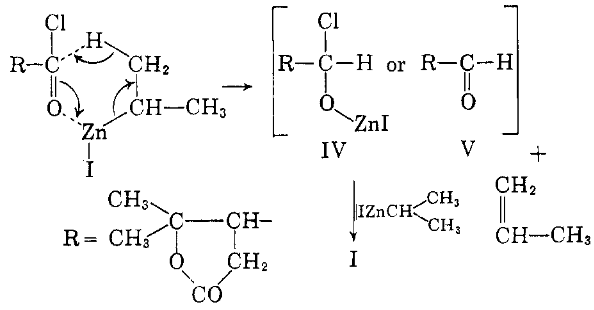


Fig. 1. Proton NMR spectrum at 40 mc. in carbon tetrachloride of the product obtained from reaction of a mixture of II and isopropyl terebate with isopropylzinc iodide

proton at lower magnetic field than 85 cps. (standard: benzene), on which the group of lines due to an α-proton of the isopropoxyl group of isopropyl terebate is centered.[9]

On the basis of the evidence presented above, it may be concluded that the reaction does not involve the ketone (II) as an intermediate. Probably, the reaction may proceed through the following route, the acid chloride being reduced *before* condensation rather than *after* condensation:



Scheme B

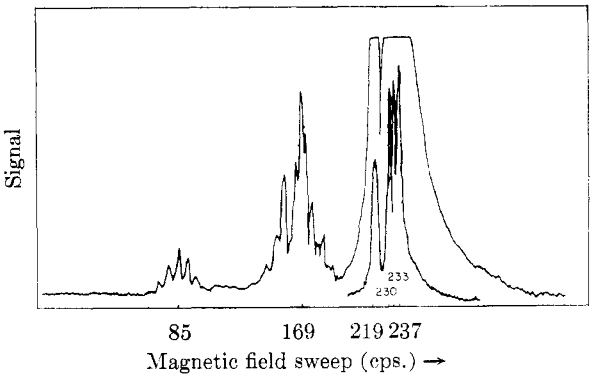


Fig. 2. Proton resonance spectrum of isopropyl terebate at 40 mc. in carbon tetrachloride

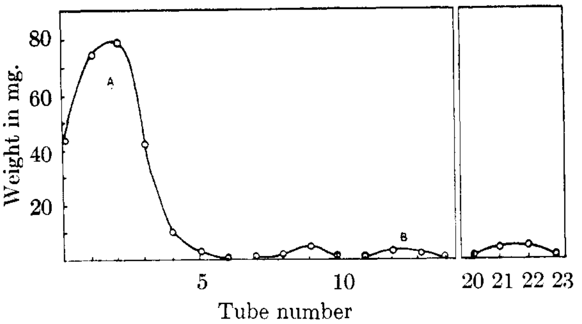


Fig. 3. Distribution curve of a high boiling fraction from reaction of terebic acid chloride and isopropyl zinc iodide

The intermediate may be either the α-haloalcoholate (IV) or the aldehyde (V). As the intermediates IV and V are anticipated to be reactive enough to combine easily with a further mole of the Blaise reagent, the suggested mechanism B affords a more reasonable explanation for the absence of any carbonyl compound in the reaction mixture. However, further studies are necessary before the detailed mechanism of the above reaction of the Blaise reagent can be elucidated. As a reaction similar to the first step of the scheme B, the reduction of acid chlorides to aldehydes and to the corresponding primary alcohols by the Grignard reagents may be mentioned.[10]

At an early stage of the present work, it was noted that treatment of terebic acid with thionyl chloride, which had been kept in the laboratory for over ten years, resulted in the formation of a compound $C_7H_8O_3$, m.p. 44°, and did not afford any detectable amount of the desired acid chloride. Similar observation has been made by Barbier and Loquin,[11] who regarded the product as caronic acid anhydride. However, the product has now been identified as teraconic acid anhydride by the melting point of

---

(7) The authors are very pleased to express sincere thanks to Prof. Genjiro Hazato of Tohoku University, Sendai, and his associates as well as to Dr. Ichiro Yamaguchi of Research Institute for Atomic Energy, Japan, for the measurement of the NMR spectra.

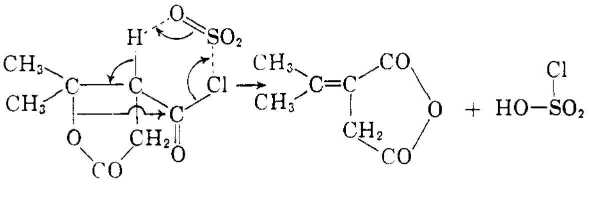
(8) Pyrocin exhibits double lines at 56 and 47.5 cps. Well defined methyl proton peaks appear at 190, 204, and 211 cps (Y. Ikenokami and A. Suzuki, unpublished observation).

(9) Comparison of the NMR spectra of the mixture with that of pure isopropyl terebate (Fig. 2) provides evidence for the ratio of the ketone (II) to the ester in the reaction mixture. As the line spacing between the septet due to α-proton of the isopropoxyl group is 7 cps., the peaks at 230 and 237 cps. (Fig. 2) with identical spacing may be ascribed to β-protons of the same isopropoxyl group. The remaining peaks at 219 and 233 cps. must then be due to the unequivalent geminal methyl groups on the lactone ring. Therefore, shifts at 237 (overlapped by methyl resonance of isopropoxyl group) and 245 cps. in Fig. 1 may be assigned to dimethyl protons of the isopropyl group of the ketone (II). The ratio of the area under the peak at 245 cps. to that under the peak at 230 cps. may therefore be regarded to present the approximate ratio of the ketone (II) to the ester.

(10) M. S. Kharasch and O. Reinmuth, *loc. cit.*, pp. 725–727.

(11) Ph. Barbier and R. Loquin, *Compt. rend.*, **153**, 188 (1911); *Bull. soc. chim. France*, **13**, 223 (1913).

the product as well as by melting and mixed melting point and infrared determination of the hydrolysis product, teraconic acid. As Barbier and Loquin's product melted at 44°, it actually may have been teraconic anhydride. The anhydride may be formed through the action of impurities such as sulfur trioxide in deteriorated thionyl chloride on the acid chloride as follows, as treatment of the acid chloride with a small amount of sulfur trioxide gave teraconic anhydride in excellent yield:



EXPERIMENTAL[12]

Terebic acid. The method of preparation described in the literature[1] gave a mixture of unidentified acids. It was modified as follows. To 108 g. of sodium methoxide in 400 ml. of anhydrous ether was added a mixture of 120 g. of acetone and 145 g. of methyl succinate under cooling with ice, and the resulting mixture was allowed to stand for 2 days at room temperature. Concd. hydrochloric acid (700 ml. rather than 350 ml.) and water (350 ml.) were poured into the mixture. After removal of ether, the residue was heated under reflux for 12 hr. Hot water (400 ml.) was added to the mixture, and the solution was decolorized with Norite and allowed to stand overnight. Terebic acid, which separated, was collected and recrystallized from water; yield 65 g.

Teraconic anhydride. A mixture of terebic acid (9 g.), thionyl chloride (15 ml., an old sample was used without purification) and dry benzene (40 ml.) was refluxed until no more hydrogen chloride gas evolved (for about 20 hr.). After removal of benzene and excess thionyl chloride, the residue was distilled *in vacuo* and a fraction boiling at 137–145° (9 mm.) was collected; yield 4.6 g. On being put aside, the distillate soon solidified. After recrystallization from carbon disulfide, the solid product melted at 44°.

Anal. Calcd. for $C_7H_8O_3$: C, 59.99; H, 5.75. Found: C, 60.15; H, 5.63.

Teraconic acid was obtained by hydrolysis of the anhydride with water. The acid decomposed at 160–161° when rapidly heated and at 154–156° on slow heating, and no melting point depression was observed on admixture with authentic sample.[13]

Terebic acid chloride. A mixture of thionyl chloride (30 ml.) purified by Fieser's procedure,[14] terebic acid (18 g.), and dry benzene (80 ml.) was heated under reflux until no more hydrogen chloride gas evolved (for about 9 hr.). The mixture was distilled and a fraction boiling at 123–129° (10 mm.) was collected; yield 17 g. ν_{max}^{film} 1785 cm.$^{-1}$ (C=O). Absence of absorption bands characteristic of the acid anhydride group indicated that no detectable amount of teraconic anhydride was produced in this case. Newly purchased, unpurified thionyl chloride gave an essentially same result. Addition of a small quantity of water or sulfur monochloride, a possible impurity of the commercial thionyl chloride, also did not alter the result.

The reaction of terebic acid chloride with sulfur trioxide was examined as follows. A mixture of terebic acid chloride (1.1 g.) and a small amount of sulfur trioxide in 4 ml. of benzene was heated under reflux for 13 hr. On removal of benzene, the residue was solidified, m.p. 41–43°. Recrystallization from carbon disulfide raised the melting point to 44°. No depression in melting point was observed on admixture with teraconic anhydride which was prepared above. When phosphorus trichloride was used instead sulfur trioxide, the acid chloride was recovered unchanged.

Reaction of isopropylzinc iodide with terebic acid chloride. Zinc-copper couple (60 g. weight ratio 10:1), isopropyl iodide (50 g.), and 25 ml. of ligroin (b.p. 87–95°) were placed in a three necked flask equipped with an inlet tube for nitrogen, a reflux condenser, and a mercury sealed stirrer. A slow stream of nitrogen was introduced and stirring and heating were continued for 10 hr. After cooling, dry benzene was added to the reaction mixture. A portion of the solution was submitted for analysis.[15] A portion of isopropylzinc iodide solution (containing 0.04 mole of the reagent) was placed in a flask equipped with a condenser, a mercury sealed stirrer, a dropping funnel and an inlet tube for nitrogen gas. Terebic acid chloride (3.6 g.; 0.02 mole) in 15 ml. of dry benzene was added with stirring and passing nitrogen, under cooling with ice. After the stirring had been continued for 2 hr., the reaction mixture was allowed to stand at room temperature for a week. The viscous mixture was hydrolysed with 70 g. of ice and 30 ml. of 6*N* hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers were washed successively with water, 5% sodium carbonate solution, and again with water and dried with anhydrous sodium sulfate. In this way, 3.1 g. of a neutral product was obtained. Distillation of the product gave 1.7 g. of crude pyrocin, b.p. 135–145° (35 mm.) and 0.6 g. of an unknown product, b.p. 115–135° (6 mm.) The former fraction crystallized after being kept overnight at −35°. Recrystallization from petroleum ether (b.p. 30–60°) gave pure *dl*-pyrocin, m.p. 61–62° (lit.,[1] m.p. 61–62°). The fraction, b.p. 115–135° (6 mm.) was fractionated by countercurrent distribution in the glass apparatus designed by Craig with the system *n*-hexane and 85% aqueous methanol as solvents. The distribution curve was plotted with weight of material in each tube as ordinates and the tube numbers as abscissas. Fig. 3 illustrates the result obtained using this method on 0.47 g. of the above unknown substance. The material of the cut A became a scaly crystalline product. Recrystallization from *n*-hexane gave isopropyl terebate, m.p. 42.5–43.5°, ν_{max}^{nujol} 1770 cm.$^{-1}$ (γ-lactone) 1720 cm.$^{-1}$ (ester).

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.78; H, 8.12.

The cut B gave *dl*-pyrocin. An authentic sample of isopropyl terebate was prepared by the reaction of terebic acid with an excess of isopropyl alcohol in the presence of a small amount of concd. sulfuric acid; m.p. 43°, mixed m.p. 43°.

---

[12] All melting points and boiling points are uncorrected. Infrared spectra were taken on a Koken model DS-301 infrared spectrophotometer. The workers wish to thank Mr. O. Yonemitsu of the Pharmaceutical Institute of Hokkaido University for the spectral data and Miss N. Fujino for the microanalyses.

[13] H. Stobbe, *Ber.*, **36**, 197 (1903).

[14] L. F. Fieser, *Experiments in Organic Chemistry*, rev. 3rd ed., D. C. Heath and Company, Boston, 1955, p. 345.

[15] The analysis was effected by adaptation of H. Gilman's gas analysis method for Grignard Reagent (H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923)) and by the gravimetric determination of zinc in the solution by the pyrophosphate method (I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, The Macmillan Company, London, 1936, p. 345). The two methods afforded consistent results.

Reaction of diisopropylcadmium with terebic acid chloride. An ether solution (47.5 cc.) of isopropylmagnesium bromide (0.065 mole[16]) was cooled to 0°, and 10 g. (0.037 mole) of powdered anhydrous cadmium bromide was added in several portions during about 5 min. The solution was stirred under ice-cooling until a negative Gilman test for Grignard reagent was obtained (usually in about 30 min.). A solution of 5.5 g. (0.031 mole) of terebic acid chloride in 20 ml. of benzene was added during about 5 min. After stirring has been continued for 4 hr. under ice-cooling and for 2 hr. at room temperature, the reaction vessel was kept air-tight and allowed to stand for a week. After addition of ice and 6*N* hydrochloric acid and extraction of the aqueous layer with ether, the total ether solution was successively washed once with water, twice with 5% sodium carbonate solution, and three times with sodium chloride solution; then it was dried. There remained 3.8 g. of a neutral product C; $\nu_{max}^{CCl_4}$ 1780 cm.$^{-1}$ (lactone), 1730 cm.$^{-1}$ (ester), 1710 cm.$^{-1}$ (ketone). Distillation gave 2.8 g. of colorless liquid, b.p. 138–141° (8 mm.). Upon seeding, it formed colorless crystals (2 g.; 32%), which were identified with isopropyl terebate by mixed melting point determination. When the oily portion of the distillate was allowed to stand for a long time (about 1 month) with Brady reagent in ethanol, a 2,4-dinitrophenylhydrazone (1.2 g.; 10.6% based on terebic acid chloride) was obtained. A sample for analysis was prepared by recrystallization from methanol; it formed orange needles, m.p. 175–176.5°.

Anal. Calcd. for $C_{16}H_{20}O_6N_4$: C, 52.74; H, 5.53. Found: C, 52.80; H, 5.67.

Reaction of the ketone (II) *with Blaise reagent.* The above mixture C (900 mg.; prepared in another run) containing the ketone (II) and isopropyl terebate was dissolved in 2 ml. of dry benzene. The solution was added with stirring under cooling with ice to 7.5 ml. of isopropylzinc iodide-benzene solution which contained 0.002 mole of the reagent. After the stirring was continued for 2 hr., the reaction mixture was allowed to stand at room temperature for 8 days. The reaction mixture was hydrolyzed with ice and 6*N* sulfuric acid; the separated organic layer and ether extracts were combined and washed successively with water, 5% sodium bicarbonate, and saturated sodium chloride aqueous solution. After having been dried with anhydrous sodium sulfate, the solvent was removed under reduced pressure. A pale orange-red oily residue (750 mg.) was obtained. The residue was negative to Baeyer reagent to which pyrocin is positive. On treatment with Brady's Reagent, the residue afforded dinitrophenyl hydrazone of the ketone (II). The NMR spectrum of the residue was reproduced in Fig. 1.

CHEMISTRY DEPARTMENT
FACULTY OF SCIENCE
HOKKAIDO UNIVERSITY
SAPPORO, JAPAN

---

(16) Analysed by Gilman's method; *cf.* ref. 13.

The Preparation of Acetylated Aldonic Acids

ROBERT BARKER

Received March 7, 1960

The fully acetylated aldonic acids are important as intermediates in the synthesis of ketones[1] and some aldoses.[2] However, attempts to acetylate the aldonic acids or their salts have demonstrated that the yield of the desired product not only depends upon the stereochemistry of the acid but, with any given acid, varies markedly with the particular salt employed.[3]

The most generally applicable method for the preparation of acetylated aldonic acids involves formation of the amide, followed by acetylation, and then regeneration of the free acid from the amide,[4] although in some instances the use of this procedure has proved difficult.[5]

This report describes a method for the preparation of acetylated aldonic acids in good yields from the salts of the acids. The yields obtained are virtually independent of the salt used.

EXPERIMENTAL

A solution prepared at room temperature of 1.75 g. (12.9 mmoles) of fused zinc chloride in 25 ml. of acetic anhydride was cooled to −5° and 5 g. (24.3 mmoles) of finely divided potassium arabinonate was added. The suspension was then saturated with dry hydrogen chloride, care being taken to maintain a reaction temperature of less than 5°. When saturated, the mixture was set at room temperature and protected from atmospheric moisture by a calcium chloride tube. After standing at room temperature for periods varying from 5 to 18 hr. the reaction mixture was chilled in an ice bath and small portions of chipped ice were added cautiously to destroy the excess acetic anhydride. To ensure complete destruction of the anhydride, the reaction mixture was left at 0° for 1 hr., then diluted to approximately 100 ml. with water, and extracted six to eight times with 30-ml. portions of chloroform or dichloromethane. The extracts were dried over sodium sulfate, filtered from the drying agent, and concentrated *in vacuo* at 40° to a yellow sirup. This sirup was twice concentrated *in vacuo* with 40-ml. portions of toluene, then dissolved in 25 ml. of warm toluene, and the solution cooled. Crystallization occurred spontaneously within a few hours. The yield varied from 6.0 to 6.8 g. (74–84%) and the material melted at 135–136°, with $[\alpha]^{25}_{D}$ +32.0° (*c* 4.0, chloroform).

The yields of acetylated aldonic acids and their physical constants are listed in Table I. All of the acetates were prepared in a similar fashion to that described above except that the ammonium salts were allowed to react for a longer time because of their slower solubilization in the reaction mixture.

NATIONAL INSTITUTES OF ARTHRITIS AND
METABOLIC DISEASES
NATIONAL INSTITUTES OF HEALTH
PUBLIC HEALTH SERVICE
U. S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
BETHESDA 14, MD.

---

(1) M. L. Wolfrom, D. I. Weisblat, E. F. Evans, and J. B. Miller, *J. Am. Chem. Soc.* **79**, 6454 (1957) and previous communications in the series.

(2) E. W. Cook and R. T. Major, *J. Am. Chem. Soc.*, **58**, 2410 (1936).

(3) K. Ladenburg, M. Tishler, J. W. Wellman, and R. D. Babson, *J. Am. Chem. Soc.*, **66**, 1217 (1944).

(4) G. B. Robbins and F. W. Upson, *J. Am. Chem. Soc.*, **60**, 1788 (1938).

(5) G. B. Robbins and F. W. Upson, *J. Am. Chem. Soc.*, **62**, 1074 (1940).

(6) C. D. Hurd and J. C. Sowden, *J. Am. Chem. Soc.*, **60**, 235 (1938).

(7) Crystallized from water as a monohydrate.

(8) E. W. Cook and R. T. Major, *J. Am. Chem. Soc.*, **58**, 2474 (1936).