These results compare favorably with those previously reported on silver[4] and polonium.[6]

Filtration Efficiency.—Filter papers of various relative retentivities and glass frits of various degrees of porosity were used to separate the radiocolloids at *p*H values of 7.0 and 10.0. As the relative retentivities of Schleicher and Schnell filter papers decreased and as the porosity of the frits increased, the per cent. radiocolloid removed decreased.

Effect of Stirring.—To test the effect of previous agitation upon the extent of radiocolloid removal, a series of samples originally 0.01 *N* in nitric acid was rapidly stirred for 60 min. after adjustment of the *p*H, and the removable activity was compared to that for similar samples which were not stirred. At a *p*H value of 7.0, 27% of the activity could be removed from the stirred samples by filtration through filter paper as compared to 38% for those not stirred. These values are the averages for four determinations, the standard deviations being 2.1 and 2.6 percentage points, respectively. Similar results were obtained for filtration through a glass frit and for centrifugation. Results showing a decrease in removal for stirred samples were also obtained at a *p*H value of 10.01. These results might be interpreted as the breaking up of the radiocolloidal aggregates into smaller groups which were not removed with as great an efficiency.

Diffusion.—The diffusion coefficients of the beryllium were determined at several *p*H values using the method of Anderson and Saddington.[7] At a *p*H at 2.0 the diffusion coefficient was 0.34 cm.^{2}/day; at *p*H 6.0 it was 0.29 cm.^{2}/day; the value was 0.13 cm.^{2}/day at a *p*H of 8.0 and 0.11 cm.^{2}/day at *p*H 10.0. Each determination was made in triplicate and no standard deviation exceeded 0.02 cm.^{2}/day. Assuming the validity of the Einstein–Stokes equation, the average radii of the aggregates were calculated to be 7 Å. at *p*H 2.0 increasing to 22 Å. at *p*H 10.0. Similar results are reported by Hevesy and Paneth for polonium,[8] and Schubert and Conn for zirconium and barium.[9]

Acknowledgment.—The authors wish to express their gratitude to the U. S. Atomic Energy Commission for the grant of funds which made this work possible.

---

[6] G. Bouissieres, R. Chastel and L. Vigneron, *Comp. rend.*, **224**, 43 (1947).

[7] J. S. Anderson and K. Saddington, *J. Chem. Soc.*, S 381 (1949).

[8] G. Hevesy, *Phil. Mag.*, **25**, 390 (1913); **27**, 586 (1914); F. Paneth, *Kolloid Z.*, **13**, 1 (1913).

[9] J. Schubert and E. E. Conn, *Nucleonics*, **4**, No. 6, 2 (1949).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TENNESSEE
KNOXVILLE 16, TENNESSEE

3-Methyl-5-anisyl-4-carbethoxy-2-cyclohexene-1-one

BY WALTER T. SMITH, JR., AND DANIEL S. P. EFTAX

RECEIVED APRIL 9, 1953

The preparation of 3-methyl-5-substituted-4-carbethoxy-2-cyclohexene-1-ones by the acid-catalyzed monodecarbethoxylation of 3-methyl-5-substituted-4,6-dicarbethoxy-2-cyclohexene-1-ones has been reported only in those cases in which the 5-substituent is alkyl.[1] Various earlier attempts to accomplish the monodecarbethoxylation have been unsuccessful in those cases in which the 5-substituent is aryl.[2,3]

Horning and Field[4] devised an alternate method for the preparation of 3-methyl-4-carbethoxy-5-anisyl-2-cyclohexene-1-one. The final step in their method was the cyclization of ethyl α,γ-diacetyl-β-anisylbutyrate with phosphoric acid in acetic acid. On this final step the yield of crude product was 22%.

A reinvestigation of the action of sodium ethoxide on ethyl anisal-bis-acetoacetate has shown that the product of this reaction is not 3-methyl-5-anisyl-2-cyclohexen-1-one as previously reported,[5] but that this reaction provides a new and improved method for the synthesis of 3-methyl-5-anisyl-4-carbethoxy-2-cyclohexene-1-one. The yield in the last step is 47%. The method has the further advantage that the starting material can be prepared in good yield in only one step from anisaldehyde.[5]

The identity of the product is established by comparison with the melting points previously reported[4] for the compound itself and for its dinitrophenylhydrazone. The *p*-nitrophenylhydrazone was also prepared. In addition, the monoester was converted to the known 3-methyl-5-anisyl-2-cyclohexene-1-one by alkaline saponification, followed by decarboxylation.

By the procedures described here, together with methods previously reported,[6] it is possible to use ethyl anisal-bis-acetoacetate as the common starting material for the preparation not only of 3-methyl-5-anisyl-2-cyclohexen-1-one, but also for the 4-carbethoxy derivative and the 4,6-dicarbethoxy derivative.

Experimental

3-Methyl-4-carbethoxy-5-anisyl-2-cyclohexene-1-one.—Ethyl anisal-bis-acetoacetate (60 g., 0.16 mole) was dissolved in 240 ml. of absolute ethanol containing 1.9 g. (0.082 mole) of sodium and refluxed for five hours. At the end of this period a small amount of sodium carbonate (4.8 g.) precipitated on cooling and was separated by filtration. The remaining orange solution was poured into 250 ml. of water containing chipped ice and 15 ml. of concd. hydrochloric acid; 40 g. (87%) of pale yellow solid separated. Subsequent recrystallizations from 95% ethanol yielded 21.5 g. (47%) of colorless crystals, m.p. 71–73°. The 2,4-dinitrophenylhydrazone melted at 182.5–183.5°.[4]

The yellow *p*-nitrophenylhydrazone[7] was recrystallized from 95% ethanol and melted at 195–196°.

Anal. Calcd. for $C_{23}H_{25}O_5N_3$: C, 65.25; H, 5.96; N, 9.92. Found: C, 65.16; H, 5.98; N, 10.06.

3-Methyl-5-anisyl-2-cyclohexene-1-one.—3-Methyl-4-carbethoxy-5-anisyl-2-cyclohexene-1-one (13 g., 0.043 mole) was dissolved in 100 ml. of 95% ethanol and the solution was added to 60 ml. of water containing 8 g. of sodium hydroxide; the mixture was refluxed for one-half hour, cooled to room temperature, acidified with 40 ml. of 1:1 hydro-

---

[1] E. C. Horning, M. O. Denekas and R. E. Field, *J. Org. Chem.*, **9**, 547 (1944).

[2] E. Knoevenagel, *Ann.*, **303**, 223 (1898).

[3] E. C. Horning and R. E. Field, THIS JOURNAL, **68**, 384 (1946).

[4] E. C. Horning and R. E. Field, *ibid.*, **68**, 387 (1946).

[5] W. T. Smith, Jr., and P. G. Kort, *ibid.*, **72**, 1877 (1950).

[6] E. C. Horning and R. E. Field, *ibid.*, **68**, 384 (1946).

[7] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Ed., John Wiley and Sons, Inc., 1948, p. 171.

chloric acid and refluxed for 15 minutes. At the end of this period the light brown mixture was poured into 500 ml. of water whereupon 10 g. of brown solid separated. The melting point was 60–61.5°. Recrystallization from 50 ml. of 95% ethanol gave 7.5 g. (77%) of pale yellow crystals, m.p. 62.5–63.5°. A mixed melting point with an authentic sample prepared according to the procedure of Horning and Field[4] showed no depression.

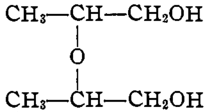
DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

Synthesis and Identification of Dipropylene Glycol Isomers

BY A. R. SEXTON AND E. C. BRITTON

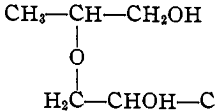
RECEIVED JANUARY 31, 1953

When one mole of propylene oxide is treated with propylene glycol, three isomers of dipropylene glycol may theoretically result.



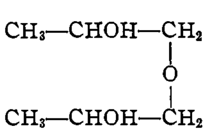
$$\begin{array}{c}\mathrm{CH_3{-}CH{-}CH_2OH}\\ |\\ \mathrm{O}\\ |\\ \mathrm{CH_3{-}CH{-}CH_2OH}\end{array}$$

I, 2,2′-oxydi-1-propanol (diprimary alcohol)



$$\begin{array}{c}\mathrm{CH_3{-}CH{-}CH_2OH}\\ |\\ \mathrm{O}\\ |\\ \mathrm{H_2C{-}CHOH{-}CH_3}\end{array}$$

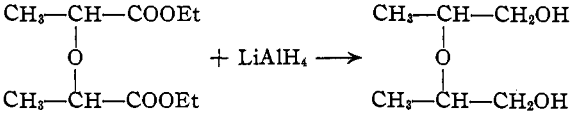
II, 2-(2-hydroxypropoxy)-1-propanol (primary-secondary alcohol)



$$\begin{array}{c}\mathrm{CH_3{-}CHOH{-}CH_2}\\ |\\ \mathrm{O}\\ |\\ \mathrm{CH_3{-}CHOH{-}CH_2}\end{array}$$

III, 1,1′-oxydi-2-propanol (disecondary alcohol)

The three isomers have been prepared and their physical properties determined. The diprimary alcohol I was prepared in 91% yield by the reduction of diethyl dilactate with lithium aluminum hydride.



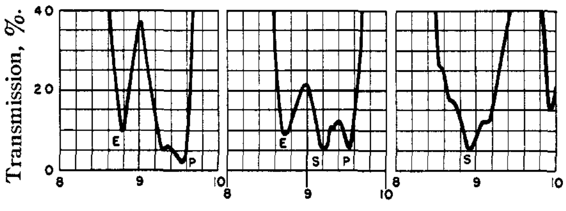
$$\begin{array}{c}\mathrm{CH_3{-}CH{-}COOEt}\\ |\\ \mathrm{O}\\ |\\ \mathrm{CH_3{-}CH{-}COOEt}\end{array} + \mathrm{LiAlH_4} \longrightarrow \begin{array}{c}\mathrm{CH_3{-}CH{-}CH_2OH}\\ |\\ \mathrm{O}\\ |\\ \mathrm{CH_3{-}CH{-}CH_2OH}\end{array}$$

The synthesis of the primary-secondary isomer (II) was based on the work of earlier investigators[1-4] which showed that addition of propylene oxide to an alcohol with alkaline catalyst yields largely a secondary alcohol. On this basis 1-methoxy-2-propanol[1] was treated with propylene oxide using sodium catalyst to give 1-(2-methoxyisopropoxy)-2-propanol, b.p. 76–78° (10 mm.). This was heated with 48% hydrobromic acid to give methyl bromide and 2-(2-hydroxypropoxy)-1-propanol in 52% yield.

The disecondary isomer (III) was prepared by treating propylene oxide with propylene glycol using sodium as the catalyst. This gave largely the disecondary isomer since propylene oxide reacts much faster with a primary alcohol than with a secondary alcohol. The product was distilled and on recrystallization from diethyl ether melted at 45–46.5°.

A study of infrared absorption curves (Fig. 1) in the region of 8 to 10 μ showed the three isomers to be distinctively different. The compounds were studied in 1% solution of carbon disulfide in 1-mm. cells.

The absorption curve for the ether linkage is designated by E, the primary OH curve by P and the secondary OH curve by S.



Wave length in microns.

Fig. 1.—Left curve, 2,2′-oxydi-1-propanol; middle curve, 2-(2-hydroxypropoxy)-1-propanol; right curve, 1,1′-oxydi-2-propanol.

Experimental

I. Preparation of 2,2′-Oxydi-1-propanol.—The apparatus consisted of a 5-l., 5-neck flask equipped with a stirrer, thermometer, dropping funnel, nitrogen inlet and reflux condenser. The condenser was vented through a Dry Ice trap and calcium chloride drying tube.

After sweeping the flask with nitrogen, 45 g. (1.15 moles) of finely powdered lithium aluminum hydride was added. The flask was cooled in an ice–water-bath. With stirrer going and nitrogen bubbling through, 1500 g. of dry diethyl ether was added slowly. The ice-bath was removed and the mixture refluxed on a water-bath 3 hours to dissolve the lithium aluminum hydride. To this mixture 218 g. (1.08 mole) of dilactic acid diethyl ester[5] in 286 g. of dry diethyl ether was added dropwise over a period of two hours at 15–18°. The temperature was controlled by adding ice to the water-bath. The mixture was then slowly warmed to reflux and held at this temperature for 4 hours.

Fifty grams of ethyl acetate was added dropwise to destroy any unreacted lithium aluminum hydride, followed by slow addition of 250 cc. of water and finally 4–6 moles of 35% hydrochloric acid. The nitrogen was then shut off and the ether distilled off on a steam-bath. The still residue (966 g.) was passed through Dowex-50 cation exchange resin to remove the lithium and aluminum. The filtrate was distilled under vacuum to remove water and hydrochloric acid, and gave 122 g. (0.91 mole) of 2,2′-oxydi-1-propanol boiling at 102° at 5 mm. and at 225.7° at 760 mm. It did not solidify at −40° and had specific gravity 1.0316 (25/25), 1.0018 (60/4); $n^{25}\mathrm{D}$ 1.4410, $n^{60}\mathrm{D}$ 1.4296.

Anal. Calcd. for $C_6H_{14}O_3$: C, 53.71; H, 10.52. Found: C, 53.63; H, 10.53.

Its **bis-*p*-nitrobenzoate**, prepared in 86.5% yield, melted at 142–143°.

Anal. Calcd. for $C_{20}H_{20}N_2O_9$: N, 6.48. Found: N, 6.54.

Its **bis-triphenylmethyl ether**, prepared in 70% yield,[6] melted at 131–132°.

Anal. Calcd. for $C_{44}H_{42}O_3$: C, 85.40; H, 6.84. Found: C, 85.2; H, 7.0.

II. Synthesis of 2-(2-Hydroxypropoxy)-1-propanol.—The apparatus was the same as described under I. Nine hundred grams (10 moles) of 1-methoxy-2-propanol[1] and 4 g. of metallic sodium were added to the flask. The mixture was heated to 80° and 406 g. (7 moles) of propylene oxide was added dropwise at 80–100° over a period of 4 hours. The mixture was distilled on a $1^{1}/_{4}''$ × 4′ column packed with $^{3}/_{16}''$ KA2S stainless steel saddles at a 10/1 reflux ratio to give 430 g. (2.9 moles) of 1-(2-methoxyisopropoxy)-2-propanol, b.p. 76–78° (10 mm.). Two moles of this was mixed with 3 moles of 48% hydrogen bromide and refluxed at 80–108° until no more methyl bromide was liberated. The methyl bromide (88.5% of theory) was collected in a Dry Ice trap. The residue was passed through a bed of Amber-

---

(1) H. C. Chitwood and B. T. Freure, THIS JOURNAL, **68**, 680 (1946).

(2) R. G. Kadesch, *ibid.*, **68**, 41 (1946).

(3) P. D. Bartlett, *ibid.*, **70**, 926 (1948).

(4) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R*), **14**, 1038 (1944).

(5) Pierre Vieles, *Ann. chim.*, [11] **3**, 143 (1935).

(6) Prepared according to M. K. Seikel and E. H. Huntress, THIS JOURNAL, **63**, 593 (1941).