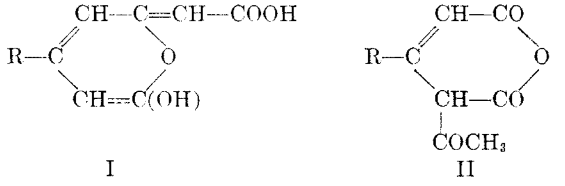
β-Arylglutaconic Acids. III.[1] The Action of Acetic Anhydride and Sodium Acetate on β-(2-Methoxy-4-methylphenyl)glutaconic Anhydride

J. J. NERURKAR[2] AND V. M. BHAVE

Received January 22, 1960

Under the conditions of the Perkin reaction, β-(4-methoxyphenyl)glutaconic anhydride has been shown to give a condensation product thought to be the corresponding glutaconylacetic acid (I).[3] Similar results were obtained earlier by other workers in the case of phthalic anhydride.[4,5] Gogte,[6] however, claims that the condensation product can be represented better by structure II than by structure I, since he also obtained it from β-(4-methoxyphenyl)-glutaconic anhydride under the conditions of Einhorn's acetylation method.[7]


I II

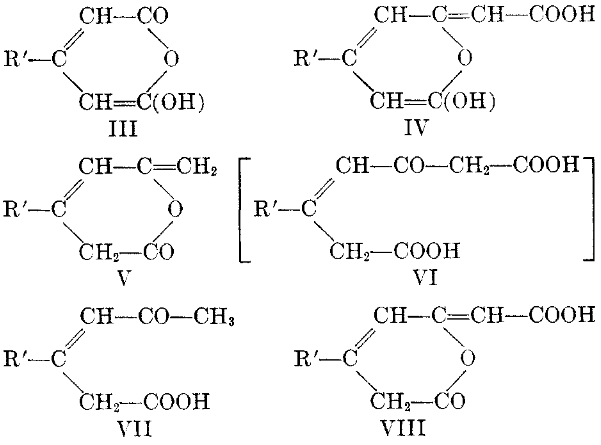
R = 4-Methoxyphenyl

This structural discrepancy has been resolved by Bhave on the basis of chemical evidence,[8] which indicates that the compound is a lactonic acid (I) rather than a ketonic anhydride (II).

In the present studies, we have collected further experimental and physical evidence in support of structure I by preparing similar compounds from an analogous anhydride, namely β-(2-methoxy-4-methylphenyl)glutaconic anhydride, and studying their infrared spectra.[9]

β-(2-Methoxy-4-methylphenyl)glutaconic anhydride (III), the intermediate for the present work, was obtained in 94% yield from the corresponding glutaconic acid[10] by the action of acetic anhydride at reflux temperature. The infrared spectrum of III had strong absorption peaks at 5.65 μ and 5.76 μ, characteristic of unstrained six-membered anhydride attached to an aromatic nucleus.[11] When III was subjected to the action of acetic anhydride in presence of fused sodium acetate, following the general procedure of Bhave,[3] an acidic substance (IV) was obtained in 67% yield. The infrared spectrum of IV does not show absorption attributable to an anhydride linkage, thus indicating the invalidity of structure II, but it has a broad peak between the range 5.69–5.78 μ, probably due to fusing of the carboxylic carbonyl absorption at 5.7 μ and δ-lactonic carbonyl absorption at 5.75 μ.[12] The acid IV gave a positive ferric chloride test (intense violet coloration) suggesting that it is enolic in nature.

When IV was heated above its melting point or treated with mineral acids, it lost a molecule of carbon dioxide affording a neutral compound (V) in 68% yield. The infrared spectrum of V has a single strong peak at 5.75 μ characteristic of δ-lactones.[12] It is apparent that this evidence is not in accord with a ketonic anhydride structure II. Also, IV as well as V failed to give a positive 2,4-dinitrophenylhydrazine test.


III IV V VI VII VIII

R′ = 2-Methoxy-4-methylphenyl

Alkaline hydrolysis of IV was accompanied by decarboxylation giving 3-(2-methoxy-4-methylphenyl)-5-keto-3-hexenoic acid (VII) in 46% yield. This suggests that the intermediate keto dicarboxylic acid (VI) was unstable and readily decarboxylated to a more stable monocarboxylic acid (VII). The presence of a keto function in VII was indicated through the preparation of a phenylhydrazone and semicarbazone. When VII was heated with acetic anhydride at reflux temperature, it gave rise to the lactone V in 58% yield. This lactone failed to give a positive ferric chloride test. Alkaline hydrolysis of V followed by a careful neutralization yielded the parent keto acid (VII). All these observations show a close parallelism between the behavior of IV and phthalylacetic acid[4,5] and thus further support the glutaconylacetic acid structure assigned to IV.

---

[1] Parts I and II: (a) *J. Org. Chem.*, **24**, 520 (1959); (b) *J. Org. Chem.*, **24**, 2055 (1959).

[2] Present address: Laboratory of Pharmaceutical Chemistry, The University of Kansas, Lawrence, Kan.

[3] D. B. Limaye and V. M. Bhave, *J. Univ. Bombay*, **2**, 82 (1933); [*Chem. Abstr.*, **28**, 6128 (1934)].

[4] S. Gabriel and A. Newman, *Ber.*, **26**, 951 (1893).

[5] S. Gabriel and G. Gieber, *Ber.*, **29**, 25 (1893).

[6] G. R. Gogte, *Proc. Ind. Acad. Sci.*, **7A**, 214 (1938); [*Chem. Abstr.*, **32**, 5389 (1938)].

[7] A. Einhorn and F. Hollandt, *Ann.*, **301**, 95 (1898).

[8] V. M. Bhave, *Rasayanam*, **1**, 127 (1938); [*Chem. Abstr.*, **33**, 1669 (1939)].

[9] Infrared spectra were determined using a Perkin-Elmer Infracord in chloroform solution in the region 5–6 μ.

[10] G. R. Gogte, M.S. thesis, University of Bombay, 1932, p. 72.

[11] B. R. Brown and A. R. Todd, *J. Chem. Soc.*, 1280 (1954).

[12] R. S. Rasmussen and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1073 (1949).

As mentioned earlier, IV is enolic in nature and we were interested to see if it could be converted into its keto form, an observation made earlier by Bhave in the case of similar compounds.[13] When IV was therefore subjected to the action of concentrated sulfuric acid, an isomeric high melting substance (VIII) was obtained. Unlike IV, VIII did not give any coloration with ferric chloride, but, like IV, it gave the keto acid VII by treatment with alkali and the lactone V by treatment with hydrochloric acid. From these observations and by analogy with previous work,[3,13] the high melting compound VIII can be considered as the keto form of the enolic compound IV. The reverse change, namely, the conversion of the keto VIII to the enol IV has not been observed.

EXPERIMENTAL[14]

3-(2-Methoxy-4-methylphenyl)glutaconylacetic acid (IV). This acid was prepared following the general procedure of Bhave.[3] To an intimate mixture of 11.5 g. (0.05 mole) of β-(2-methoxy-4-methylphenyl)glutaconic anhydride (III) and an equal quantity of powdered fused sodium acetate, 15 ml. of acetic anhydride was added. The mixture was heated on a steam bath for about 10 min. The resulting hot red solution was poured with stirring into 200 ml. water, filtered, and to the clear filtrate, 20 ml. of concd. hydrochloric acid was added. The precipitated solid was collected, washed with several portions of water and the dry solid was crystallized from acetic acid to give 9.5 g. (67% yield) of IV as gray crystals, m.p. 138–139°. A pure sample was obtained by two recrystallizations from alcohol, m.p. 142–142.5°.

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.11; neut. equiv., 274.0. Found: C, 65.37; H, 4.82; neut. equiv., 271.7.

3-(2-Methoxy-4-methylphenyl)-5-keto-3-hexenoic acid (VII). A solution of 13.7 g. (0.05 mole) of IV in 250 ml. of 1*N* sodium hydroxide was kept at room temperature for 12 hr. and then heated on a steam bath for 0.5 hr. to effect complete hydrolysis. After the alkaline solution had been washed with several portions of ether, it was carefully neutralized with dilute hydrochloric acid at ice-bath temperature. The precipitated gummy substance was taken up in ether and the ethereal extracts, after having been washed with several portions of water, were concentrated. The residual gum solidified upon trituration with acetic acid. Recrystallization of the solid from acetic acid gave 5.7 g. (46% yield) of VII as colorless crystals, m.p. 102–104° dec.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.74; H, 6.45; neut. equiv., 248.0. Found: C, 67.90; H, 6.71; neut. equiv., 250.1.

A *semicarbazone* of VII was prepared in usual manner, m.p. 164–165.5°.

Anal. Calcd. for $C_{15}H_{19}N_3O_4$: neut. equiv., 305.0. Found: neut. equiv., 304.2.

A *phenylhydrazone* of VII was prepared by heating a solution of VII in glacial acetic acid with an equimolar quantity of phenylhydrazine on a steam bath for 15 min. The hydrazone was recrystallized from alcohol to give colorless plates, m.p. 182–183°.

Anal. Calcd. for $C_{20}H_{22}N_2O_3$: neut. equiv., 338.0. Found: neut. equiv., 340.0.

3-(2-Methoxy-4-methylphenyl)-5-keto-3-hexenoic acid lactone (V). *Method A.* A hard glass test tube containing 5 g. of IV was heated in an oil bath at 155–160° for 0.5 hr. After the evolution of carbon dioxide had subsided, the contents of the tube was thoroughly washed with 5% sodium bicarbonate solution. The solid residue was collected, washed with several portions of water, and after drying was recrystallized from alcohol to give 2.8 g. (68% yield) of V, m.p. 74–75°.

Method B. A mixture of 5 g. of IV and 10 ml. of concd. hydrochloric acid was heated at reflux temperature on a sand bath for 2 hr. The contents of the flask were poured into water and the solid was collected on a filter. It was washed with several portions of water, dilute sodium hydroxide solution and again with water. After drying, it was recrystallized from alcohol (60%) to give V in 53% yield, m.p. 74–75.5°. A mixed melting point of this sample with the one obtained by method A showed no depression.

Method C. A mixture of 5 g. of VII in 7.5 ml. of acetic anhydride was heated on a steam bath for 2 hr. The contents of the flask was poured into water with stirring and the resulting solid mass was processed as in method B, to give V in 58% yield, m.p. 73.5–74.5°.

Anal. Calcd. for $C_{14}H_{14}O_3$: C, 73.05; H, 6.09. Found: C, 73.21; H, 6.37.

3-(2-Methoxy-4-methylphenyl)glutaconylacetic acid (keto form) (VIII). A mixture of 10 g. of finely powdered enolic glutaconylacetic acid (IV) and 10 ml. of concd. sulfuric acid was heated cautiously at 80° for 2 min. The resulting red solution was filtered through a sintered glass funnel and the clear filtrate was slowly poured into 150 ml. of water. The gummy mass that separated was washed with several portions of water and then after drying, was triturated with acetic acid, affording a solid. It was recrystallized from acetic acid to give 6.2 g. (62% yield) of VIII, m.p. 218–220°.

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.11; neut. equiv., 274.0. Found: C, 65.82; H, 5.18; neut. equiv., 275.2.

Laboratory of Chemistry
Ramnarain Ruia College
University of Bombay
Bombay, India

---

(13) V. M. Bhave, M.S. thesis, University of Bombay, 1932.

(14) All melting points are uncorrected.

Bisarene-Chromium Compounds from Aryl Chlorides[1]

Richard W. Bush[2] and H. R. Snyder

Received January 26, 1960

Bisarene-chromium compounds of benzene, toluene, *p*-xylene, mesitylene, hexamethylbenzene, tetralin, and biphenyl have been prepared by the action of anhydrous chromic chloride upon the appropriate aromatic hydrocarbon in the presence of anhydrous aluminum chloride and powdered aluminum, the so-called reducing Friedel-Crafts conditions.[3] Only by the alternative synthesis, from arylmagnesium bromides, have bisarene-chromium compounds been prepared that contain substituents other than alkyl and aryl on the aromatic rings. By carbonating the mixture from the reac-

---

(1) Grateful acknowledgment is made of the partial support of this research by a grant from the National Science Foundation (G6223).

(2) National Science Foundation Fellow, 1956–1957. Phillips Petroleum Co. Fellow, 1957–1958.

(3) (a) E. O. Fischer and W. Hafner, *Z. anorg. u. allgem. Chem.*, **286**, 146 (1956); (b) E. O. Fischer and D. Seus, *Chem. Ber.*, **89**, 1809 (1956).