The picrate was prepared in and recrystallized from 95% ethanol, m. p. 194–195° (cor.).

Anal. Calcd. for $C_{18}H_{16}N_4O_7$: C, 54.00; H, 4.03; N, 14.00. Found: C, 54.15; H, 4.17; N, 13.97.

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The Addition of Malonic Esters to an Acetylenic Ketone

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Recent communications from this Laboratory described some of the reactions of *o*-chlorophenylbenzoylacetylene.[1,2,3,4] The present report further defines the behavior of this unsaturated ketone, outlining the addition of malonic esters and the nature of some of the cyclic products formed from the primary addition compounds.

The addition of malonic ester to phenylbenzoylacetylene was carefully studied by Kohler[5] and the addition of malonic ester to phenyl-*p*-nitrobenzoylacetylene and to phenyl-*p*-methylbenzoylacetylene was used by Barat[6] as a method of identifying these acetylenic ketones.

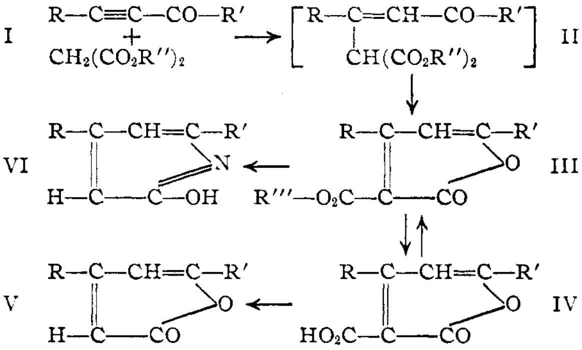
The behavior of *o*-chlorophenylbenzoylacetylene (I) closely parallels that of the unsubstituted analog,[5] the first isolable substance being the cyclized product III, an α-pyrone, formed by the loss of a molecule of alcohol by the primary addition product II. The formation of these pyrone esters constitutes a very interesting example of rapid ester interchange, the alcohol used as the solvent determining the alkyl group of the carboxylate, regardless of the particular malonic ester used. For example, the use of ethyl malonate and methanol gives the methyl ester of the pyrone acid while the use of methyl malonate and butanol gives the butyl ester of the pyrone acid. Moreover, one pyrone ester is converted into another by the action of the appropriate alcohol in the presence of a trace of sodium alcoholate.

Kohler[5] was unable to obtain the pyrone acid corresponding to IV by a simple basic hydrolysis of the pyrone esters, deep-seated decompositions destroying the bulk of the pyrone structure. The method which he finally employed was time-consuming, laborious and gave at best a 70% yield of the acid. In the present study, two simple methods have been developed which give good yields of the pyrone acid IV. Basic hydrolysis, using acetone as the solvent and one equivalent of aqueous sodium hydroxide, converts the esters quantitatively into the acid while acidic hydrolysis, using acetic acid as the solvent and aqueous sulfuric acid, converts the esters into a mixture of the acid and the pyrone V, the extent of decarboxylation of the acid increasing with time. There is no indication that Kohler tried either of these methods. The identity of the acid IV is certain since it is converted quantitatively into the esters from which it is formed either by the use of silver oxide and the appropriate alkyl halide or by the use of sulfuric acid and the appropriate alcohol.

The pyrone V is best prepared by refluxing a solution of the pyrone acid in acetic acid and aqueous sulfuric acid, the conversion being essentially complete. The action of an excess of sodium alcoholate on the pyrone esters, the chemical method of Kohler, gives a large amount of oily products and a low yield of the pyrone.

The *o*-chloropyrone esters, like the unsubstituted compounds, are readily converted into pyridine derivatives by the action of an alcoholic solution of ammonia.

The above reactions are summarized in structural form below, where R represents the *o*-chlorophenyl group, R′ the phenyl group, R″ the alkyl group of the malonic ester and R‴ the alkyl group of the alcohol used as the solvent.



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Experimental

The *o*-chlorophenylbenzoylacetylene was prepared as described previously[1]; the methyl and ethyl malonates were Eastman Kodak Co. products.

The Pyrone Esters, III.—The pyrone esters were prepared by malonic ester synthesis, by interconversion, and also by the esterification of the pyrone acid IV. In the following three paragraphs, each of these methods is illustrated by a general procedure and the particular reactions studied are indicated.

A small amount of an alcoholic solution of sodium alcoholate (the alcohol being the same as that used for the solution of the acetylenic ketone) was added to a warm solution of 5 g. of the acetylenic ketone and a slight excess of malonic ester in 50 ml. of alcohol. After cooling to room temperature, the solution was acidified with glacial acetic acid, the red color of the solution fading to a pale yellow. The solution was then diluted with water to the point of turbidity and left in the refrigerator overnight. The solid product was filtered, washed with water, allowed to dry and finally recrystallized from acetone or ether. The methylpyrone ester was prepared by using methanol and either methyl malonate or ethyl malonate, the ethyl ester by using 95% ethanol and *either* malonic ester, the propyl ester by using propanol-1 and *either* malonic ester, and the

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(1) Bickel, THIS JOURNAL, **69**, 73, 2134 (1947).

(2) Bickel, *ibid.*, **70**, 763 (1948).

(3) Bickel, *ibid.*, **71**, 336 (1949).

(4) Bickel and Fabens, *ibid.*, **71**, 1450 (1949).

(5) Kohler, *ibid.*, **44**, 379 (1922).

(6) Barat, *J. Indian Chem. Soc.*, **7**, 851 (1930).

butyl ester by using butanol-1 and *either* malonic ester. In the case of the reactions using butanol, the solution was concentrated by a current of air after acidification, the butyl ester then being taken up in ether and handled in the usual way. The yields of esters ranged from 70 to 85%.

A warm alcohol solution of one of the pyrone esters was treated with a trace of sodium alcoholate, allowed to cool to room temperature, acidified with glacial acetic acid and then worked up as in the preceding paragraph. Each of the pyrone esters was converted into each of the other esters by this method. No other products were detected.

The pyrone acid IV was esterified either by refluxing an anhydrous ether solution with an excess of silver oxide and an excess of alkyl iodide or by refluxing an alcoholic solution with concentrated sulfuric acid, the ester products being isolated in the usual way. Each of the four esters was obtained as the sole product, except for traces of recovered pyrone acid when the Fischer method was used.

Methyl 4-(*o*-chlorophenyl)-6-phenyl-2-pyrone-3-carboxylate is fairly soluble in acetone, sparingly soluble in methanol and ether, and insoluble in petroleum ether. It crystallizes as pale yellow stout plates and melts at 121–122°.

Anal. Calcd. for $C_{19}H_{13}O_4Cl$: C, 67.0; H, 3.85. Found: C, 66.9; H, 3.88.

Ethyl 4-(*o*-chlorophenyl)-6-phenyl-2-pyrone-3-carboxylate is very soluble in acetone, soluble in ethanol, sparingly soluble in ether and insoluble in petroleum ether. It crystallizes as very pale yellow thin plates and melts at 133–134°.

Anal. Calcd. for $C_{20}H_{15}O_4Cl$: C, 67.6; H, 4.26. Found: C, 67.9; H, 4.35.

Propyl 4-(*o*-chlorophenyl)-6-phenyl-2-pyrone-3-carboxylate is very soluble in acetone, soluble in propanol and ether, and sparingly soluble in petroleum ether. It crystallizes as very pale yellow long thin plates and melts at 101°.

Anal. Calcd. for $C_{21}H_{17}O_4Cl$: C, 68.4; H, 4.65. Found: C, 68.4; H, 4.90.

Butyl 4-(*o*-chlorophenyl)-6-phenyl-2-pyrone-3-carboxylate is very soluble in acetone, butanol and ether, and sparingly soluble in petroleum ether. It crystallizes as very pale yellow long thin plates and melts at 62°.

Anal. Calcd. for $C_{22}H_{19}O_4Cl$: C, 68.9; H, 5.01. Found: C, 69.0; H, 5.13.

The Pyrone Acid, IV.—The next two paragraphs indicate the formation of the pyrone acid by basic hydrolysis and by acidic hydrolysis of the pyrone esters.

One equivalent of 0.2 normal aqueous sodium hydroxide (73.5 ml.) was added over a period of thirty minutes to a warm solution of 5.00 g. of the methyl pyrone ester in 100 ml. of alcohol-free acetone. After standing for one hour, the yellow solution was diluted with about 200 ml. of water and extracted with ether. The ether solution, twice extracted with sodium bicarbonate solution, gave 0.46 g. of unchanged methylpyrone ester. The combined aqueous solution, acidified with hydrochloric acid, gave a precipitate of the pyrone acid which was filtered, washed with water, allowed to dry and finally crystallized from ether. The weight of pyrone acid was 4.25 g., a 98% yield based on the ester consumed. In another run, one normal sodium hydroxide was used and the time of standing before extraction was increased to five hours. The amount of recovered ester was 0.75 g. and the weight of pyrone acid was 3.91 g., indicating that the more dilute base gives the better result.

A mixture of 4.95 g. of the methylpyrone ester, 50 ml. of glacial acetic acid and 50 ml.of six normal sulfuric acid was refluxed for one and one-half hours, cooled, diluted with water and extracted with ether. The ether solution was washed with water and then extracted with sodium bicarbonate solution. The extracted ether solution gave 1.20 g. of the pyrone V; the sodium bicarbonate extract gave 3.30 g. of the pyrone acid IV, a 70% yield of acid based on the methyl ester used. In another run, an increase of the refluxing period to four hours gave more of the pyrone, 2.70 g., at the expense of the acid produced, 1.50 g.

Hydrolysis of the pyrone esters by an excess of base resulted in a much lower yield of the pyrone acid and of the pyrone. The bulk of the material was converted into an oily mixture which has resisted identification.

4-(*o*-Chlorophenyl)-6-phenyl-2-pyrone-3-carboxylic acid is soluble in acetone, insoluble in petroleum ether and moderately soluble in ether. It dissolves with difficulty in ether but forms supersaturated solutions from which it precipitates when seeded or scratched. The acid crystallizes from ether as clusters of small stout sulfur-yellow plates and melts at about 178–180° with decomposition.

Anal. Calcd. for $C_{18}H_{11}O_4Cl$: C, 66.1; H, 3.40. Found: C, 66.0; H, 3.28.

The Pyrone, V.—The best method of preparing the pyrone appears to be the one described in the preceding section, namely, the acidic hydrolysis of the pyrone esters and the subsequent decarboxylation of the acid formed. One may start either with the pyrone ester or the pyrone acid. For example, 5.0 g. of the recrystallized pyrone was obtained when 6.0 g. of the pyrone acid was refluxed for eleven hours with 60 ml. of glacial acetic acid and 60 ml. of six normal sulfuric acid, a 95% conversion into the pyrone.

The action of an excess of alcoholic sodium hydroxide or alcoholic sodium alcoholate on the pyrone esters or the pyrone acid gave a mixture of products, the best yield of the pyrone obtained in this way being about 50%.

4-(*o*-Chlorophenyl)-6-phenyl-2-pyrone is soluble in glacial acetic acid, moderately soluble in acetone and methanol, sparingly soluble in ether and insoluble in petroleum ether. It crystallizes as long colorless needles, resembling fine glass wool, and melts at 141°.

Anal. Calcd. for $C_{17}H_{11}O_2Cl$: C, 72.2; H, 3.93. Found: C, 72.1; H, 4.04.

The Hydroxy Pyridine, VI.—Five grams of the methylpyrone ester was added to 30 ml. of methanol saturated with ammonia gas. The ester dissolved completely in one and one-half hours, giving a yellow solution from which colorless crystals began to separate in another hour. After standing overnight, the solid was filtered and washed with methanol, the yield of product being 2.5 g.

2-Hydroxy-4-(*o*-chlorophenyl)-6-phenylpyridine is very sparingly soluble in the common solvents, crystallizes as long thin colorless plates and melts at 232°.

Anal. Calcd. for $C_{17}H_{12}ONCl$: C, 72.6; H, 4.30. Found: C, 72.6; H, 4.50.

The filtrate from the above hydroxypyridine was evaporated in a current of air, giving an oily mixture from which only one pure substance could be obtained. This substance was β-methoxy-2-chlorochalcone,[1,3,7] identified by a mixed melting point with a known sample. The formation of this compound can be logically explained only by assuming that *o*-chlorophenylbenzoylacetylene was formed by a cleavage of the pyrone ring and that methanol then added to the acetylene.

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[7] Bickel, THIS JOURNAL, 68, 865 (1946).

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Action of Organometallic Compounds on Geoisomeric Styrenes

BY J. C. BOND AND GEORGE F WRIGHT

The reaction of an excess of phenyllithium or phenylmagnesium bromide with either *cis*- or *trans*-styryl cyanide[1] gives β,β-diphenylpropiophenone and the known isomer of benzalacetophenone. A mixture of the geoisomers of styryl

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[1] Ghosez, *Bull. soc. chim. Belg.*, 41, 477 (1932).