came off. Continued elution with 2% ethanol in petroleum ether slowly removed the oleanolic and ursolic acids as a mixture. The isomers were readily separated in crude form at this point by boiling in methanol and filtering or decanting the partially cooled methanol solution. The supernatant or filtrate contained the oleanolic acid, since ursolic acid is only slightly soluble in hot methanol.

Isolation of Oleanolic Acid as the Acetate.—Oleanolic acid, obtained in amorphous form by evaporation of the methanol solution, was converted to the acetate for preliminary identification by boiling with acetic anhydride in pyridine. Samples of the acetate from each plant part melted sharply between 258 and 261° after several crystallizations from methanol. A composite sample from all plant parts containing oleanolic acid consisted of needles, m.p. 259–261° after two crystallizations from methanol.[12]

Anal. Calcd. for $C_{32}H_{50}O_4$: C, 77.06; H, 10.10. Found: C, 76.80; H, 9.88.

Oleanolic Acid.—Each of the oleanolic acid acetate samples was saponified with 5% alcoholic KOH to the free acid. After several crystallizations from methanol, needles melting sharply between 295 and 302° were obtained in each case. None of the samples depressed the melting point of an authentic sample of free oleanolic acid.[13] A composite sample of all of the free acid fractions, after two crystallizations from acetone, consisted of needles, m.p. 302–303°.[12] It gave a characteristic color in the Liebermann–Burchard test.

Anal. Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.58. Found: C, 78.66; H, 10.38.

Oleanolic Acid Benzoate.—A composite sample of the free acid was boiled with benzoyl chloride in pyridine, yielding a benzoate, m.p. 259–261°, after several crystallizations from methanol.[14]

Isolation of Ursolic Acid as the Acetate.—Crude ursolic acid obtained as outlined above consisted of an amorphous, green powder which resisted all attempts to purify it by crystallization from various solvents. Samples from each plant part, however, were readily converted to the crystalline acetate by boiling in acetic anhydride–pyridine mixture. Each preparation melted sharply between 284 and 287° after several crystallizations from acetone or methanol. A composite sample from all plant parts, after two crystallizations from acetone, consisted of needles, m.p. 286–287°.[15]

Anal. Calcd. for $C_{32}H_{50}O_4$: C, 77.06; H, 10.10. Found: C, 77.04; H, 10.12.

Ursolic Acid.—Saponification of each of the acetate samples with 5% alcoholic KOH gave an amorphous white powder, m.p. 260–285°, which also resisted numerous attempts at crystallization from various solvents. Except in one case (mature roots) the acid was finally obtained in crystalline form by treating the saponified product according to the procedure of King, *et al.*[16] A composite sample from all plant parts, after two crystallizations from ethanol, consisted of needles, m.p. 283–285°,[15] undepressed by admixture with an authentic sample of ursolic acid.[13] It gave a characteristic color in the Liebermann–Burchard test.

Anal. Calcd. for $C_{30}H_{48}O_4$: C, 78.89; H, 10.58. Found: C, 78.62, H, 10.80.

Ursolic acid monoacetyl methyl ester, prepared according to the procedure of Rowe, *et al.*,[6] melted at 247°, in agreement with the recorded value.

Ursolic acid acetate acid chloride, prepared according to the procedure of Sando,[17] melted at 221°, in agreement with the recorded value.

Acknowledgments.—We wish to thank Mr. Albert Kihm and Mr. Robert Manning for technical assistance, and the General Appropriations Fund of the University of Kansas for financial support during this investigation.

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(12) A. Winterstein and G. Stein, *Z. physiol. Chem.*, **199**, 64 (1931), give m.p. 259–264° for oleanolic acid acetate and m.p. 305–308° for free oleanolic acid.

(13) Kindly supplied from the collection of Dr. C. E. Sando at the U. S. Department of Agriculture.

(14) Y. Obata, *J. Agr. Chem. Soc. Japan*, **17**, 219 (1941), gives m.p. 260–262° for oleanolic acid benzoate. See *C. A.*, **45**, 3912c (1951).

(15) Rowe, *et al.*, ref. 6, give m.p. 288–289° for ursolic acid acetate and m.p. 282–284° for free ursolic acid.

(16) N. M. King, A. Chatterjee and L. M. Parks, *J. Am. Pharm. Assoc.*, **39**, 595 (1950).

(17) C. E. Sando, *J. Biol. Chem.*, **90**, 477 (1931).

The Reaction of Ethyl Trichloroacetate with Aromatic Grignard Compounds

BY A. KALUSZYNER AND S. REUTER

RECEIVED MAY 18, 1953

Henry[1] has described the reaction between methylmagnesium bromide and ethyl trichloroacetate (I) as leading to the expected trichloro-*t*-butyl alcohol, without indicating the yield. Experiments with aromatic Grignard compounds, undertaken in an attempt to synthesize substances of the general formula CCl_3CAr_2OH, have led to unexpected results.

The reaction of I with phenylmagnesium bromide (4 moles per mole ester) did not yield the chlorinated tertiary alcohol in isolable quantities. Apart from about 0.4 mole of biphenyl, a yield of 1 mole of chlorobenzene was obtained, identified by boiling point, density and refractive index. In the aqueous layer obtained in the decomposition of the reaction product, one third of the chlorine of the ester I was recovered in form of chloride ion. Phenyllithium reacts with I in the same manner.

The analogous reaction with *p*-tolylmagnesium bromide gave 0.6 mole of *p*-chlorotoluene, 0.8 mole of 4,4′-dimethylbiphenyl and in the aqueous layer, 80% of the chlorine of I as chloride ion. The reaction with *p*-chlorophenylmagnesium bromide yielded 0.2 mole of *p*-dichlorobenzene, 0.8 mole of 4,4′-dichlorobiphenyl and 72% of the chlorine atoms of I in ionic form.

It appears, therefore, that ethyl trichloroacetate reacts with arylmagnesium bromides according to the following equation to give the corresponding aryl chloride

$$\mathrm{ROOC{\cdot}CCl_3 + ArMg\ Br \longrightarrow ArCl + (ROOC{\cdot}CCl_2)^{-}MgBr^{+}} \quad (1)$$

In the case of phenylmagnesium bromide, all of the trichloroacetate reacts in that manner, in that of *p*-tolylmagnesium and of *p*-chlorophenylmagnesium bromide, only 60 and 10%, respectively.

Replacement of MgX in Grignard compounds by chlorine has been known to occur with substances containing "positive chlorine," such as aryliodonium chloride,[2] ethyl hypochlorite,[3] N-chloropiperidine[4] and benzene sulfochloride.[5] One has, therefore, to conclude that in ethyl trichloroacetate (I), the accumulation of chlorine atoms gives them an electropositive character.

For the formation of chloride ion and the biaryl compound in the reaction between an arylmagnesium bromide and ethyl trichloroacetate, a number of possibilities exist. In this respect, it is re-

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(1) L. Henry, *Bull. soc. chim. Belg.*, **20**, 152 (1906); *Chem. Zentr.*, **77**, 1178 (1906).

(2) H. Hepworth, *J. Chem. Soc.*, **119**, 1244 (1921).

(3) N. N. Melnikow, *Chem. Zentr.*, **107**, II, 2896 (1936).

(4) R. I. W. Le Fèvre and P. I. Markham, *J. Chem. Soc.*, 703 (1934).

(5) R. I. W. Le Fèvre, *J. Chem. Soc.*, 1245 (1932); *cf.* H. Gilman and R. E. Fothergill, THIS JOURNAL, **51**, 3501 (1929).

called[6] that DDT and its analogs react with Grignard compounds to give substances of the formulas: $(RC_6H_4)_2CHCHCl_2$, $(RC_6H_4)_2CHCCl{=}CClCH(C_6H_4R)_2$ and $(RC_6H_4)_2CHCH{=}CHCH(C_6H_4R)_2$. Although we have not succeeded in elucidating the fate of the trichloroacetate molecule, the following conclusions can be drawn from the experimental material. In the reaction of I with phenylmagnesium bromide, all of the chloride ion and of the biphenyl must derive from an interaction of the Grignard compound with $(ROOCCCl_2)^-MgBr^+$. In the other two cases, both this type of reaction can occur, but equally a direct interaction of the Grignard compound with I, *e.g.*, according to the equation

$$ROOCCCl_3 + 2ArMgBr \longrightarrow ArAr + (ROOCCCl_2)^-MgBr^+ + MgBrCl$$

In all three instances, for each mole of biaryl isolated, approximately three equivalents of chloride ion are found.

The reductive dehalogenation of trichloroacetic acid has been observed in other reactions.[7,8]

It is interesting that according to Pepper and Kulka[9] *p*,ω,ω,ω-tetrachloroacetophenone and *p*-chlorophenylmagnesium bromide give *p*,ω,ω-trichloroacetophenone. It could be shown that also in the reaction between ω-trichloroacetophenone and phenylmagnesium bromide (4 moles per mole), 43% of the chlorine reappears in the form of chloride ions; apart from biphenyl (1.7 moles per mole ketone), no defined organic material could, however, be isolated in this case.

In contradistinction to I, ethyl trifluoroacetate reacts normally with Grignard compounds. This reaction will be described in a forthcoming communication.

Experimental

Ethyl trichloroacetate (I) had b.p. 167°, n^{20}_{D} 1.4505. **ω-Trichloroacetophenone**, b.p. 254–255°, was prepared from trichloroacetyl chloride and benzene[10] and ***p*-chlorobromobenzene**, m.p. 67°, according to Mouneyrat and Pouret.[11]

General Procedure.—A quantity of 0.1 mole of ethyl trichloroacetate (or trichloroacetophenone) and 0.4 mole of the Grignard compound in ether was employed. The second component was added at 0° to the Grignard solution and the reaction completed by refluxing for 90 minutes. (In one experiment, the mixture was kept at 0° for 12 hours, but the result was the same.) The product was decomposed with ice-cold distilled water and dilute sulfuric acid. In the aqueous layer, chloride ion was determined in the usual manner. The ethereal layer was washed with 5% sodium carbonate solution, dried and concentrated and the residue subjected to fractional distillation.

Reaction of I with Phenylmagnesium Bromide.—In two experiments, 11.3 and 10.0 g. of chlorobenzene was isolated (0.1 and 0.09 mole, respectively); b.p. 132°, d^{28}_{4} 1.104, n^{20}_{D} 0.5252. The quantities of biphenyl were 5.7 g. (0.037 mole) and 8.0 g. (0.050 mole), respectively. Thirty-five and thirty-seven per cent. of the total chlorine of I were found in the aqueous layer.

Reaction of I with *p*-Tolylmagnesium Bromide.—*p*-Chlorotoluene (7.5 g., 0.06 mole) was identified by permanganate oxidation to *p*-chlorobenzoic acid, m.p. 238°; **4,4′-dimethylbiphenyl** (11.0 g., 0.076 mole) by melting point (120°) and mixed m.p. Eighty per cent. of the total chlorine of I was recovered in the aqueous layer.

Reaction of I with *p*-Chlorophenylmagnesium Bromide.—Both ***p*-dichlorobenzene** (2.5 g., 0.017 mole) and **4,4′-dichlorobiphenyl** (9.0 g., 0.04 mole) were identified by m.p. (52–53°, 146–147°) and comparison with authentic specimens. Seventy-five per cent. of the total chlorine had been converted into ionic form.

Reaction of I with Phenyllithium.—The reaction between I (0.05 mole) and phenyllithium (0.2 mole, 31.5 g. of bromobenzene and 2.8 g. of lithium) was carried out as described above, but in an atmosphere of nitrogen. The products obtained were: chlorobenzene (6.3 g., 0.06 mole); biphenyl (2.5 g., 0.016 mole) and chloride ion (31% of the total chlorine in the quantity of the ester employed).

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[6] W. Awe and J. Reinecke, *Experientia*, **6**, 185 (1950).

[7] H. W. Doughty and D. A. Lacoss, THIS JOURNAL, **51**, 853 (1929).

[8] Rathke, *Ann.*, **161**, 166 (1872).

[9] J. M. Pepper and M. Kulka, THIS JOURNAL, **72**, 1417 (1950).

[10] H. Biltz, *J. prakt. Chem.*, [2] **142**, 196 (1937).

[11] A. Mouneyrat and Ch. Pouret, *Bull. soc. chim. France*, **19**, 801 (1898).

2,3-Bis-(*p*-aminophenyl)-2,3-butanediol

BY NELSON J. LEONARD, SHERLOCK SWANN, JR., AND GLENN FULLER

RECEIVED JUNE 10, 1953

Because of increasing interest in 2,3-bis-(*p*-aminophenyl)-2,3-butanediol (I)[1] as an immediate precursor of compounds having pronounced physiological activity,[2] we wished to provide a method for the synthesis of I by the electrolytic reduction of *p*-aminoacetophenone which would require only readily available apparatus. The electrolytic reduction has been carried out under the following conditions to give acceptable yields of 2,3-bis-(*p*-aminophenyl)-2,3-butanediol dihydrochloride (55–59%): the cathode used was tin,[3] the anode, platinum,[4] both anolyte and catholyte were 1.6 *N* hydrochloric acid, the temperature was maintained at 24–30°, and the initial cathode current density was in the range 0.01–0.02 amp. per cm.².

Experimental

Electrolytic Reduction of *p*-Aminoacetophenone.—The tin cathode (of 99.9% purity or better), with a surface area of 100 cm.², was cast in a graphite mold initially at a temperature of 70°. It was prepared prior to use by the customary procedure.[5] The anode was of smooth platinum. A porous alundum diaphragm was first cleaned in 20% nitric acid, soaked in 20% aqueous sodium silicate, then in 20% sulfuric acid and finally in 20% hydrochloric acid.[5] The catholyte was prepared by dissolving 13.5 g. (0.1 mole) of *p*-aminoacetophenone (Eastman Kodak Co. material recrystallized) in 100 ml. of 1.6 *N* hydrochloric acid. The anolyte was 1.6 *N* hydrochloric acid. The electrolysis cell was assembled in the usual manner,[5] and stirring was effected by a magnetic stirrer. The line potential was 6 v. The temperature of the cell was maintained at 24–30° while a current of 1 amp. was allowed to flow through the solution (100 ml. of 1 *M* *p*-aminoacetophenone hydrochloride). The initial cathode current density was therefore 0.01 amp. per cm.². During the course of the reduction, the current diminished to 0.84 amp. after 4 hours. Approximately 1.5 l. of hydrogen was evolved, the rate of evolution increasing toward the end of the reaction. After 5.3 hours

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[1] M. J. Allen and A. H. Corwin, THIS JOURNAL, **72**, 114 (1950).

[2] *E.g.*, Amphenone "B": A. E. Heming, D. E. Holtkamp, J. F. Kerwin, L. F. Mansor and J. G. Dacanay, *Proc. Soc. Exptl. Biol. Med.*, **80**, 154 (1952).

[3] S. Swann, Jr., P. E. Ambrose, R. C. Dale, R. C. Rowe, H. M. Ward, H. D. Kerfman and S. Axelrod, *Trans. Electrochem. Soc.*, **85**, 231 (1944).

[4] Past experience indicates that an anode of carbon or graphite would be equally satisfactory.

[5] S. Swann, Jr., "Electrolytic Reductions" in A. Weissberger, editor, "Technique of Organic Reactions," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1948.