

Reactions of Substituted Phenacyl Bromides
with Various Bases: *p*-Methyl- and *p*-Methoxyphenacyl Bromide. II
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Received December 11, 1987

The products obtained from the reaction of *p*-methyl- and *p*-methoxyphenacyl bromide with various bases are described.

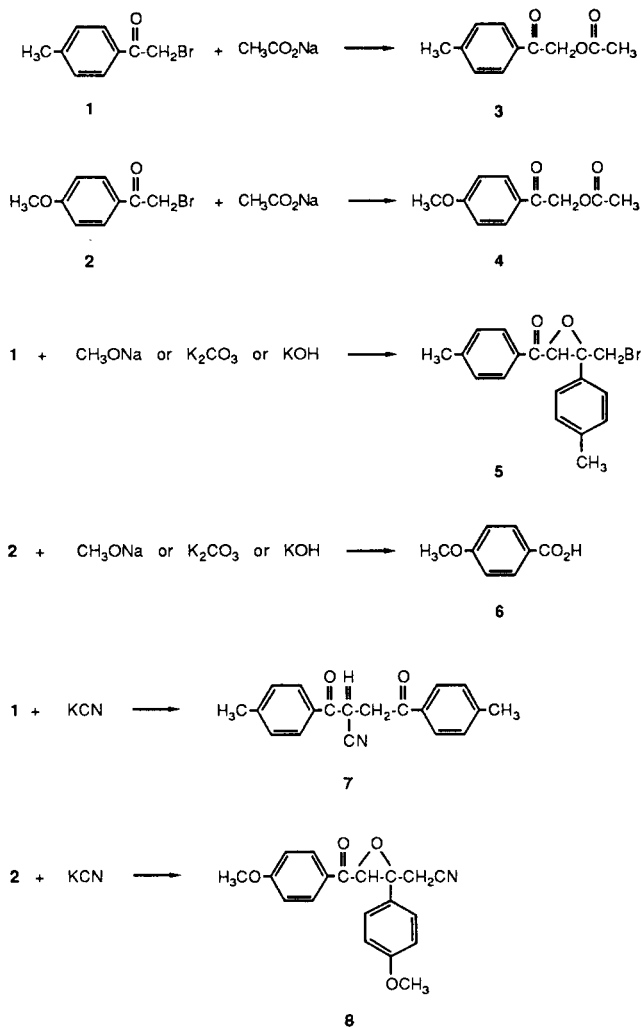
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The first paper in the continuing study of the reactions of substituted phenacyl bromides dealt with reactions of *o*- and *p*-nitrophenacyl bromides [2]. In this communication we wish to report on the results of the reactions of *p*-methyl- (**1**) and *p*-methoxyphenacyl bromide (**2**) with different bases. Karavan [3] has reported the isolation of 2-cyano-4-oxo-4-(4-methylphenyl)butanenitrile from the reaction of **1** and the sodium salt of malononitrile in a sodium ethoxide-ethanol solution. Charpentier-Morize [4] has reported that when **2** was treated with potassium carbonate in aqueous dioxane that *p*-methoxyphenacyl alcohol and *p*-methoxybenzoic acid were obtained as products. Temnikova [5] has reported that the reaction of **2** with sodium methoxide in aqueous dioxane gave only *p*-methoxyphenacyl alcohol as the product but if the reaction media was aqueous methanol, *p*-methoxyacetophenone, *p*-methoxybenzoic acid, and *p*-methoxyphenacylmethyl ether were obtained. Thus, the product(s) depend upon the base used as well as the solvent for the reaction media.

In this study we have looked at the reaction of **1** and **2** with sodium methoxide, potassium hydroxide, potassium carbonate, potassium cyanide, and sodium acetate in methanol.

When **1** or **2** was treated with sodium acetate only the corresponding *p*-methylphenacyl acetate (**3**) and *p*-methoxyphenacyl acetate (**4**) were obtained as products. When **1** was treated with sodium methoxide, potassium carbonate, or potassium hydroxide only 4-oxo-2,3-epoxy-2,4-bis(4-methylphenyl)-1-bromobutane (**5**) was obtained as the product. However, when **2** was treated with these same reagents only *p*-methoxybenzoic acid (**6**) was isolated.

The treatment of **1** with potassium cyanide yielded 1,4-dioxo-1,4-bis(4-methylphenyl)-2-cyanobutane (**7**) as the product. This seemingly unusual product is not without precedence since the formation of the symmetrical dibenzoyl ethylene has been previously reported as being obtained from the reaction of phenacyl chloride and potassium hydroxide in ethanol [6]. When **2** was treated with potassium cyanide, 5-oxo-3,4-epoxy-3,5-bis(4-methoxyphenyl)pentanenitrile (**8**) was obtained.



EXPERIMENTAL

Melting points were determined with a Mel-Temp capillary melting point apparatus previously calibrated. The ir spectra were recorded with a Perkin-Elmer Model 567 spectrophotometer. Chemical shifts are reported in δ units. Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, Indiana. Molecular weight was determined by Galbraith Laboratories, Inc., Knoxville, Tennessee.

p-Methylphenacyl Acetate (**3**).

A solution of anhydrous sodium acetate (0.82 g, 10 mmoles) in 20 ml of methanol was added dropwise with stirring to a solution of **1** in 10 ml of methanol. After 72 hours at reflux the mixture was poured over 200 g of ice. The resulting precipitate was collected and when recrystallized from ethanol afforded 0.63 g (33%) of colorless crystals, mp 84-85°; ir (potassium bromide): 1740 and 1690 cm^{-1} (C=O); pmr (deuteriochloroform): δ = 7.2-7.9 (d, ArH, 4H), 5.25 (s, CH_2 , 2H), 2.5 (s, CH_3 , 3H), and 2.3 (s, CH_3 , 3H).

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_3$: C, 68.76; H, 6.25. Found: C, 69.02; H, 6.37. *p*-Methoxyphenacyl Acetate (**4**).

A solution of anhydrous sodium acetate (0.82 g, 10 mmoles) in 25 ml of methanol was added dropwise with stirring to a solution of **2** (2.29 g, 10 mmoles) in 25 ml of methanol at ambient temperature. The resulting solution was heated to reflux for 48 hours before pouring over 350 g of ice. Recrystallization of the resulting precipitate afforded 0.9 g (43%) of colorless crystals, mp 56°; ir (potassium bromide): 1740 and 1695 (C=O), 1230 and 1085 cm^{-1} (ArOCH₃); pmr (deuteriochloroform): δ = 7.9-7.0 (d, ArH, 4H), 5.2 (s, CH_2 , 2H), 3.9 (s, CH_3O , 3H), 2.2 (s, CH_3 , 3H).

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_4$: C, 63.44; H, 5.82. Found: C, 63.35; H, 5.83.

4-Oxo-2,3-epoxy-2,4-bis(4-methylphenyl)-1-bromobutane (**5**).

To a solution of **1** (2.13 g, 10 mmoles) in 25 ml of methanol was added dropwise a solution of sodium methoxide (0.54 g, 10 mmoles) in 25 ml of methanol. The mixture was stirred for 4 hours at ambient temperature and then refluxed for 4 hours before pouring over 200 g of ice. The resulting precipitate was recrystallized from ethanol (decolorizing carbon) yielding 1.07 g (32%) of colorless crystals, mp 136-137°; ir (potassium bromide): 1680 (C=O), 1240 and 860 cm^{-1} (epoxy); pmr (carbon tetrachloride): δ = 6.6-7.2 (m, ArH, 8H), 4.0 (s, epoxy H), 3.45 (q, CH_2Br , 2H), 2.0 (s, CH_3 , 3H), and 1.85 (s, CH_3 , 3H).

Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{BrO}_2$: C, 62.63; H, 4.92. Found: C, 63.01; H, 5.13.

1,4-Dioxo-1,4-bis(4-methylphenyl)-2-cyanobutane (**7**).

To a solution of **1** (2.3 g, 10 mmoles) in 15 ml of methanol was added dropwise potassium cyanide (0.65 g, 10 mmoles) in 20 ml of methanol. After stirring at ambient temperature for one hour the resulting precipitate was collected. The filtrate was poured over 200 g of ice yielding additional product. The combined precipitates were crystallized

from ethanol affording 0.11 g (39%) of colorless crystals, mp 148-150°; ir (potassium bromide): 2240 (CN), 1695 and 1660 cm^{-1} (C=O); pmr (deuteriochloroform): δ 8.1-7.2 (m, ArH, 8H), 5.1 and 4.95 (2d, CHCN, 1H), 4.15, 3.95, 3.6 and 3.4 (4d, CH_2 , 2H) 2.45 (s, CH_3 , 3H), and 2.2 (s, CH_3 , 3H).

Anal. Calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}_2$: C, 78.35; H, 5.84; N, 4.81; Mol. Wt. 291. Found: C, 78.50; H, 5.83; N, 4.75; Mol. Wt. 301.

5-Oxo-3,4-epoxy-3,5-bis(4-methoxyphenyl)pentanenitrile (**8**).

A solution of potassium cyanide (1.43 g, 22 mmoles) in 75 ml of methanol was added dropwise with stirring to a solution of **2** (5.0 g, 22 mmoles) in 75 ml of methanol at ambient temperature. After stirring for three hours, the reaction mixture was heated to reflux for three hours. The solution was allowed to cool before pouring over 300 g of ice. The resulting pale yellow solid was collected and recrystallized from ethanol yielding 1.54 g (43%) of colorless crystals, mp 135°; ir (potassium bromide): 2245 (CN), 1685 (C=O), 1240 and 850 (epoxy), 1270 and 1175 cm^{-1} (ArOCH₃); pmr (deuteriochloroform): δ = 8.1-7.1 (m, ArH, 8H), 5.1 (m, epoxy H), 3.9 (s, OCH₃, 6H), 3.5 (q, CH_2 , 2H).

Anal. Calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}_4$: C, 70.59; H, 5.26; N, 4.33. Found: C, 70.77; H, 5.35; N, 4.40.

Acknowledgement.

We are grateful to the Faculty Research Committee of Middle Tennessee State University, Murfreesboro, Tennessee for the support of this research.

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