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α , β —UNSATURATED KETONES OBTAINED FROM ACETOPHENONE AND THEIR REACTION WITH PHENYLHYDRAZINE

L. CHAS. RAIFORD AND GLEN V. GUNDY

In an earlier paper¹ it was reported that when the bromine and chlorine substitution products of vanillin were condensed with acetophenone in the presence of sodium hydroxide, as indicated by Schmidt² and extended by Claisen and collaborators,³ both mono- and diacetophenone derivatives were obtained, regardless of the relative amounts of aldehyde and ketone used. It was clearly of interest to test this behavior when a substituent is present in the acetophenone used. These experiments have been repeated with various substituted acetophenones, and it may be stated at once that although several modifications of the method of condensation were tried⁴ no diacetophenone derivatives were obtained.

It was proposed also to use these monoacetophenone derivatives in a continuation of our studies⁵ on the rearrangement of the hydrazones of α , β —unsaturated ketones into the isomeric pyrazolines. Here it was desired particularly to test further Straus'⁶ claim that "when halogen or the nitro radical is present in either the ketone or the hydrazine residue of such hydrazones the closing of the pyrazoline ring occurs readily; but that when both are substituted with such groups the hydrazone is quite stable and energetic treatment is required to rearrange it."

In the present study the behavior of a number of the unsymmetrical ketones derived from substituted acetophenones toward phenylhydrazine and the p-nitro compound have been examined. The most suitable solvent in which to conduct the reaction is glacial acetic acid. In a few cases it was possible to bring about the reaction at room temperature, but in most instances it was necessary to heat the mixture. In those cases where both methods could be used they gave the same product which indicated that the latter

¹ Raiford and Gundy, *J. Am. Chem. Soc.*, 54, 1911 (1932).

² Schmidt, *Ber.*, 14, 1459 (1881).

³ Claisen and others, *Ann.*, 223, 137 (1884); *Ber.*, 20, 657 (1887).

⁴ Glaser and Triemer, [*J. prakt. chem.*, 116, 331 (1927)] used a mixture of glacial acetic and concentrated hydrochloric acids, while Rao, Srikantia and Iyengar [*Helv. chim. Acta.*, 12, 581 (1929)] used an acetic acid solution of ammonium acetate at the room temperature, and at the boiling point.

⁵ Raiford and Davis, *J. Am. Chem. Soc.*, 50, 156 (1928); Raiford and Entrikin, *ibid.*, 55, 1125 (1933); Raiford and Hill, *ibid.*, 56, 174 (1934).

⁶ Straus, *Ber.*, 51, 1458 (1918).

was a pyrazoline rather than a hydrazone.⁷ Thus, phenylhydrazine was added to an acetic acid solution of 5-bromovanillal-acetophenone, the liquid was divided into two portions, one was boiled for half an hour and the other was allowed to remain at room temperature for forty-eight hours. The same product crystallized from each mixture. This substance was also obtained when the reactants were dissolved in 70 per cent alcohol and the mixture allowed to stand, though the separation of crystals was much slower than when acetic acid was present.

The identity of the above product was further tested by attempts to reduce it by the method described by Tafel⁸ and used extensively by Auwers and Kreuder.⁹ They found that, in general, the phenylhydrazones of α , β —unsaturated ketones can be reduced to give aniline as one product. In the present work it has been found that hydrazones from this and other classes of ketones undergo the change indicated, but that pyrazolines do not. For example, when a boiling alcoholic solution of the hydrazone of benzalacetophenone was treated with sodium, 38 per cent of the required aniline¹⁰ was obtained and some of the hydrazone was recovered. Treated in the same way the phenylhydrazone of 5-bromovanillin gave 54 per cent¹¹ of the required aniline. On the other hand, when 1, 3, 5-triphenylpyrazoline was suspended in alcohol at 50-60° and treated with excess of sodium amalgam while the mixture was kept acid with acetic acid, 94 per cent of the pyrazoline was recovered. In a second experiment the method was modified to the extent that the liquor was stirred vigorously and a constant stream of carbon dioxide was passed in. The amount of starting material recovered was 90 per cent. In a third experiment where Schlenk's method¹² was employed, the pyrazoline recovered represented 92 per cent of the starting material.

With more highly substituted compounds the results were similar to the extent that no aniline was obtained. Thus with the pyrazolines obtained by action of 4-nitrophenylhydrazine on 5-bromo- and 6-bromovanillal-acetophenone, respectively, 86 per cent of starting material was recovered in each case. Treatment of certain compounds that contained bromine caused loss of halogen from a

⁷ The phenyl hydrazones of α , β —unsaturated ketones are usually rearranged to the isomeric pyrazolines by boiling acetic acid, but there are exceptions. Auwers and Voss [Ber., 42, 4418 (1909)] failed to rearrange the product obtained from cinnamic aldehyde and p-nitrophenylhydrazine, although the compound was shown by reduction to be a hydrazone.

⁸ Tafel, Ber., 22, 1854 (1889).

⁹ Auwers and Kreuder, Ber., 58, 1983 (1925).

¹⁰ This was found to be more suitable than Tafel's method.

¹¹ Raiford and Hilman, J. Am. Chem. Soc., 49, 1572 (1927).

¹² Schlenk, J. prakt. chem., [2] 78, 57 (1908).

portion of the material. When the pyrazoline obtained by the action of phenylhydrazine on benzal-4-bromoacetophenone was tested it gave 12 per cent of 1, 3, 5-triphenylpyrazoline and 72 per cent of the starting material, while that one obtained from 5-bromovanillal-4-bromoacetophenone gave 10 per cent of 1, 3-diphenyl-5-(3-methoxy-4-hydroxyphenyl)-pyrazoline and 63 per cent of starting material. This shows that the method used might not be suitable for the hydrazones if bromine is present as a substituent.

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