[Contribution from the Chemical Laboratory of the University of Washington]

# BETA-TOLOXY-PROPIONIC ACIDS AND THE CORRESPONDING CHROMANONES

By S. G. Powell and Norman G. Johnson

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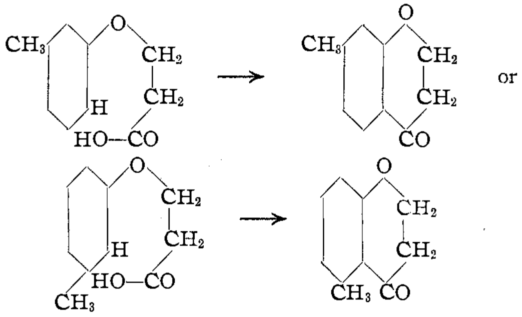
It was shown in a previous paper[1] that γ-phenoxypropyl alcohol is readily oxidized to β-phenoxypropionic acid, which in turn is smoothly dehydrated to chromanone. A study of the preparation of other β-aryloxypropionic acids and the corresponding chromanones was then begun. After this investigation was well under way, several papers by other investigators, bearing on this same subject, appeared. Arndt and Källner[2] describe the preparation of chromanone from β-phenoxypropionic acid, their results agreeing in every way with those already reported by one of us.[1] Krollpfeiffer and Schultze[3] describe the preparation of 6-methyl-chromanone from β-(*p*-toloxy)-propionic acid. In view of this, although the investigation is by no means completed, it seemed desirable to report at this time such results as have so far been obtained.

This paper describes the preparation of β-(*m*-toloxy)- and β-(*p*-toloxy)-propionic acids and the corresponding chromanones. The investigation is being continued and further results will be reported in a later communication.

The β-toloxy-propionic acids were obtained by oxidation of the corresponding alcohols. Attempts to prepare β-(*o*-toloxy)-propionic acid in a similar manner have so far been unsuccessful. The chromanones were readily obtained by heating a benzene solution of the acid with phosphorus pentoxide. The β-(*p*-toloxy)-propionic acid yields 6-methyl-chromanone, identical with that described by Auwers and Krollpfeiffer[4] and later by Krollpfeiffer and Schultze.[3] β-(*m*-Toloxy)-propionic acid, on the other hand, can yield either 5- or 7-methyl-chromanone.



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[1] Powell, This Journal, **45**, 2708 (1923).

[2] Arndt and Källner, *Ber.*, **57B**, 202 (1924).

[3] Krollpfeiffer and Schultze, *Ber.*, **57B**, 206 (1924).

[4] Auwers and Krollpfeiffer, *Ber.*, **47**, 2585 (1914).

As Perkin and Robinson[5] and later Pfeiffer and Oberlin[6] found that β-(*m*-anisoxy)-propionic acid yields 7-methoxy-chromanone, it is assumed that the product obtained from β-(*m*-toloxy)-propionic acid is 7-methylchromanone.

**γ-(*m*-Toloxy)-propyl Alcohol,** $CH_3.C_6H_4.O.(CH_2)_3OH$.—This was prepared by the same method as that described for the preparation of γ-phenoxy-propyl alcohol.[1] One hundred g. of trimethylene-chlorohydrin is added to a solution of 108 g. of *m*-cresol in 400 g. of aqueous sodium hydroxide solution and the mixture boiled under a reflux condenser for 30 minutes. An oily layer separates after about three minutes, but the boiling is continued to insure completion of the reaction. The toloxy-propyl alcohol is taken up in ether, the ether solution washed with 5% sodium hydroxide solution, then with water and finally dried over sodium sulfate. After removal of the ether, the residue is distilled and the desired alcohol is obtained, as an oily liquid; b. p., 146–147° (13 mm.). On standing, the oil solidifies to a mass of colorless crystals; m. p., 30–31°; yield, 135 g., or 80%.

*Anal.* Subs., 0.2456: $CO_2$, 0.3880; $H_2O$, 0.0984. Calc. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.4. Found: C, 71.60; H, 8.4.

**β-(*m*-Toloxy)-propionic Acid,** $CH_3.C_6H_4.O.CH_2.CH_2.COOH$.—As in the case of β-phenoxy-propionic acid, it was found that the best results were obtained by oxidizing small quantities at a time.

Ten g. of the alcohol is added to a solution of 40 g. of crystallized magnesium sulfate in 100 cc. of water and 260 cc. of a 5% solution of potassium permanganate is added drop by drop while the mixture is constantly stirred. When the color of the permanganate has completely disappeared, a slight excess of sodium bisulfite is added and the mixture acidified with dil. sulfuric acid. The mixture of toloxy-propionic acid and unoxidized alcohol is dissolved in ether and the ether solution is extracted with dil. sodium hydroxide solution. The alkaline extract is then acidified with dil. sulfuric acid, when the β-(*m*-toloxy)-propionic acid separates. It crystallizes from hot water in long, shining needles; m. p., 105°; yield, 4.5 g., or 41%.

*Anal.* Subs., 0.2340: $CO_2$, 0.5692; $H_2O$, 0.1276. Calc. for $C_{10}H_{12}O_3$: C, 66.7; H, 6.7. Found: C, 66.4; H, 6.1.

AMIDE.—Three g. of the acid is warmed for a few minutes with a slight excess of thionyl chloride and the resulting solution poured into concd. aqueous ammonia. The amide is filtered off and recrystallized from hot water; m. p., 108°.

*Anal.* Subs., 0.1985: 11.1 cc. of 0.1 *N* $H_2SO_4$ (Kjeldahl). Calc. for $C_{10}H_{13}O_2N$: N, 7.82. Found: 7.83.

**7-Methyl-chromanone.**—Twenty-five g. of phosphorus pentoxide is added to a solution of 10 g. of β-(*m*-toloxy)-propionic acid in 150 cc. of dry benzene and the mixture boiled under a reflux condenser for one hour. The benzene solution is removed and the residue extracted several times with dry benzene. The united benzene solutions are washed with dil. alkali, then with water and finally dried over calcium chloride. After removal of the benzene, the residue is distilled when the methyl-chromanone is obtained as a slightly yellow, highly refracting liquid with the characteristic lemon-like, chromanone odor; b. p., 138° (13 mm.).

*Anal.* Subs., 0.2019: $CO_2$, 0.5529; $H_2O$, 0.1136. Calc. for $C_{10}H_{10}O_2$: C, 74.1; H, 6.2. Found: C, 74.5; H, 6.2.

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[5] Perkin and Robinson, *Proc. Chem. Soc.*, **28,** 7 (1913).

[6] Pfeiffer and Oberlin, *Ber.*, **57B,** 208 (1924).

OXIME.—Three g. of methyl-chromanone, 3 g. of hydroxylamine hydrochloride, 6 g. of potassium carbonate and 50 cc. of alcohol are boiled under a reflux condenser for six hours. The oxime is then precipitated by the addition of water, filtered off and crystallized from hot water, from which it separates in beautiful, white needles; m. p., 98–99°.

*Anal.* Subs., 0.2491: 16.4 cc. of $N_2$ (20°, 760 mm.; over 50% KOH). Calc. for $C_{10}H_{11}O_2N$: N, 7.9. Found: 7.7.

**γ-(*p*-Toloxy)-propyl Alcohol,** $CH_3.C_6H_4.O.(CH_2)_3OH$.—This compound was prepared from *p*-cresol and trimethylene-chlorohydrin in the same manner as was the *meta* derivative. It forms a viscous, colorless liquid which solidifies on cooling to form a mass of fine crystals; b. p., 171° (39 mm.); m. p., 21–22°; yield, 80%.

*Anal.* Subs., 0.1794: $CO_2$, 0.4708; $H_2O$, 0.1324. Calc. for $C_{10}H_{14}O_2$: C, 72.30; H, 8.4. Found: C, 71.70; H, 8.2.

**β-(*p*-Toloxy)-propionic Acid,** $CH_3.C_6H_4.O.CH_2.CH_2.COOH$.—This acid has already been described by Krollpfeiffer and Schultze.[3] It is also readily obtained by oxidation of γ-(*p*-toloxy)-propyl alcohol; 10 g. of the alcohol, treated as described for the *meta* derivative, yields 4.5 g. of the acid (41%).

AMIDE.—Three g. of the acid is warmed for a few minutes with a slight excess of thionyl chloride and the mixture then poured into concd. aqueous ammonia. On cooling, the amide slowly separates and is removed and recrystallized from hot water. It is obtained as colorless needles; m. p., 128°.

*Anal.* Subs., 0.1384: 7.40 cc. of 0.1 *N* $H_2SO_4$ (Kjeldahl). Calc. for $C_{10}H_{13}O_2N$: N, 7.82. Found: 7.48.

**6-Methyl-chromanone.**—This compound has been prepared by Auwers and Krollpfeiffer[4] who obtained it by treating *m*-(β-iodopropionyl)-*p*-cresol with alkali, and more recently by Krollpfeiffer and Schultze[3] who obtained it by dehydration of β-(*p*-toloxy)-propionic acids. The β-(*p*-toloxy)-propionic acid obtained by us was dehydrated in the same manner as described for the *meta* compound and the results were found to agree in every way with those of Krollpfeiffer and Schultze.

## Summary

1. γ-(*m*-Toloxy)- and γ-(*p*-toloxy)-propyl alcohols have been prepared and described.
2. β-(*m*-Toloxy)-propionic acid has been prepared.
3. β-(*p*-Toloxy)-propionic acid has been prepared in a new way.
4. 7-Methyl-chromanone has been prepared and described.

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