Friedel-Crafts Reaction of Ethylene with Benzoyl Chloride

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In a previous paper[1] a synthesis of 2-amino-1-phenyl-1,3-propanediol, starting with phenyl vinyl ketone, was described. In an attempt to prepare this latter compound by condensing ethylene and benzoyl chloride,[2] it was noticed that when an excess of aluminum chloride was employed, the desired ketone could hardly be obtained, and another ketone (I) was formed. The new ketone was a saturated compound containing chlorine, but was readily converted to an unsaturated ketone (II) on treatment with alkali. The conditions for the preparation and the structure of the unsaturated ketone were studied, and the compound has now been shown to be seneciophenone. The product (I), which could not be obtained in pure state, may consist mainly of β-chloro isovalerophenone, which would readily be converted to the unsaturated ketone by the well known α,β-elimination reaction of β-substituted carbonyl compounds. Treatment of ethylene in tetrachloroethane with benzoyl chloride and anhydrous aluminum chloride gave a chlorine containing oil (I) in 30–50% yield. Next, the relation between the amount of the catalyst and the yield of the reaction product was examined; the employment of 1.2 moles of the catalyst reduced the yield to 20–30%, and 2 moles afforded a polymeric substance as the main product. The product (I) changes rapidly into a purple, a green, and finally a dark brown. The 2,4-dinitrophenylhydrazone of I, which contains no chlorine, melted at 180–181°. Upon redistillation, the dark brown oil lost hydrogen chloride and converted into a stable substance (II), b.p. 102–104° (4 mm.), of pale yellow color. The stable ketone (II) can, however, more conveniently be obtained by distillation after the treatment of the reaction mixture with diluted aqueous alkali. The compound (II) readily consumed permanganate in acetone solution, contained no chlorine, and formed a 2,4-dinitrophenylhydrazone, $C_{17}H_{16}N_4O_4$, m.p. 180–181°, which was identical with the derivative prepared from the product (I). The elemental composition of the dinitrophenylhydrazone suggests that one mole of benzoyl chloride reacted with two moles of ethylene. The partial structure of the compound (II) may therefore be formulated as $C_6H_5COC_4H_7$. Hydrogenation of this ketone in the presence of palladium-on-charcoal resulted in the uptake of one mole of hydrogen and afforded a saturated ketone. The melting point of the 2,4-dinitrophenylhydrazone of the latter compound was in agreement with that of isovalerophenone,[3] and the identity of these two compounds was confirmed by mixed melting point determination. The presence of an isobutyl skeleton has thus been demonstrated. Since the dehydrochlorination occurs in general readily at the α,β-position of a β-chloro ketone, it may be reasonably considered that the double bond of the compound (II) is situated at α,β-position relative to the carbonyl group. This assumption is consistent with the fact that the same 2,4-dinitrophenylhydrazone is obtained from (I) and (II). Further evidences supporting this hypothesis were obtained by the ozonization experiment. Treatment of the compound (II) the ozone yielded as expected, acetone along with phenylglyoxylic acid. The unsaturated ketone is therefore almost certainly seneciophenone. The identity of these two substances was finally conclusively established by the synthesis of the latter compound and by the melting and mixed melting point determination of 2,4-dinitrophenylhydrazones and of dibromides from both origins.

II

The reaction seems quite interesting in that the isobutenyl group is introduced by one step with the action of C_2 olefin; similar instances, so far as the writers are aware, have not hitherto been reported.

EXPERIMENTAL[4]

Condensation of ethylene and benzoyl chloride in the presence of 1.5 moles aluminum chloride. A mixture of benzoyl chloride (20 g.) and powdered anhydrous aluminum chloride (28 g.) was carefully heated in a reaction vessel and after cooling, 80 cc. of dry tetrachloroethane was added to dissolve the mixture. Dry ethylene was then passed into the solution for 20 hr. at 0–5° with vigorous stirring. The reaction mixture was poured on ice containing hydrochloric acid; the product was taken up in ether and the extract was dried over calcium chloride. After removal of the solvent the residue was distilled *in vacuo* and a pale yellow oil (I) boiling at 120° (4 mm.) was collected. From ethanol 2,4-dinitrophenylhydrazone was crystallized in reddish orange needles, m.p. 180–181°. The product (I) changed rapidly into a dark brown viscous oil by way of purple and green. Redistillation of the dark brown oil gave a stable, pale yellow oil (II), b.p. 102–104° (4 mm.), which readily consumed potassium permanganate in acetone solution.

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(1) T. Matsumoto and K. Hata, *J. Am. Chem. Soc.*, **79**, 5506 (1957).

(2) J. F. Norris and H. B. Couch, *J. Am. Chem. Soc.*, **42**, 2329 (1920).

(3) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2012 (1950). A melting point 123–124° is recorded for *n*-valerophenone 2,4-dinitrophenylhydrazone [H. A. Fahim and A. Mustafa, *J. Chem. Soc.*, 519 (1949)]. A synthetic sample prepared in this Laboratory however melted at 163–164°.

(4) Melting points are uncorrected.

When the ethereal extract of the reaction mixture was thoroughly washed with 2*N* aqueous sodium hydroxide before being dried and evaporated, distillation gave directly product II, (7–12.5 g.; 30–50% yield). The 2,4-dinitrophenylhydrazone obtained from II was crystallized from ethanol in reddish orange needles and melted at 180–181°.

Anal. Calcd. for $C_{17}H_{16}O_4N_4$: C, 59.99; H, 4.74; N, 16.46. Found: C, 59.87; H, 4.89; N, 16.45.

A mixture of the 2,4-dinitrophenylhydrazone from I and II had m.p. 180–181°. Semicarbazone and phenylhydrazone could not be obtained under the usual conditions.

With an excess of aluminum chloride (1.2 moles). A mixture of benzoyl chloride (11.5 g.) and powdered aluminum chloride (13.1 g.) was prepared and the reaction was run for 11 hr. as described before. The product, worked up as in the foregoing section, gave the compound (II) (2.5 g.; 20% yield) and phenyl vinyl ketone (5.1 g.), characterized as 1,3-diphenylpyrazoline.[1]

Condensation with 2 moles of aluminum chloride. The reaction was effected in just the same way as described above, by the use of 2 moles of aluminum chloride. Working up of the reaction mixture gave a resinous product which could hardly be distilled.

Catalytic hydrogenation of (II). Hydrogenation of the compound II (1.8 g.) in ethyl acetate (20 cc.) was carried out in the presence of 10% palladized charcoal (0.2 g.); one equivalent of hydrogen (182 cc.) was absorbed after shaking for 18 min. The solution was then filtered from the catalyst, evaporated under reduced pressure and distilled to afford 0.8 g. (81%) of phenyl isobutyl ketone, which was characterized by the 2,4-dinitrophenylhydrazone, m.p. 131.5–132°, undepressed on admixture with a synthetic sample.[5]

Ozonolysis. A solution of (II) (1.5 g.) in ethyl acetate (20 cc.) was treated with ozone at −15°. After the reaction was completed, water was added to the solution to extract any soluble substance formed, and the aqueous layer was then distilled. Volatile component was collected in a flask containing alcohol. On treatment of the alcoholic solution with 2,4-dinitrophenylhydrazine, yellow precipitates were obtained. Recrystallization from alcohol gave yellowish orange needles, melting at 128°, which showed no depression in melting point on admixture with 2,4-dinitrophenylhydrazone of acetone. After removal of the volatile fraction, the aqueous solution was extracted with ether. Evaporation of ether left phenylglyoxylic acid, m.p. 66°.

Identification of (II) with seneciophenone. Seneciophenone was prepared by the condensation of benzene and 3,3-dimethylacryloyl chloride according to Smith and Engelhart.[6] 2,4-Dinitrophenylhydrazone had melting and mixed melting point 180–181°.[7] A solution of (II) in chloroform was cooled in an ice bath and the theoretical amount of bromine was added. Evaporation of the resultant mixture under reduced pressure left a white solid, which was recrystallized from methanol in white needles, m.p. 78–79°.

Anal. Calcd. for $C_{11}H_{12}Br_2O$: C, 41.28; H, 3.78. Found: C, 40.97; H, 3.79.

No depression in melting point was observed on admixture of the dibromide with dibromoseneciophenone.[6]

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[5] Authentic sample of phenyl isobutyl ketone was prepared according to G. Schroeter, *Ber.*, **40**, 1601 (1907).

[6] L. I. Smith and V. A. Engelhart, *J. Am. Chem. Soc.*, **71**, 2671 (1949).

[7] E. A. Braude and J. A. Coles reported the m.p. 185–186° in ref. 3.

Derivatives of Ferrocene. IV. Ferrocene-Containing Unsaturated Ketones[1]

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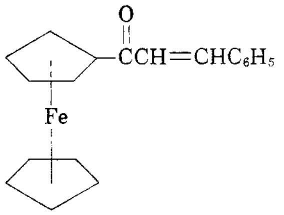
We wish to report the synthesis of a ferrocene analog of chalcone, cinnamoylferrocene (I), and the attempted preparation of both ferrocenyl vinyl ketone and ferrocenyl isopropenyl ketone. These ketones were desired as part of a program designed to study vinyl polymers containing the ferrocene unit, vinylferrocene[2] being the only other ferrocene-containing vinyl monomer thus far described in the literature.



I

Cinnamoylferrocene was prepared in 81.5% yield by the Friedel-Crafts reaction of equimolar quantities of ferrocene, *trans*-cinnamoyl chloride and aluminum chloride in methylene chloride solution. Ketone I was also prepared in 47% yield by the Claisen-Schmidt condensation of acetylferrocene, benzaldehyde, and sodium hydroxide in aqueous ethanolic solution. The Friedel-Crafts procedure is to be preferred in view of the excellent yields obtained, the simplicity of the preparation, and the purity of the product.

Catalytic hydrogenation of I in the presence of platinum on charcoal produced the saturated ferrocenyl ketone, β-phenylpropionylferrocene. Ketone I also reacted readily with hydroxylamine in ethanolic potassium hydroxide solution to form a derivative, cinnamoylferrocene oxime.

In an attempt to prepare ferrocenyl vinyl ketone by a method similar to that for the preparation of phenyl vinyl ketone,[3] acetylferrocene, paraformaldehyde, and dimethylamine hydrochloride were reacted in absolute ethanol to produce a 68% yield, based on recovered acetylferrocene, of β-dimethylaminopropionyl ferrocene hydrochloride. Pyrolysis of this hydrochloride by steam distillation did not produce any of the desired product, however, and only a brown polymeric residue was isolated, even in the presence of a polymerization inhibitor such as hydroquinone.

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[1] For paper III of this series, see M. Vogel, M. D. Rausch, and H. Rosenberg, *J. Org. Chem.*, **22**, 1016 (1957).

[2] R. S. Arimoto and A. C. Haven, *J. Am. Chem. Soc.*, **77**, 6295 (1957).

[3] C. Mannich and G. Heilner, *Ber.*, **55**, 356 (1922).