acid and 0.43 g. (0.004 mole) of phenylhydrazine. The pyrazole was isolated in the usual way,[1,2] m.p. 128–129°, wt. 0.81 g. (67% yield). This product was identical with an authentic sample of 1-phenyl-3-(*p*-biphenylyl)-5-methylpyrazole.[1]

trans-**1,2-Dimethyl-3-(*p*-phenylbenzoyl)-ethylenimine (Vb).**—An 8.0 g. (0.036 mole) sample of *p*-phenylcrotonophenone in 40 ml. of benzene was treated with an ether solution of methylamine (0.144 mole) using ice-bath cooling. To this solution was added 9.26 g. (0.036 mole) of iodine dissolved in 120 ml. of benzene. The iodine color disappeared completely in 1 hr. The benzene layer was separated from the oily methylamine hydroiodide, washed with water, dried and evaporated to leave a red colored oil. This crude product was crystallized from petroleum ether (b.p. 40–50°) to give 7.0 g. of a nearly colorless product, m.p. 65–67°.

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.01; H, 6.93; N, 5.43.

This product decomposed in the air at room temperature to a red oil in a few hours.

cis- and *trans*-**1-Cyclohexyl-2-methyl-3-(*p*-phenylbenzoyl)-ethylenimines, VIa and VIb. A. Reaction of α-Bromo-*p*-phenylcrotonophenone with Cyclohexylamine.**—To a solution of 6.0 g. (0.020 mole) of α-bromo-*p*-phenyl-crotonophenone (II) in 50 ml. of dry benzene was added 4.5 g. (0.044 mole) of cyclohexylamine. The reaction mixture was stirred for 3 hr. and allowed to stand 12 hr. in the ice-chest. The reaction mixture was worked up and the crude product separated by a chromatographic method as previously described for the reaction using the analogous α,β-dibromo-*p*-phenylbutyrophenone.[1] The yield of crude, mixed product was 6.1 g. (95%), m.p. 110–118°. The first eluates from the chromatographic separation of a 3.0-g. sample of the mixed product produced 0.98 g. (34% of the total material recovered) of the *trans* isomer VIb, m.p. 141–142°. The final eluates contained the low melting, *cis* isomer VIa, m.p. 127–128°, wt. 1.8 g. (62% of the total material recovered). Both products were nearly colorless.

B. Reaction of *p*-Phenylcrotonophenone with Bromine and Cyclohexylamine.—A 5-g. (0.0225 mole) sample of the unsaturated ketone[1] was dissolved in 12 ml. of benzene and 9 g. (0.091 mole) of cyclohexylamine. The solution was cooled and 3.6 g. (0.0225 mole) of bromine in 50 ml. of benzene was added over a period of 20 minutes with stirring. The nearly colorless reaction mixture, after standing at room temperature for 12 hr., was filtered to remove 8.1 g. (0.045 mole) of cyclohexylamine hydrobromide. The filtrate was washed with water, dried and concentrated under reduced pressure to give 6.25 g. (0.0195 mole) of a colorless crystalline product, m.p. 112–124°. A chromatographic separation of 2 g. of this material produced 0.51 g. of a mixed product, m.p. 110–121°, in the first eluate and 1.47 g. of the pure *cis* isomer, m.p. 127–129°, in later eluates.

C. Reaction of *p*-Phenylcrotonophenone with Cyclohexylamine and N-Bromocyclohexylamine.—A 4.4-g. (0.02 mole) sample of the unsaturated ketone was dissolved in 10 ml. of benzene and 1.98 g. (0.02 mole) of cyclohexylamine. After standing for 30 minutes, 25 ml. of a benzene solution containing about 3.56 g. (0.02 mole) of N-bromocyclohexylamine[13] was added rapidly. After standing at room temperature for 14 hr., the cyclohexylamine hydrobromide, 3.4 g. (0.0189 mole), was removed and the filtrate worked up to give 6.35 g. (99% yield) of solid material, m.p. 114–122°. One recrystallization from petroleum ether (b.p. 60–70°) gave 6.3 g. of colorless crystalline solid, m.p. 120–128°. A 1.0-g. sample of this material was chromatographed to give as a first eluate 0.25 g. of a mixed product, m.p. 109–120°, and in later eluates 0.74 g. of the pure *cis* isomer, m.p. 128–129°.

D. Reaction of β-Cyclohexylamino-*p*-phenylbutyrophenone with N-Bromocyclohexylamine. The β-cyclohexylamino-*p*-phenylbutyrophenone was prepared from 2.2 g. of *p*-phenylcrotonophenone and 1.0 g. of cyclohexylamine in 8 ml. of abs. ethanol upon standing in the refrigerator fo three days. The yield was 2.9 g., m.p. 84.5–85.5°.

Anal. Calcd. for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36. Found: C, 82.43; H, 8.61; N, 4.34.

A 1.6-g. (0.005 mole) sample of the β-aminoketone was dissolved without heating in 5 ml. of benzene and a solution of 0.89 g. (0.005 mole) of N-bromocyclohexylamine[13] in 15 ml. of benzene was added rapidly. After standing at room temperature for 12 hr. the working up of the reaction mixture produced 0.87 g. (97% yield) of cyclohexylamine hydrobromide and 1.33 g. (85% yield) of the pure *cis* isomer, m.p. 127–128°.

An attempt to add one molar equivalent of N-bromocyclohexylamine[13] to 2.22 g. of *p*-phenylcrotonophenone in benzene solution produced only small amounts of cyclohexylamine hydrobromide and 2.0 g. of unchanged unsaturated ketone.

Chromatographic Separation of *cis*- and *trans*-1-Cyclohexyl-2-phenyl-3-(*p*-phenylbenzoyl)-ethylenimines.—A 0.50-g. sample of a 50–50 mixture of the *cis* and *trans* isomers which had been separated previously by fractional crystallization[2] was re-separated by the chromatographic method.[1] The first eluates contained 0.24 g. (50% of the total material recovered) of the low melting *trans* isomer, m.p. 118–119°, while the final eluates produced the same amount of the higher-melting *cis* form, m.p. 144–146°. Both of these products were colorless.

(13) Using the procedure outlined for N-bromomorpholine, see ref. 7a, benzene solutions of N-bromocyclohexylamine were freshly prepared from one equiv. of bromine and two equiv. of cyclohexylamine and used immediately after removing the cyclohexylamine hydrobromide by filtration.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORY OF THE INDIAN INSTITUTE OF SCIENCE, BANGALORE]

Hydrolysis of Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-2-pentenoate and Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-valerate

BY D. K. BANERJEE AND T. R. KASTURI

RECEIVED SEPTEMBER 5, 1956

Hydrolysis of ethyl 4-(1-carbethoxy-2-oxocyclopentyl)-2-pentenoate (Ia) and ethyl 4-(1-carbethoxy-2-oxocyclopentyl)-valerate (Ib) with 10% sulfuric acid yielded the normal products Ic and Id, respectively. Treatment of Ia with hydrochloric acid yielded a mixture of II, a rearrangement product, and Ic.

In the course of a synthetic project currently in progress in our laboratory, the introduction of the bile acid side chain was contemplated by the condensation of a cyclopentanone-2-carboxylic ester derivative with ethyl 4-bromo-2-pentenoate followed by hydrolysis and reduction. Recently Herz[1] has shown that such condensation products, after reduction, on hydrolysis with hydrochloric acid yield rearranged products. We have now reinvestigated this step and it has been possible to obtain the desired normal hydrolysis product in good yield by using 10% sulfuric acid.

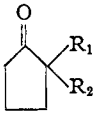
At first the hydrolysis of ethyl 4-(1-carbethoxy-2-oxocyclopentyl)-2-pentenoate(Ia)[1a] under the condition of Herz[2] was studied, as in this case

(1) (a) W. Herz, THIS JOURNAL, **78**, 1485 (1956); (b) **78**, 2529 (1956).

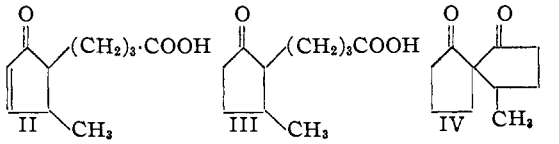
(2) These experiments were completed before the appearance of the second paper[1b] of Herz, where he has expressed the intention of studying the hydrolysis of Ia.

a similar rearrangement should lead to the formation of a cyclopentenone derivative easily detectable by the ultraviolet absorption spectrum. However, the treatment of Ia with hydrochloric acid yielded a mixture which could be resolved by chromatography on an acid-washed alumina column into two components. One of these has been assigned the structure of 4-(5-methyl-2-oxocyclopent-3-enyl)-butyric acid (II), a rearrangement product, for the following reasons: (1) its ultraviolet spectrum had absorption maximum characteristic of α,β-unsaturated ketone, (2) it yielded a semicarbazone and a red 2,4-dinitrophenylhydrazone which also had absorption maxima typical of α,β-unsaturated ketonic derivatives, (3) on catalytic hydrogenation it yielded a product identical with 4-(5-methyl-2-oxocyclopentyl)-butyric acid (III) previously obtained by Herz[1a] as a rearrangement product by the hydrolysis of ethyl 4-(1-carbethoxy-2-oxocyclopentyl)-valerate (Ib). The second product yielded a semicarbazone and a yellow 2,4-dinitrophenylhydrazone which showed absorption maxima characteristic of those of a saturated ketone, and on ozonolysis furnished 2-(2-oxocyclopentyl)-propionic acid (Ie). This has been assigned the structure of 4-(2-oxocyclopentyl)-2-pentenoic acid (Ic), the normal product of hydrolysis. When Ia was hydrolyzed with 10% sulfuric acid, only Ic could be isolated in 93% yield.

Hydrolysis of the hydrogenated keto ester Ib with 10% sulfuric acid also gave the corresponding normal product Id, as proved by its identity with 4-(2-oxocyclopentyl)-valeric acid obtained by the hydrogenation of Ic, and was found to be different from the rearranged keto acid III.

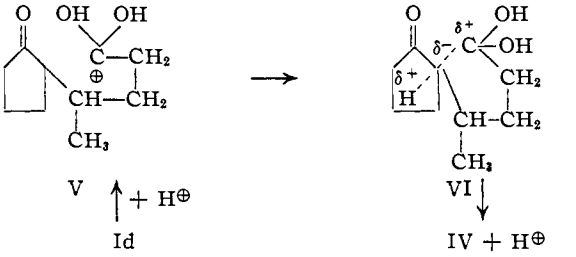


	R_1	R_2
Ia,	$-COOC_2H_5$	$-CH(CH_3)CH{=}CHCOOC_2H_5$
Ib,	$-COOC_2H_5$	$-CH(CH_3)CH_2CH_2COOC_2H_5$
Ic,	$-H$	$-CH(CH_3)CH{=}CH-COOH$
Id,	$-H$	$-CH(CH_3)CH_2CH_2COOH$
Ie,	$-H$	$-CH(CH_3)COOH$
If,	$-COOH$	$-CH(CH_3)CH_2CH_2-COOH$



To explain the rearrangement, Herz[1a] assumed the formation of a diketone IV *via* the normal keto acid Id. We considered that IV might have been formed *via* the keto diacid If. The normal keto acid Id, however, on treatment with hydrochloric acid yielded the rearranged product III, thus proving the correctness of Herz's suggestion regarding the intermediate product.

For this rearrangement,[3] we suggest that the β-diketone IV[1a] is formed through a transition state VI and elimination of proton, which may be visualized through an electrophilic attack of the dioxycarbonium ion V, formed from the carboxylic group of the keto acid Id in the presence of hydrogen ion, on the ketomethine carbon atom. Presumably a lower hydrogen ion concentration leads to the formation of mainly the normal product.



Experimental[4]

Ethyl 4-(1-Carbethoxy-2-oxocyclopentyl)-2-pentenoate[1a] (Ia).—In our hands alkylation of 2-carbethoxycyclopentanone with ethyl 4-bromo-2-pentenoate ($n^{22}D$ 1.4850) gave a higher yield (77%, reported[1a] 60%) of the condensation product Ia, b.p. 155–156° (1 mm.), $n^{23}D$ 1.4780.

Hydrolysis of Ia.—(a) A mixture of 10 g. of Ia and 40 ml. of concentrated hydrochloric acid was refluxed for 15 hr. and 5.5 g. of a product, b.p. 160–165° (1 mm.), $n^{24}D$ 1.4994, was isolated through its sodium salt as described by Herz for the hydrolysis of Ib.[1a]

The semicarbazone, m.p. 184–185°, ultraviolet spectrum $\lambda_{max}^{alcohol}$ 230 mμ (log ε 4.01), 261 mμ (log ε 4.02), prepared by the sodium acetate method, is obviously a mixture of the semicarbazones of II and Ic, as evident from ultraviolet data.

Anal. Calcd. for $C_{10}H_{17}N_3O_3$: N, 17.57. Found: N, 17.4.

The crude **2,4-dinitrophenylhydrazone** prepared by usual methods melted at 100–110° and was a mixture of yellow and red crystals. The yellow solid (0.1 g.) was separated from 0.25 g. of this mixture by trituration with dry benzene. After repeated crystallization from ethanol it was obtained as clusters of needles, m.p. 194–196°; ultraviolet spectrum $\lambda_{max}^{alcohol}$ 229 mμ (log ε 4.11), 364 mμ (log ε 4.31).

Anal. Calcd. for $C_{16}H_{18}N_4O_6$: N, 15.47. Found: N, 15.19.

The aforementioned benzene filtrate was passed through a column of 10 g. of acid-washed alumina,[5] which on evaporation yielded 0.11 g. of the red **2,4-dinitrophenylhydrazone** which crystallized in red silky needles from ethanol, m.p. 131–132°; ultraviolet spectrum $\lambda_{max}^{alcohol}$ 256 mμ (log ε 4.23), 387 mμ (log ε 4.4).

Anal. Calcd. for $C_{16}H_{18}N_4O_6$: N, 15.47. Found: N, 15.38.

The column was further eluted with ethyl acetate when a small quantity of the yellow **2,4-dinitrophenylhydrazone**, m.p. 194–196°, was obtained.

A solution of 1 g. of the aforementioned acid mixture, obtained by hydrolysis of Ia, in 10 ml. of benzene was chromatographed over a column of 30 g. of acid-washed alumina. Elution with benzene gave 0.5 g. of **4-(2-oxocyclopentyl)-pentenoic acid (Ic)**, which showed no absorption maximum characteristic of conjugated ketones and gave only the aforementioned yellow 2,4-dinitrophenylhydrazone, m.p. 194–196°.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.93; H, 7.69. Found: C, 65.42; H, 7.89.

Further elution with ether yielded, after initial separation of a small quantity of the acid mixture, 0.4 g. of **4-(5-methyl-2-oxocyclopent-3-enyl)-butyric acid (II)** whose ultraviolet spectrum had $\lambda_{max}^{alcohol}$ 235 mμ, and gave the afore-

(3) An alternative mechanism for this type of rearrangement was previously suggested by F. Ramirez and A. P. Paul, THIS JOURNAL, **77**, 1035 (1955), on the basis of the mechanism proposed by M. J. S. Dewar ("The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 126) for acid-catalyzed Claisen condensation proceeding through the enol. The present mechanism may also be extended to explain the acid-catalyzed Claisen condensation through an oxycarbonium ion.

(4) All melting points and boiling points are uncorrected and ranges of temperature less than one degree have not been recorded.

(5) We are indebted to Merck and Co. Inc., Rahway, N. J., for a gift of acid-washed alumina, 9R8094.

mentioned red 2,4-dinitrophenylhydrazone, m.p. 130–132°.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.93; H, 7.69. Found: C, 65.52; H, 7.86.

The semicarbazone crystallized in shiny needles from ethanol, m.p. 208–210°, ultraviolet spectrum $\lambda_{max}^{alcohol}$ 266 mμ (log ε 4.17).

Anal. Calcd. for $C_{11}H_{17}N_3O_3$: N, 17.57. Found: N, 17.32.

(b) A mixture of 10 g. of Ia and 150 ml. of 10% sulfuric acid was refluxed for 36 hr. On working up in the usual way, 6 g. (93%) of Ic, b.p. 158–160° (1 mm.), $n^{28}D$ 1.4985, was isolated.

The yellow 2,4-dinitrophenylhydrazone melted at 194–196° and remained undepressed on admixture with the previously described yellow 2,4-dinitrophenylhydrazone.

The semicarbazone crystallized in plates from ethanol, m.p. 185–186°, ultraviolet spectrum $\lambda_{max}^{alcohol}$ 227 mμ (log ε 4.3).

Anal. Calcd. for $C_{11}H_{17}N_3O_3$: N, 17.57. Found: N, 17.31.

4-(5-Methyl-2-oxocyclopentyl)-butyric Acid (III).—A solution of 80 mg. of 4-(5-methyl-2-oxocyclopent-3-enyl)-butyric acid (II) in 10 ml. of ethanol was hydrogenated in the presence of 15 mg. of platinum oxide catalyst. The theoretical amount of hydrogen was absorbed in 3 hr. The product was worked up in the usual manner to yield 70 mg. of III, b.p. 110–115° (bath temperature) (1 mm.).

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.22; H, 8.70. Found: C, 64.76; H, 8.70.

The semicarbazone, m.p. 195–196°, did not depress the melting point (195–196°) of the semicarbazone of III prepared according to Herz.[1a] In this connection it may be mentioned that the crude semicarbazone of Herz's hydrolysis product melted at 160–170°.

4-(2-Oxocyclopentyl)-valeric Acid (Id).—A solution of 2 g. of 4-(2-oxocyclopentyl)-2-pentenoic acid (Ic) in 40 ml. of ethanol was hydrogenated in the presence of 0.2 g. of 10% palladium–charcoal catalyst. The theoretical amount of hydrogen was absorbed in 4 hr. The product was worked up in the usual manner to yield 1.7 g. of Id, b.p. 110–115° (bath temperature) (1 mm.), $n^{23}D$ 1.4740.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.22; H, 8.70. Found: C, 64.85; H, 8.98.

The semicarbazone crystallized in thin plates from ethanol, m.p. 184–185°.

Anal. Calcd. for $C_{11}H_{19}N_3O_3$: N, 17.43. Found: N, 17.68.

Hydrolysis of Ib.—Hydrolysis of 2 g. of ethyl 4-(1-carbethoxy-2-oxocyclopentyl)-valerate, b.p. 146–148° (1 mm.), $n^{23}D$ 1.4640, prepared by the method of Herz[1a] from Ia in almost quantitative yield (reported[1a] 80%), was carried out with 10% sulfuric acid as before to yield 1.1 g. of **4-(2-oxocyclopentyl)-valeric acid** (Id), b.p. 110–115° (bath temperature) (1 mm.), $n^{23}D$ 1.4738.

The semicarbazone, m.p. 184–185°, did not depress the melting point of the semicarbazone of Id prepared by hydrogenation of Ic, but depressed that of the semicarbazone of III by 24°.

Ozonolysis of Ic.—A current of ozonized oxygen was bubbled through a solution of 2 g. of Ic in 30 ml. of purified ethyl acetate and cooled to 0°. Ozonization was over in about 2 hr. Ethyl acetate was removed *in vacuo* at room temperature, when 2.5 g. of a sirupy liquid was obtained. The ozonide was decomposed with 20 ml. of distilled water, by heating for 4 hr. on a steam-bath. The cooled solution was thrice extracted with ether. Oxalic acid could be detected in the aqueous solution. The ether extract was separated into 0.5 g. of an acidic product, b.p. 85–90° (bath temp.) (1 mm.), and 0.8 g. of a neutral fraction. The semicarbazone of the acidic fraction crystallized in small fragile needles from hot water and melted at 185–186°, which remained undepressed on admixture with an authentic sample of the semicarbazone of 2-(2-oxocyclopentyl)-propionic acid (Ie).[6]

Rearrangement of Id to III.—A mixture of 0.5 g. of Id and 5 ml. of concentrated hydrochloric acid was refluxed for 7 hr. Excess of hydrochloric acid was removed *in vacuo* to yield 0.4 g. of a product, b.p. 110–115° (bath temp.) (1 mm.), $n^{24}D$ 1.4758.

The semicarbazone, m.p. 195–196°, did not depress the melting point of the semicarbazone of III, but depressed that of the semicarbazone of Id by 12°.

(6) F. Sorm, Z. Sormova and L. Sedivy, *Collection Czechoslov. Chem. Communs.*, **12**, 554 (1947); *C. A.*, **42**, 7742[b] (1948).

BANGALORE 3, INDIA

[CONTRIBUTION FROM THE NOYES LABORATORY, UNIVERSITY OF ILLINOIS]

Selective Side Chain Metalation of Duryl *o*-Tolyl Ketone[1]

BY REYNOLD C. FUSON, WILLIAM C. HAMMANN[2] AND PAUL R. JONES[3]

RECEIVED SEPTEMBER 24, 1956

Treatment of duryl *o*-tolyl ketone with *n*-butyllithium, followed by carbonation, gave *o*-duroylphenylacetic acid. When oxygen was passed through the reaction mixture, the product was 2,2′-diduroylbibenzyl. The structures of these compounds were established by independent syntheses.

The facility of the displacement of substituents such as methoxyl from an *o*-position in highly hindered diaryl ketones[4] by the action of Grignard reagents is ascribed to electron withdrawal from the ring by the carbonyl group. The electron deficit at the *o*-position must be greatly enhanced by the polarization of the ketone function through its coördination with the magnesium atom of the reagent. The same influence would be expected to confer increased mobility on the hydrogen atoms of a methyl group in an *o*-position. To test this idea we have studied the metalation of duryl *o*-tolyl ketone with *n*-butyllithium.

This ketone offers special interest since it possesses three methyl radicals in positions *ortho* to the carbonyl group. From the work of Kadesch and Weller[5] it seems safe to assume that resonance interaction of the carbonyl group with the durene ring cannot be important and hence that the methyl groups of this ring would show an activity not greatly different from that of those in durene itself. Moreover, in the infrared spectrum of acetodurene,[6] the band assigned to the carbonyl function is at a considerably higher frequency than a similar band in the spectrum of acetophenone. Similarly, the band attributable to the ketone group in duryl *o*-tolyl ketone is much higher (1672 cm.$^{-1}$) than that of benzophenone (1655 cm.$^{-1}$),[7]

(1) This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

(2) Rohm and Haas Fellow, 1950–1951.

(3) Allied Chemical and Dye Corporation Fellow, 1954–1955.

(4) R. C. Fuson and S. B. Speck, THIS JOURNAL, **64**, 2446 (1942).

(5) R. G. Kadesch and S. W. Weller, *ibid.*, **63**, 1310 (1941).

(6) H. S. Killam, private communication.

(7) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).