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°.

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[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]

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[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).

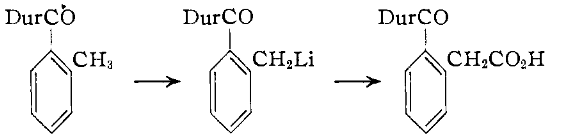
[5] R. G. Kadesch and S. W. Weller, *ibid.*, **63**, 1310 (1941).

[6] H. S. Killam, private communication.

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

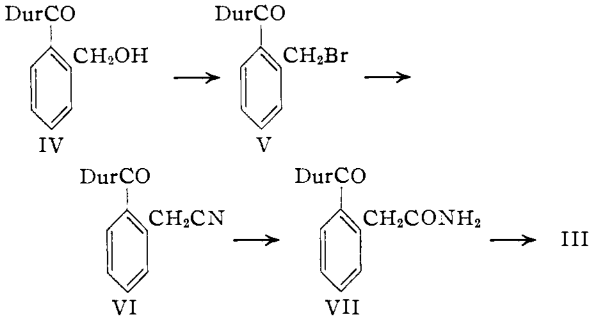
which shows that conjugation with the carbonyl function is reduced.

In our work duryl *o*-tolyl ketone was treated with *n*-butyllithium, and then carbon dioxide was passed into the mixture. In support of the original hypothesis, the acid proved to be *o*-duroylphenylacetic acid (III), a fact which shows that the corresponding lithium compound II was an intermediate in the reaction.

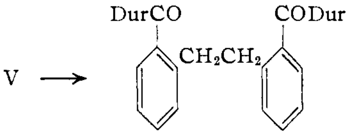


I II III

The acid was synthesized by the following series of steps.



When oxygen was passed into the mixture instead of carbon dioxide, a neutral compound was obtained, which has been shown to be the coupling product, 2,2′-diduroylbibenzyl (VIII). This procedure was patterned after that used by Faber and Nauta.[8] The bibenzyl VIII was made independently by the action of *n*-butyllithium on the bromide V.



VIII

The first step in the independent synthesis of the acid III was the formation of *o*-duroylbenzyl alcohol by the condensation of durylmagnesium bromide with phthalide—a procedure which had proved to be successful for the preparation of several benzyl alcohols.[9] While previous workers had obtained products resulting from a twofold addition of the organometallic compound to phthalide, the bulky duryl reagent, as expected, reacted only once. The yield of *o*-duroylbenzyl alcohol was 70%.

The complications that had been encountered in the preparation of durylmagnesium bromide, formerly made by the entrainment method,[10] were obviated by the use of finely ground magnesium.[11] This method appears to be superior for the preparation of Grignard reagents from unreactive halides. When mesitylmagnesium bromide was employed in a similar manner, *o*-mesitoylbenzyl alcohol was obtained.

It might be expected that the methylene group of *o*-duroylphenylacetic acid, which is vinylogous with duroylacetic acid, would be uncommonly reactive. Although this reactivity was not studied deliberately, it is held to be responsible for the pronounced readiness of the corresponding nitrile, ester and amide to form tarry products.

The intermediary amide VII, obtained by the hydrolysis of *o*-duroylphenylacetonitrile (VI) with alkaline hydrogen peroxide, could also be prepared from the acid III by a modification of the method for esterification recently described by Brewster and Ciotti.[12]

Experimental[13]

***o*-Mesitoylbenzyl Alcohol.**—Mesitylmagnesium bromide was prepared from 10 g. of finely ground magnesium and 80 g. of bromomesitylene dissolved in 120 ml. of anhydrous ether. After the addition of the bromide, which required 1.5 hr., the mixture was heated under reflux for 1.5 hr. and then cooled in an ice-bath to 10°. A solution of 26.8 g. of phthalide in 100 ml. of dry, thiophene-free benzene was added over a period of 1 hr. while the mixture was stirred and kept at 10° by means of an ice-bath. The mixture was stirred for 1 hr. longer as it was allowed to warm to room temperature; then it was decomposed with a solution of 3 moles of ammonium chloride. The organic layer was removed, washed twice with water and dried over anhydrous magnesium sulfate. Filtration of the solution and removal of the solvent at reduced pressure left a yellow oil. Its infrared spectrum[14] contains bands assignable to a hydroxyl group (3440 cm.$^{-1}$) and to a hindered, conjugated carbonyl function (1665 cm. $^{-1}$). A portion of the oil, after being refrigerated for several days, became crystalline. It was collected and washed with low-boiling petroleum ether, m.p. 77–83°. After three recrystallizations of the solid from cyclohexane the melting point was 87–89°.

Anal.[15] Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.36; H, 7.36.

The acetate was made by treating a pyridine solution of crude *o*-mesitoylbenzyl alcohol with an excess of acetyl chloride. After the initial reaction had subsided, the solution was warmed on a steam-bath several minutes and poured into water. The mixture was extracted with ether; the ether was removed and the residue taken up in aqueous ethanol. After the red solution had been allowed to stand in the refrigerator for a period of 5 months, a crystalline solid had separated. It was collected on a filter, m.p. 101–107°. By recrystallization from 95% ethanol the *o*-mesitoylbenzyl acetate was obtained in the form of colorless prisms, m.p. 106.5–108°.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.97; H, 7.03.

The infrared spectrum contains bands assignable to an aliphatic ester function (1747, 1227 cm.$^{-1}$), to a hindered, conjugated carbonyl group (1669 cm.$^{-1}$) and to the mesityl group (850 cm.$^{-1}$).

***o*-Duroylbenzyl Alcohol (IV).**—Durylmagnesium bromide was prepared from 24 g. of finely ground magnesium and an ethereal solution of 213 g. of bromodurene. After a small quantity of the solution had been added, with stirring, to the magnesium, 1 ml. of ethyl bromide was added. A vigorous reaction began, and the remainder of the solution was added in 30 minutes; during the last 15 minutes the mixture was heated at reflux temperature. Stirring and heating under reflux were continued for 5 hr., and the resulting brown mixture was cooled in an ice-bath. A solution of 67 g. of phthalide in 100 ml. of anhydrous, thiophene-free ben-

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[8] A. C. Faber and W. T. Nauta, *Rec. trav. chim.*, **62**, 469 (1943).

[9] A. Guyot and J. Catel, *Bull. soc. chim.*, [3] **35**, 567 (1906); A. Ludwig, *Ber.*, **40**, 3060 (1907); F. Seidel, *ibid.*, **61B**, 2267 (1928).

[10] R. C. Fuson and R. Gaertner, *J. Org. Chem.*, **13**, 496 (1948).

[11] H. Gilman and C. H. Meyers, THIS JOURNAL, **45**, 159 (1923).

[12] J. H. Brewster and C. J. Ciotti, Jr., *ibid.*, **77**, 6214 (1955).

[13] All melting points are corrected.

[14] The infrared spectra were determined by Mr. James Brader, Mrs. M. Louise Griffing and Miss Helen Miklas.

[15] Microanalyses were performed by Mrs. R. Maria Benassi, Mrs. Lucy Chang, Mr. Joseph Nemeth and Mr. R. J. Nesset.

zene was added dropwise in 1 hr. During this time the mixture was stirred constantly and kept in the ice-bath. After it had warmed to room temperature, the mixture was heated under reflux for 1 hr. and decomposed with a solution of 53.5 g. of ammonium chloride in 250 ml. of water. Dilute hydrochloric acid was added in order to lower the *p*H to 7. The ether–benzene layer was removed and the water layer extracted twice with ether. The organic layer, to which these extracts were added, was washed with water and dried over anhydrous magnesium sulfate; then the solution was filtered and the ether removed at reduced pressure. The residue was purified by fractional crystallization from 95% ethanol; the first three crops, consisting largely of durene, bromodurene and phthalide, were discarded. The crude alcohol, weighing 94.7 g. (70%), was recrystallized several times from cyclohexane, m.p. 135.5–139°. A mixture melting point with an authentic sample of *o*-duroylbenzyl alcohol showed no depression.

The infrared spectrum contains bands assignable to a primary alcohol function (3520, 1033 cm.$^{-1}$), a hindered, conjugated carbonyl group (1661 cm.$^{-1}$) and to *o*-disubstituted benzene (756 cm.$^{-1}$).

o-**Duroylbenzyl Bromide (V).**—Into a solution of 29.5 g. of *o*-duroylbenzyl alcohol in 200 ml. of dry methylene chloride, cooled in an ice-bath, was bubbled 8.5 g. of anhydrous hydrogen bromide, with constant shaking. After the addition, which required 15 minutes, the solution was allowed to stand in the ice-bath for 1.5 hr. while the bath came to room temperature; then it was poured into a mixture of ice and water; the organic layer was removed, washed twice with saturated sodium bisulfite and once with water and dried over anhydrous magnesium sulfate. By filtration of the solution and evaporation of the solvent at reduced pressure, there was obtained 20.6 g. (59%) of *o*-duroylbenzyl bromide, m.p. 141–148°. The product, after being recrystallized three times from cyclohexane (the first time in the presence of decolorizing charcoal), melted at 144.5–148.5°.

Anal. Calcd. for $C_{18}H_{19}BrO$: C, 65.27; H, 5.78; Br, 24.13. Found: C, 65.34; H, 6.03; Br, 23.94.

The infrared spectrum of the unrecrystallized product contains a band assignable to a hindered, conjugated carbonyl group (1668 cm.$^{-1}$) and none assignable to a hydroxyl function.

o-**Duroylbenzyl Methyl Ether.**—To a solution of 0.4 g. of commercial sodium methoxide in 25 ml. of anhydrous methanol, cooled in an ice-bath, was added 1 g. of *o*-duroylbenzyl bromide, and the orange mixture was allowed to stand overnight at room temperature. It was then heated under reflux for 2 hr., cooled and diluted with 50 ml. of water; a light orange precipitate appeared. Colorless prisms melting at 101–109° were obtained by sublimation of the orange solid at 95° (0.5 mm.), yield 0.25 g. (30%). After recrystallization of the product from high-boiling petroleum ether at −70° and a second sublimation, the melting point was unchanged.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.84; H, 7.91.

Absorption bands that are attributed to a hindered, conjugated carbonyl group (1670 cm.$^{-1}$) and to an ether function (1110 cm.$^{-1}$) are present in the infrared spectrum of the once-sublimed product.

Selective Side Chain Metalation of Duryl *o*-**Tolyl Ketone with** *n*-**Butyllithium.**—A solution of 0.02 mole of *n*-butyllithium in 25 ml. of anhydrous ether was added, with stirring, to a solution of 5.1 g. of duryl *o*-tolyl ketone in 50 ml. of anhydrous ether maintained at −30° in a bath of acetone and solid carbon dioxide in an atmosphere of nitrogen. The addition required 30 minutes, and stirring was continued for 1 hr. At the end of this period a stream of carbon dioxide gas was passed through the solution for 1 hr. The reaction mixture was decomposed with ice and 20 ml. of 10% sulfuric acid solution and the ether layer extracted with three 25-ml. portions of 5% sodium carbonate. Acidification of the sodium carbonate solution gave 1 g. (17%) of a solid, which, after several recrystallizations from ethanol, was in the form of colorless prisms, m.p. 206–208.5°.

Anal. Calcd. for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.90; H, 6.81.

The ether solution was found to contain two neutral compounds which have the composition of butylation products of duryl *o*-tolyl ketone; these substances are still under investigation.

Ethyl *o*-**Duroylphenylacetate.**—A solution of 0.2 g. of unrecrystallized *o*-duroylphenylacetic acid, 10 ml. of absolute ethanol and five drops of concentrated sulfuric acid was heated under reflux on a steam-bath for 8 hr. The colorless solution, when allowed to stand overnight, deposited a colorless crystalline solid, which was collected on a filter and dried by suction, yield 0.4 g. (64%), m.p. 150–152.5°. By recrystallization of the product from 95% ethanol colorless prisms were obtained, m.p. 151–153°.

Anal. Calcd. for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.64; H, 7.34.

The infrared spectrum contains bands assignable to an ester function (1742, 1167 cm.$^{-1}$) and to a hindered, conjugated ketone group (1673 cm.$^{-1}$).

o-**Duroylphenylacetonitrile (VI).**—A mixture of 2.8 g. of *o*-duroylbenzyl bromide, 1 g. of sodium cyanide, 10 ml. of water and 60 ml. of ethanol was taken into solution by warming on a steam-bath; the solution was heated under reflux for 5 hr. It was poured into water and the mixture extracted with two portions of ether. The extracts were combined, washed with water and dried over anhydrous sodium sulfate. An orange solid remained after filtration of the ethereal solution and removal of the solvent at reduced pressure. It was sublimed at 120° (0.05 mm.), yield 1.7 g. (74%), m.p. 123–128°. By recrystallization of the nitrile from methanol, the melting point was raised to 128.5–130°.

Anal. Calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.91; N, 5.05. Found: C, 82.13; H, 6.72; N, 4.80.

The infrared spectrum contains bands attributable to a nitrile function (2260 cm.$^{-1}$) and to a hindered, conjugated carbonyl group (1667 cm.$^{-1}$).

o-**Duroylphenylacetamide (VII). A. From** *o*-**Duroylphenylacetic Acid.**[12]—A solution of 1 g. of *o*-duroylphenylacetic acid, 1.26 g. of benzenesulfonyl chloride and 20 ml. of pyridine was stirred at ice-bath temperature for 10 minutes. Then 6 ml. of concentrated ammonia was added, and the solution was stirred in the cold for 2 hr. It was poured on ice and the mixture extracted with three portions of ether. The combined ether extracts were washed three times with 5% sodium carbonate and twice with saturated sodium sulfate, and the solvent was removed. The brown residue was recrystallized from 95% ethanol; yield 0.08 g. (8.1%), m.p. 206.5–208°.

Anal. Calcd. for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.17; H, 7.40; N, 4.58.

The infrared spectrum contains bands assignable to the amino group of a primary amide (3360, 3178, 1625 cm.$^{-1}$), to an amide carbonyl function (1635 cm.$^{-1}$), to a hindered, conjugated carbonyl group (1674 cm.$^{-1}$) and to *o*-disubstituted benzene (751 cm.$^{-1}$).

By acidification of the sodium carbonate washing, 0.66 g. (66%) of *o*-duroylphenylacetic acid was recovered.

B. From *o*-**Duroylphenylacetonitrile (VI).**—A mixture of 0.7 g. of *o*-duroylphenylacetonitrile, 1.5 g. of 30% hydrogen peroxide, 1 ml. of 5% sodium hydroxide solution and 36 ml. of 95% ethanol was heated in an oil-bath at 50–58° for 5.5 hr. The nitrile went into solution after a few minutes, and gas evolution occurred during the first hour. At the end of the heating period, the mixture was acidified and evaporated to dryness. The light green solid remaining was recrystallized from 95% ethanol; yield 0.36 g. (42%), m.p. 187–201°. After three additional recrystallizations from 95% ethanol, the *o*-duroylphenylacetamide was in the form of fine, colorless needles, m.p. 206–207.5°. A mixture melting point with a sample of the amide prepared by method A showed no depression, and the infrared spectra of the two samples are identical.

o-**Duroylphenylacetic Acid (III).**—A solution of 0.1 g. of *o*-duroylphenylacetamide, 5 ml. of glacial acetic acid and 2 ml. of dilute hydrochloric acid was heated under reflux for 7.5 hr. The solution was poured into water and the resulting yellow solid collected by filtration. It was extracted with 20 ml. of warm 5% sodium hydroxide and the alkaline filtrate acidified. The white solid so obtained was collected and dried by suction, m.p. 172–207°. It was recrystallized twice from 95% ethanol; colorless prisms were formed, m.p. 206.5–208.5°. A mixture melting point with a sample of the acid obtained by the metalation of duryl *o*-tolyl ketone showed no depression.

2,2'-Diduroylbibenzyl (VIII). A. **From Duryl *o*-Tolyl Ketone.**[8]—To a solution of 5.1 g. of duryl *o*-tolyl ketone in 60 ml. of anhydrous ether was added dropwise 25 ml. of a 1.05 *N* ethereal solution of *n*-butyllithium, while the temperature was maintained at −30° by means of a solid carbon dioxide–acetone bath. The addition, which required 10 minutes, was carried out under nitrogen and with constant stirring. The mixture was stirred at −30° for 1 hr. and then heated under reflux for 1.5 hr., while a stream of oxygen was allowed to pass slowly through it. After the mixture had been decomposed with dilute sulfuric acid, a white solid persisted between the ether and water layers. It was collected on a filter and dried, 0.37 g. (7.4%). After two recrystallizations of the solid from dimethylformamide, it was in the form of fine, colorless needles, m.p. 323.5–325.5°.

Anal. Calcd. for $C_{36}H_{38}O_2$: C, 86.01; H, 7.62. Found: C, 85.82; H, 7.69.

The infrared spectrum contains bands attributable to a hindered, conjugated carbonyl group (1660 cm.$^{-1}$) and to *o*-disubstituted benzene (757 cm.$^{-1}$).

B. **From *o*-Duroylbenzyl Bromide.**—A solution of 1.5 g. of *o*-duroylbenzyl bromide in 20 ml. of anhydrous toluene and 20 ml. of anhydrous ether was added very rapidly to 6 ml. of an ethereal solution of 0.086 *N* *n*-butyllithium, maintained at −30° by means of a solid carbon dioxide–acetone bath. The addition was carried out with constant stirring in an atmosphere of nitrogen. The solution was stirred for one minute and then poured on a large excess of powdered solid carbon dioxide. After the mixture had come to room temperature, it was decomposed with dilute sulfuric acid. A nearly white solid, which persisted between the water and organic layers, was removed with the organic layer. This mixture was extracted three times with 5% sodium carbonate and washed with saturated sodium sulfate. No precipitate appeared when the sodium carbonate washings had been combined and acidified. The white solid was separated by filtration from the organic layer, which was dried over anhydrous magnesium sulfate. After two recrystallizations of the solid from dimethylformamide, 0.14 g. (12%) of colorless needles, m.p. 323–326°, was obtained.

Anal. Calcd. for $C_{36}H_{38}O_2$: C, 86.01; H, 7.62. Found: C, 85.62; H, 7.76.

A mixture melting point with a sample of the coupling product prepared by method A showed no depression, and the infrared spectra are identical. By removal of the solvent from the dried organic layer, 0.57 g. (38%) of the original bromoketone was recovered.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Reaction of Acyl Halides with Cyclopropane

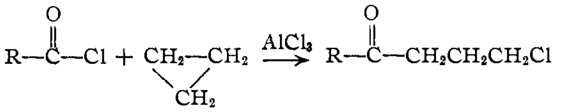
BY HAROLD HART AND OMER E. CURTIS, JR.

RECEIVED JUNE 18, 1956

Cyclopropane, with a homogeneous solution of RCOCl:$AlCl_3$ in chloroform, gave the unanticipated β-chloroketone $RCOCH(CH_3)CH_2Cl$ (II) as the major product, in addition to the expected γ-chloroketone $RCO(CH_2)_3Cl$ (I).

Attention often has been drawn[1–4] to the similarity between the cyclopropane ring and the olefinic double bond, both with regard to physical properties and chemical behavior. It is the purpose of this paper to describe results obtained from the Lewis-acid catalyzed reaction of cyclopropane with acyl halides; the corresponding reaction with olefins leads to β-chloroketones.[5]

It was anticipated that the products from acyl halides and cyclopropane would be γ-haloketones



Ia-f

R = a, CH_3; b, C_2H_5; c, *n*-C_3H_7; d, *i*-C_3H_7; e, cyclo-C_3H_5; f, C_6H_5

Opening of the cyclopropane ring here would be analogous to the formation of *n*-propyl esters from cyclopropane, acids and boron trifluoride.[6] Since γ-haloketones are readily cyclized by base to cyclopropyl ketones,[7] one would in effect have a two-step method for acylating cyclopropane. As it turned out, the anticipated reaction was accompanied by an unusual rearrangement, and the product was a mixture of two isomeric chloroketones.

The only previously reported use of cyclopropane as an acceptor in a Friedel–Crafts acylation is that of Krapivin in 1908.[8] From acetyl bromide, aluminum bromide and cyclopropane in carbon disulfide, a 15–20% yield of a ketone C_5H_8O was reported. It gave a semicarbazone, m.p. 169.5–170°, which on acid hydrolysis gave a ketone which polymerized readily and which gave a semicarbazone with a slightly higher melting point (177–178°). The product was not further characterized by Krapivin; its probable identity will be established below, but it might be noted here that the melting point of the semicarbazone does not correspond to the semicarbazones of any of the anticipated dehydrohalogenation products of Ia.

Our experimental procedure was similar to that used by Sondheimer and Woodward[5] with ethylene.

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(1) For a general review, see R. A. Raphael in E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIa, Elsevier Publishing Co., Houston Texas, 1953, pp. 25–28.

(2) E. Vogel, *Fortschr. Chem. Forsch.*, **3**, 430 (1955).

(3) (a) C. D. Lawrence and C. F. H. Tipper, *J. Chem. Soc.*, 713 (1955); (b) C. F. H. Tipper, *ibid.*, 2045 (1955).

(4) See, however, G. S. Hammond and R. W. Todd, THIS JOURNAL, **76**, 4081 (1954), for the behavior of certain cyclopropane derivatives toward free radicals.

(5) For a review of earlier work, see C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, Chapter 17. In early studies, considerable quantities of α,β-unsaturated ketones were formed with the expected β-haloketones, either directly or *via* decomposition of the latter. The technique for obtaining the β-haloketones was recently improved (see J. R. Catch, D. F. Elliott, D. H. Hey and E. R. H. Jones, *J. Chem. Soc.*, 278 (1948), and references cited there) so that the reaction has become synthetically useful. See, for example, F. Sondheimer and R. B. Woodward, THIS JOURNAL, **75**, 5438 (1953).

(6) T. B. Dorris and F. J. Sowa, *ibid.*, **60**, 358 (1938); see also ref. 3a.

(7) (a) See, for example, G. W. Cannon, R. C. Ellis and J. R. Leal, *Org. Syntheses*, **31**, 74 (1951); (b) also, H. Hart and O. E. Curtis, Jr., THIS JOURNAL, **78**, 112 (1956).

(8) S. Krapivin, *Bull. Soc. Imp. Nat. Moscow*, 1-176 (1908); *Chem. Zentr.*, **91**, I, 1335 (1910); *C. A.*, **5**, 1281 (1911). This article was available to us only as the abstract.