[Contribution from the Noyes Chemical Laboratory, University of Illinois]

o-DUROYLPHENYLLITHIUM: A KETONIC ORGANOLITHIUM COMPOUND¹

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Incompatibility of functions would appear to preclude the existence of organolithium compounds containing a carbonyl group. However, a ketone of the mesityl type in which addition reactions of the carbonyl group are practically inhibited might be expected to tolerate the presence of the organolithium function. At least one such compound has already been reported. By treating di-(2,6-xylyl) ketone with phenyllithium followed by carbon dioxide, Faber and Nauta obtained a derivative having a carbonyl group in one of the side chains (1). The intermediate formation of the corresponding ketolithium compound (I) therefore seems certain.



By treating o-bromophenyl duryl ketone with n-butyllithium at low temperatures we have succeeded in preparing the ketonic aryllithium compound, oduroylphenyllithium (II), which appears to be without precedent in the aryllithium series. The new reagent reacts normally with aldehydes and ketones. The expected carbinols are obtained with formaldehyde, benzaldehyde, acetophenone, benzophenone, fluorenone, and chalcone in yields varying from 22.4% to 78.5%.

The use of acid chlorides is especially interesting since the products are diketones which, unless both ketone groups are highly hindered, are capable of reacting further to give carbinols. Although no dicarbonyl compounds could be made with acetyl or crotonyl chloride, other acid chlorides afforded the corresponding diketones in yields as high as 71.4%. The acid chlorides were added to the reagent as quickly as possible at temperature between -60° and -55° . Cinnamoyl chloride was exceptional in that the optimum conditions involved addition of the chloride over a 10-minute period at -34° to -31.5° .

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² Rohm and Haas Fellow, 1950-1951.

In one experiment with the new reagent a small amount of the coupling product, 2,2'-diduroylbiphenyl (III), was isolated.

When treated with various sulfonyl chlorides the ketolithium compound yielded *o*-chlorophenyl duryl ketone.

EXPERIMENTAL³

o-Duroylphenyllithium. A solution of n-butyllithium was prepared according to the directions of Wittig (2) and standardized by titration with standard acid. o-Duroylbromobenzene (6.3 g.) was placed in a flask maintained at a temperature between -60° and -55° by a bath of solid carbon dioxide. Dry, oxygen-free nitrogen was passed continuously through the container and vigorous stirring was maintained at all times. Twenty milliliters of anhydrous ether and 23 ml. of 0.88 N n-butyllithium were added in the course of 5 minutes; the reaction mixture developed an orange color. The reagent prepared in this way was employed in all experiments.

2,2'-Diduroylbiphenyl. An ethereal solution of o-duroyllithium was prepared by allowing 0.04 mole of o-bromophenyl duryl ketone to react for 1 hour at -60 to -50° with an equivalent amount of n-butyllithium. One-third of the reagent, treated with carbon dioxide, gave o-duroylbenzoic acid (3) in 45% yield. A second one-third portion of the reagent was treated with an excess of benzoyl chloride in ether at -45° and to the remainder benzyl chloride was added. The reactions with the chlorides each gave a small amount of 2,2'-diduroylbiphenyl; m.p. 249-251°. A mixture melting point with an authentic specimen of this diketone (4) showed no lowering.

o-Duroylphenyl o-tolyl ketone. A solution of 3 g. of o-toluyl chloride in 15 ml. of anhydrous ether was added to the keto lithium reagent made from 6.3 g. of bromo ketone. The mixture was stirred for 10 minutes at -55° , during which time the color changed from orange to yellow. The solid carbon dioxide cooling bath was removed and stirring was continued for 25 minutes; a precipitate formed. The diketone, isolated in the usual way, melted at 181-183°; yield 4.1 g. The pure compound was obtained by recrystallization from ethanol; m.p. 188°.

Anal. Calc'd for C25H24O2: C, 84.23; H, 6.79.

Found: C, 83.95; H, 6.48.

o-Duroylphenyl mesityl ketone. A similar experiment was carried out with mesitoyl chloride (3.64 g.). The reaction mixture, however, was stirred for 30 minutes after the chloride had been added instead of 10 minutes. The diketone melted at 240-242°; yield 1.8 g. (23.4%). It was recrystallized five times from ethyl acetate; m.p. 243°.

Anal. Calc'd for C₂₇H₂₈O₂: C, 84.34; H, 7.34.

Found: C, 84.44; H, 7.11.

o-Duroylpropiophenone. In the experiment with propionyl chloride (1.85 g.) the mixture was stirred for 10 minutes after the addition of the acid chloride was complete, then for 25 minutes more after removal of the cooling bath, and finally was allowed to stand overnight. The crude diketone melted at 135.5–138.5°; yield 1.9 g. (31.7%). The pure compound was obtained by four recrystallizations from 95% ethanol; m.p. 143.5–144°.

Anal. Calc'd for C₂₀H₂₂O₂: C, 81.59; H, 7.43.

Found: C, 81.81; H, 7.50.

(o-Duroylphenyl)phenylstyrylcarbinol. To an ethereal solution of o-duroylphenyllithium (0.02 mole) was added all at once an equivalent amount (4.56 g.) of chalcone in ether. The reaction was run in an atmosphere of dry, oxygen-free nitrogen at -38° to -30° . The mixture was stirred for 30 minutes at this temperature and then for another 30 minutes after removal of the cooling bath. The color changed from nearly black to brownish-yellow. The crude carbinol melted at $203-204^{\circ}$; yield 4.1 g. (53.2%). It was purified by four recrystallizations from ethyl acetate; m.p. $207-207.5^{\circ}$.

⁸ The microanalyses were performed by Miss Emily Davis, Mrs. Katherine Pih, Mrs. Jeanne Fortney, and Mr. Joseph Nemeth.

Anal. Cale'd for C₃₂H₃₀O₂: C, 86.06; H, 6.77. Found: C, 85.99; H, 6.73.

o-Duroylchalcone. A solution of cinnamoyl chloride (0.02 mole) in 30 ml. of anhydrous ether was added over a period of 10 minutes to an ether solution of 0.02 mole of o-duroylphenyllithium at -34° to -31.5° . The blackish yellow color of the mixture changed first to black, then to red, and finally to yellow. After an additional 20 minutes of stirring, the cooling bath was removed and stirring was prolonged for 45 minutes. A colorless precipitate appeared. The chalcone was isolated by the customary procedure; m.p. 230–232.5°; yield 1.55 g. (20.9%). It was recrystallized four times from ethyl acetate; m.p. 255°.

Anal. Calc'd for C26H24O2: C, 84.75; H, 6.56.

Found: C, 84.88; H, 7.35.

Biphenylene (o-duroylphenyl)carbinol. A solution of 2 g. of fluorenone in 25 ml. of anhydrous ether was added over a period of 10 minutes to an equivalent amount (0.01 mole) of o-duroylphenyllithium -43° to -34° . The color of the reaction mixture changed from orange to yellow and, at the end of 20 minutes of stirring, was greenish yellow. Decomposition in the usual way produced 1.4 g. of the crude carbinol; m.p. 187-202°. The pure compound was obtained by recrystallization from ethyl acetate; m.p. 216-216.5°.

Anal. Calc'd for C_{\$0}H₂₆O₂: C, 86.09; H, 6.26.

Found: C, 86.20; H, 6.26.

The infrared spectrum⁴ had bands at 3445 and 1664 cm. $^{-1}$, assignable to hydroxyl and conjugated carbonyl, respectively.

(o-Duroylphenyl)phenylcarbinol. An ethereal solution of 2.14 g. of benzaldehyde was added all at once to a solution containing an equivalent amount (0.02 mole) of the keto lithium reagent at -35° to -30° . The mixture was stirred for 15 minutes before removal of the cooling bath and for the same length of time afterwards. During the course of the reaction the yellow color developed by the mixture changed to reddish brown. The crude carbinol (1.6 g.) melted at 118-119.5°. It was purified by three recrystallizations from an ethanol-water mixture; m.p. 122°.

Anal. Calc'd for C₂₄H₃₄O₂: C, 83.69; H, 7.02.

Found: C, 83.81; H, 7.23.

(o-Duroylphenyl) methylphenylcarbinol. The condensation of the keto lithium reagent with acetophenone was carried out as in the preceding experiment except that stirring was continued for 30 minutes after the bath was removed. The crude carbinol (1.9 g.) melted at 138-139°. After four recrystallizations from ethanol and water it melted at 144°. Anal. Calc'd for C_{2b}H₂₆O₂: C, 83.76; H, 7.31.

Found: C, 83.84; H, 7.38.

o-Duroylbenzyl alcohol. A stream of dry nitrogen was passed through a flask containing 10 g. of paraformaldehyde and into a second flask containing 0.02 mole of the keto lithium reagent. The apparatus was so arranged that the formaldehyde, when heat was applied, was delivered to the second flask just above the surface of the reaction mixture, which was maintained at -40°. During the first 5 minutes the color of the mixture changed from orange to a golden yellow and after 10 minutes the mixture was very turbid. The heating was discontinued and, after 10 minutes of stirring, the cooling bath was removed. Following an additional 30-minute period of stirring, the product (1.5 g.) was isolated in the usual way; m.p. 124-131°. Pure o-duroylbenzyl alcohol was obtained by four recrystallizations from ethanol and water; m.p. 140°.

Anal. Calc'd for C₁₈H₂₀O₂: C, 80.56; H, 7.51.

Found: C, 80.29; H, 7.67.

Diphenyl(o-duroylphenyl)carbinol. A solution of 3.6 g. of benzophenone in 15 ml. of anhydrous ether was added over a 5-minute period to a solution containing an equivalent amount (0.02 mole) of the keto lithium reagent at -35° to -30° . The reaction mixture was

⁴ The infrared spectra were observed and interpreted by Miss Helen Miklas and Mrs. Rosemary Hill.

stirred for 30 minutes at -30° during which time its color changed from orange to greenishyellow. The stirring was continued for 30 minutes after removal of the cooling bath. The crude product (6.1 g.), melting at 218–219°, was recrystallized three times from ethyl acetate; m.p. 219°.

Anal. Calc'd for C₃₀H₂₈O₂: C, 85.68; H, 6.71.

Found: C, 85.69; H, 6.77.

o-Chlorophenyl duryl ketone. Aluminum chloride (4 g.) was added, with stirring, to a solution of 5 g. of o-chlorobenzoyl chloride in 25 ml. of carbon disulfide. To the resulting green mixture was added over the course of 16 minutes a solution of 5.4 g. of durene in 25 ml. of carbon disulfide. After being stirred for 5 hours at room temperature, the mixture was cooled to -3.5° . The precipitate was removed and added to a mixture of 20 ml. of 20% hydrochloric acid and ice. The resulting mixture was heated for 15 minutes on a steam cone and allowed to stand overnight. The precipitate was dissolved in 95% ethanol and the solution, after treatment with Darco and Filter-Cel, was filtered and allowed to cool. The crude ketone (3.5 g.; m.p. 119-120.5°) was recrystallized four times from ethanol and water; m.p. 120.5-121°.

Anal. Cale'd for C₁₇H₁₇ClO: C, 74.85; H, 6.28; Cl, 13.00.

Found: C, 75.05; H, 6.19; Cl, 13.10.

o-Chlorophenyl duryl ketone was produced also by treatment of the keto lithium compound with benzene-, *p*-toluene-, or *p*-bromobenzene-sulfonyl chlorides. The yields, however, were low and the products extremely difficult to purify. They were shown to be identical to that made by the Friedel-Crafts method by mixture melting point determinations and by comparison of the infrared spectra.

SUMMARY

o-Duroylphenyllithium, believed to be the first ketonic aryllithium compound to be described, was made by treating o-bromophenyl duryl ketone with n-butyllithium at a temperature of -30° or lower.

The new reagent condensed with benzoyl, o-toluyl, cinnamoyl, mesitoyl, and propionyl chlorides to give the corresponding diketones.

The expected carbinols were obtained by condensation with formaldehyde, benzaldehyde, acetophenone, benzophenone, fluorenone, and chalcone.

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