

THE FORMATION OF LITHIUM AROYLNICKEL CARBOXYLATES FROM THE REACTIONS OF ARYL LITHIUMS AND NICKEL CARBONYL

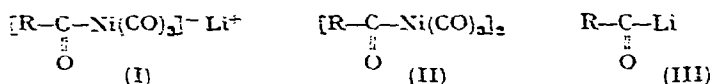
MEMBO RYANG, SONG KWANG-MYEONG, YOSHIHIKO SAWA AND SHIGERU TSUTSUMI

Department of Chemical Technology, Faculty of Engineering, Osaka University, Miyakojima-ku, Osaka (Japan)

(Received August 13th, 1965)

INTRODUCTION

In previous papers^{1,2} it has been reported that organolithium compounds reacted with nickel carbonyl or iron pentacarbonyl at low temperatures (-70 to -50°) to give ketones or acylloins and the following three complexes, (I), (II) and (III), were postulated as the possible intermediate species in the reaction with nickel carbonyl.



It would be of interest to investigate the structure and behaviors of the intermediate complexes because each of the assumed complexes represents a new type of organometallic compound with possibly novel chemical properties, the preparations of which by the earlier methods are rather difficult.

At the outset, we found that the formation of ketones and acylloins as ultimate products of the reaction between aryllithiums and nickel carbonyl can be attributed to lithium aroylnickel carbonylates as intermediates and an allusion to this complex as a precursor to ketones and acylloins has been made. During the course of our study, Fischer and Maasböl reported the formation of benzoyltungsten-carbonylate anion, which was isolated as the tetramethylammonium salt, from the reaction between phenyllithium and tungsten hexacarbonyl³.

In this report we wish to establish that the formation of lithium aroylnickel carbonylates is, in fact, antecedent to both ketones and acylloins, and to explore further the mechanism of the decomposition reaction of lithium aroylnickel carbonylates and examine some of their chemical properties.

RESULTS AND DISCUSSION

The reaction intermediates: lithium aroylnickel carbonylate

The reaction mixture obtained from the reaction of *p*-tolyllithium (0.1 mole) with nickel carbonyl (0.0375 mole) in ether solution at -70° gave *p*-toluoin in 48% yield on hydrolysis with ethanol/6*N* hydrochloric acid at -70° , and extraction of the reaction mixture with anhydrous benzene in a dry argon box below room temperature; *i.e.*, the isolation of the products without hydrolysis, yielded di-*p*-tolyl

ketone in a 29 % yield. When the reaction time was prolonged by stirring for a further 5 h at 30 or 60°, subsequent hydrolysis gave *p*-toluoin and di-*p*-tolyl ketone in yields of 36 and 25 % respectively (at 30°) and in yields of 34 and 38 % respectively (at 60°).

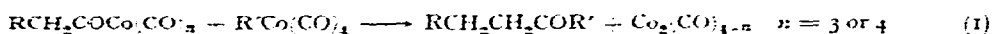
Thus it is evident that the reaction products were markedly affected by the methods of treating the reaction mixture.

A similar tendency was also observed in the reaction of *o*-tolyllithium (0.1 mole) with nickel carbonyl (0.1 mole) at -70°, from which *o*-toluoin was obtained in a 62.5 % yield on hydrolysis at -70°, and on the other hand, *o*-tolil and *o*-toluic acid in yields of 41.5 and 24.5 %, respectively, on additional stirring at higher temperature (30°) for 5 h, followed by hydrolysis. However, the reaction between 0.1 mole of *o*-tolyllithium and 0.0375 mole of nickel carbonyl gave complicated results and the precise analysis of products has not been carried out.

The above results indicate that, in the reaction of organolithium compounds with nickel carbonyl (in mole ratio of 1:1), ketones and acyloins were produced from the same intermediate complexes, but that acyloins were produced via the dimerization of the intermediate complexes, followed by hydrolysis, while ketones were produced by the thermal decomposition of the same intermediates at a higher temperature. Considering these results and our previous work on the reaction of organolithium compounds with carbon monoxide⁴, the aroyllithium (III) appears improper for the intermediate complex, precursor to ketone and acyloin.

Therefore the intermediate complex was considered to be an organonickel compound with a Ni-C σ -bond [(I) or (II)]. It is reasonable to consider the ketone and α -diketone formation to be the result of the decomposition of an aroylnickel tricarbonyl (II) and this type of reaction has been already reported by several workers: acetone formation⁵ from the decomposition of methylcobalt tetracarbonyl above -35°, the formation of tetraphenylcyclopentadienone⁶, and the formation of biacetyl by the reaction of dimethylplatinum bis(trialkylphosphine) with carbon monoxide⁷.

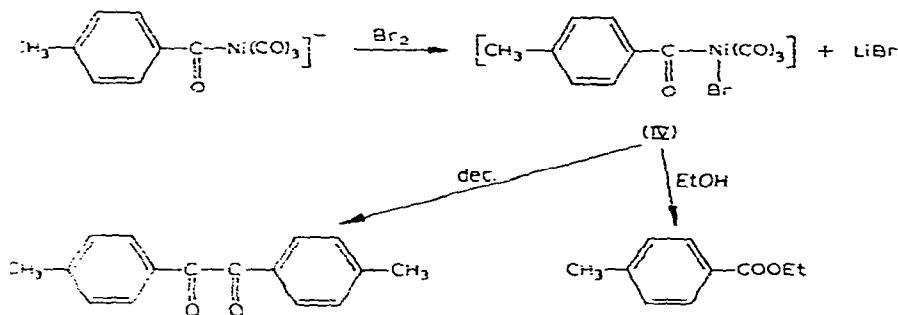
Furthermore, Bertland⁸ reported that ketones in the products of Oxo-synthesis would be produced by the interaction of acylcobalt carbonyl and alkylcobalt carbonyl (eqn. 1).



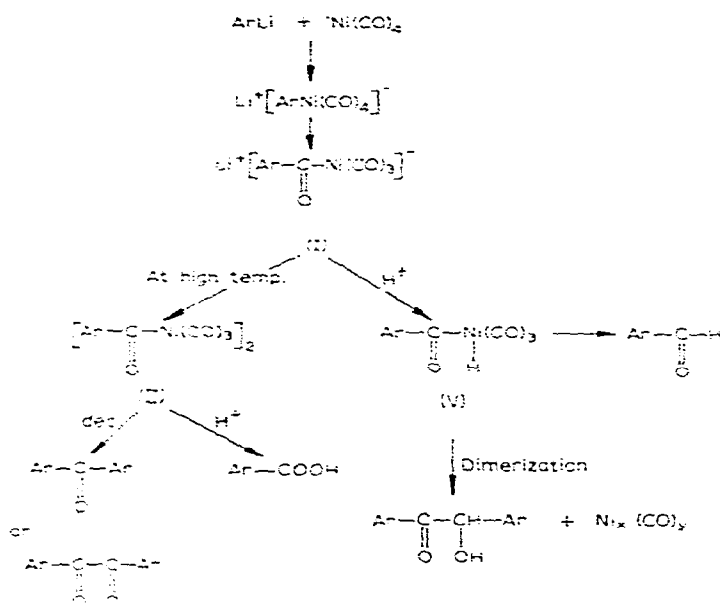
However, acyloin formation from the acylmetal carbonyl has not yet been reported, and since, in our experiment, ketone and acyloin were produced via the same intermediate complex, the assumption of lithium aroylnickel carbonylate (I) as the intermediate was preferred to the assumption of aroylnickel carbonyl (II). In accordance with this assumption the addition of bromine (0.1 mole) to the reaction mixture, obtained from the reaction between *p*-tolyllithium (0.1 mole) and nickel carbonyl (0.1 mole) at -70°, gave, after ethanolysis, *p*-tolil and ethyl *p*-toluate in yields of 72.5 and 12 % respectively.

These products were considered to be produced via the following reaction scheme; that is, the interaction of bromine and lithium *p*-toluoylnickel carbonylate gives *p*-toluoylnickel carbonyl bromide (IV)⁹, from which *p*-tolil is produced via decomposition and ethyl *p*-toluate via ethanolysis.

Since Fischer *et al.*³ have recently described the formation of lithium benzoyltungsten pentacarbonylate from the reaction of phenyllithium with tungsten hexa-




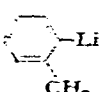
onyl, it can be generally considered that organolithium compounds easily react with mononuclear metal carbonyls to yield relatively unstable lithium acylmetal carbonylates. Furthermore, Grignard reagents react with nickel carbonyl at 0° to give the same type of complexes, and, in the case of phenylmagnesium bromide, hydrolysis at 0° gave benzoin in a 70% yield¹⁰, while further stirring at 110° for 3 h gave benzophenone (15%), benzil (25%), benzoin (10%) and benzoic acid (18%). Thus, the whole reaction scheme for the formation of ketones and acylolins may be described as the following, which are compatible with the available data.



Therein the dimerization to acylolins would not occur directly from lithium arylnickel carbonylates (I) but via arylnickel carbonylhydrides (V), formed by the protonation of (I), from which good yields of aromatic aldehydes were obtained in high diluted solution with diethyl ether². In the absence of proton donor, lithium arylnickel carbonylates (I) would decompose at higher temperature (above 30°) into arylnickel carbonyls (II), from which ketones and carboxylic acids were produced by further decomposition and hydrolysis, respectively. This consideration seemed to be supported by the following experimental results. That is, the reaction of *o*-tolyllithium with

TABLE I

THE PRODUCTS FROM THE REACTION OF ARYL LITHIUMS WITH NICKEL CARBONYL

<i>Ar-Li</i>	Treatment method ^a	<i>Ar-Li</i> to $Ni(CO)_4$ ratio			
		<i>r</i> : <i>s</i> : <i>t</i>	(yield, %) ^b	<i>r</i> : <i>t</i>	(yield, %)
CH_3 -  -Li	A	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{OH}}{\text{CH}}-Ar$	48	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{OH}}{\text{CH}}-Ar$	71
	B	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Ar$	29	$Li^+ [ArCONi(CO)_3]^-$	90
	C (60°)	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{OH}}{\text{CH}}-Ar$	34	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{OH}}{\text{CH}}-Ar$	71
		$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Ar$	38	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Ar$	—
		$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Ar$	Small amount	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Ar$	20
	 -Li	A	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{OH}}{\text{CH}}-Ar$	62	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{OH}}{\text{CH}}-Ar$
$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Ar$					
$Ar-\overset{\text{OH}}{\text{CH}}-Ar$					
etc.					
C (30°)		$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Ar$	15	$Ar-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-Ar$	42
	$Ar-COOH$	5	$Ar-COOH$	25	
	Other compounds	30			

^a The treatment of the reaction mixtures was carried by the following three methods: A: hydrolysis at -70° ; B: further stirring at 30° for 5 h and removal of solvents under reduced pressure, followed by extraction of the products with benzene (isolation of products without hydrolysis); C: further stirring at 60° (or 30°) for 5 h, followed by hydrolysis. ^b The yields were calculated on the basis of the amount of *o*-bromotoluene and *p*-bromotoluene used.

nickel carbonyl at -70° gave *o*-toluoin in a yield of 63% and *o*-toluic acid was not isolated, while during the increase of the temperature of the reaction mixture, the reddish brown color (at -70°) of the reaction mixture changed continuously to orange yellow (-20°) and to dark red ($5-30^\circ$) and on further stirring at 30° for 5 h, followed by hydrolysis, *o*-tolil and *o*-toluic acid were obtained in yields of 41.5 and 24.5%, respectively. Furthermore, recooling (to -70°) of the above mentioned reaction mixture at 30° , followed by hydrolysis at -70° , gave *o*-tolil and *o*-toluic acid in yields of 42.5 and 24%, respectively.

Hence the intermediate complex (I), the precursor to *o*-toluoin and *o*-tolualdehyde, would undergo an irreversible change with the elevation of temperature to form

o-toluoylnickel carbonyl, from which *o*-tolil would be produced on decomposition and *o*-toluic acid by hydrolysis.

The effect of the mole ratios of nickel carbonyl on the stability of the intermediate complexes

The results are summarized in Table 1. In the case of *o*-tolyl lithium, the reaction in ratio of $\text{ArLi}/\text{Ni}(\text{CO})_4 = 1:3/8$ gave the various products, whereas the increase of nickel carbonyl to *o*-tolyl lithium ratio (1:1) led to the formation of *o*-toluoin as a sole product in good yield. Therefore, when the amount of nickel carbonyl was small, the unstable intermediate complex containing two aryl groups on a nickel atom was formed and underwent various further reactions to give the various products. Furthermore, in the case of *p*-tolyl lithium (0.1 mole) and nickel carbonyl (0.1 mole), the salt-like air-sensitive (ignites in air) black powder was isolated in a crude yield of 90% (based on the assumed structure). This material was insoluble in ordinary organic solvents and gave *p*-toluoin on hydrolysis and *p*-tolil on thermal decomposition in toluene at 110°. It was therefore assumed to be a new type of metal-carbon σ -bonded complex: lithium *p*-toluoylnickel tricarbonylate $\{\text{Li}^+[\textit{p}\text{-CH}_3\text{C}_6\text{H}_4\text{CONi}(\text{CO})_3]^- \}$. The physical properties of this compound have not yet been examined.

The reaction with organic halides

The reaction with organic halides were carried out in order to study the chemical behavior of lithium *p*-toluoylnickel carbonylate (the above mentioned air-sensitive black powder).

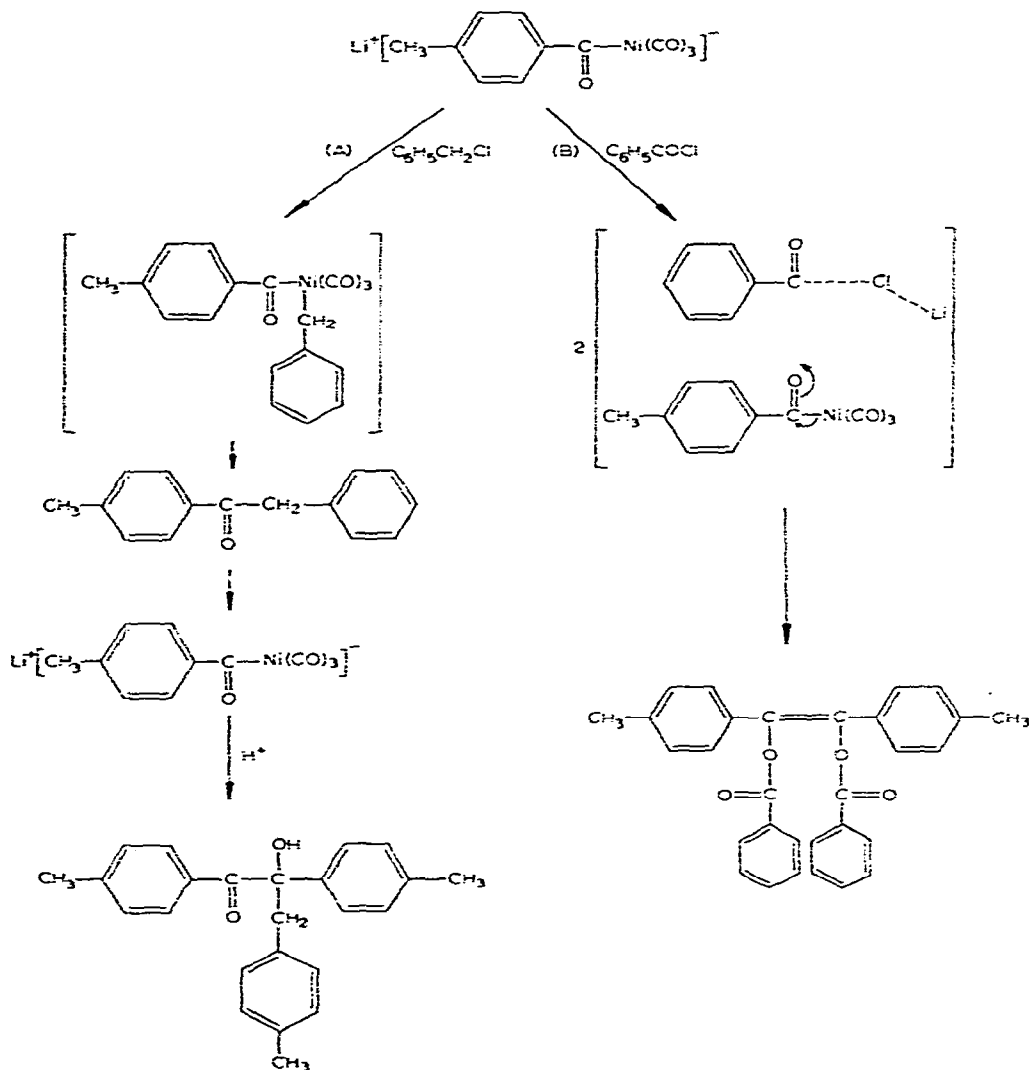
Benzyl chloride reacted with lithium *p*-toluoylnickel carbonylate in benzene solution at 80° to give α -benzyl-*p*-toluoin in a yield of 73%, which was also obtained by addition of benzyl chloride to the reaction mixture of *p*-tolyl lithium and nickel carbonyl at 50°, in a yield of 70%.

A small amount of *p*-tolyl benzyl ketone was also isolated and therefore α -benzyl-*p*-toluoin was considered to be produced by the further reaction of *p*-tolyl benzyl ketone with lithium *p*-toluoylnickel carbonylate (path A). Benzoyl chloride reacted vigorously with lithium *p*-toluoylnickel carbonylate in benzene at room temperature to give α, α' -dibenzoyloxy-4,4'-dimethylstilbene in a yield of 55% (path B).

EXPERIMENTAL

The reaction of p-tolyl lithium or o-tolyl lithium with nickel carbonyl

Into a 200 ml four-necked flask equipped with a mechanical stirrer, a low temperature thermometer, a reflux condenser protected from moisture, a gas bubbler and a dropping funnel, 40 ml of anhydrous ether (dried over sodium) were placed and, after sweeping the apparatus with dry argon, 1.6 g (0.22 g-atom) of lithium in the form of small pieces of thin foil. A solution of 17.1 g (0.1 mole) of *p*-bromotoluene or *o*-bromotoluene in 40 ml of anhydrous ether was added via the dropping funnel with stirring over a period of 30 min, while the internal temperature was maintained at 30°. After the addition had been completed, the stirring was continued for a further 2 h, after which the reaction mixture was cooled to -70° with a Dry Ice/methanol bath kept at -78°. Nickel carbonyl (17 g, 0.1 mole, or 6.3 g, 0.0375 mole) in 50 ml anhydrous ether were next introduced at -65°, and the stirring was continued for a further 3 h. The resulting reaction mixture was treated in the following three methods (A, B and C). In every case, all procedures were carried out in a dry argon box.



(A). The reaction mixture was hydrolyzed with 5 ml of ethanol and 40 ml of 6 *N* hydrochloric acid. The separated organic layer was treated with three successive 50-ml portions of 5% sodium hydroxide solution and divided into the organic layer (1), and a sodium hydroxide solution (2). The organic layer containing neutral compounds was washed with water and dried over magnesium sulfate. The brownish residual oil obtained after removal of the solvent was distilled under reduced pressure to give the products listed in Table I.

(B). The products were isolated by extraction with dry benzene without hydrolysis: for example, lithium *p*-toluoylnickel carbonylate was isolated by the following procedure. Filtration of the reaction mixture, obtained from the reaction of *p*-tolylithium (0.1 mole) with nickel carbonyl (0.1 mole) in ether solution at -70° , to remove the unreacted metallic lithium, followed by removal of solvent under reduced

pressure, gave a black powder, which then was washed with dry benzene to extract organic compounds. [In other cases, such as the reaction of *p*-tolyllithium (0.1 mole) and nickel carbonyl (0.0375 mole) or *o*-tolyllithium, ketones or α -diketones were isolated from this benzene solution.] The thus obtained benzene-insoluble, salt-like, black powder (24 g) was air-sensitive (ignited in air), insoluble in ordinary organic solvents and gave *p*-toluoin on hydrolysis and *p*-tolil on thermal decomposition in toluene at 110°. Although the physical properties of this material have not yet been examined, this compound was assumed to be lithium *p*-toluoylnickel tricarbonylate; the direct precursor to *p*-tolil, di-*p*-tolyl ketone and *p*-toluoin (a crude yield 90 %, based on the assumed structure).

(C). The reaction mixture at -70° was further stirred at higher temperature (30-60°), followed by hydrolysis with 5 ml of ethanol and 40 ml of 6 *N* hydrochloric acid. Thereafter the reaction products in Table 1 were isolated and identified by ordinary methods.

The reaction of bromine with lithium p-toluoylnickel carbonylate

Bromine (8 g, 0.05 mole) was added, at -70°, to an ether solution of lithium *p*-toluoylnickel carbonylate which had been prepared by using 8.6 g (0.05 mole) of *p*-bromotoluene, 1 g of lithium, 9.5 g (0.05 mole) of nickel carbonyl and 80 ml of anhydrous diethyl ether, and the stirring was continued for 2 h at -70°, for 10 h at room temperature. Then 20 ml of dry, pure ethanol was added and the stirring was continued for a further 5 h at 34°. The reaction mixture was hydrolyzed by 20 ml of 2 *N* hydrochloric acid and divided into a neutral part and an acidic part. The neutral part was distilled under reduced pressure to give the following fractions: (1) b.p. 95-105°/28 mm Hg, 1 g; (2) b.p. 145-165°/0.6 mm Hg, 3.7 g; and (3) b.p. 165-185°/0.6 mm Hg, 0.5 g.

The infrared spectrum of fraction (1) showed the presence of an ester group (1730, 1280, 1105 cm⁻¹) and fraction (1) was confirmed to be ethyl *p*-toluate from the results of gas-chromatographic analysis and a mixed melting point measurement of its free acid (m.p. 179°, recrystallized from water) with *p*-toluic acid (yield 12 %). Fraction (2) was recrystallized from petroleum benzine to give yellowish crystals, m.p. 102°, and identified as *p*-tolil by mixed melting point measurement (yield 73 %).

The reaction of phenylmagnesium bromide with nickel carbonyl

Nickel carbonyl (5 g, 0.028 mole) was added at -5° into the ether solution of phenylmagnesium bromide, prepared by using 4.7 g (0.03 mole) of bromobenzene, 0.73 g (0.03 g-atom) of magnesium and 50 ml of anhydrous ether. After the addition of nickel carbonyl was completed, stirring was continued for a further 2 h at room temperature. Then 80 ml of toluene was added and stirring was continued for a further 10 h at 110°. After cooling, the reaction mixture was filtered under reduced pressure. The solid material was hydrolyzed by dilute hydrochloric acid to give 0.7 g of benzoin (b.p. 140-160°/1.2 mm Hg, m.p. 133-134°, yield 10 %).

The above filtrate was distilled under reduced pressure, after the removal of toluene, to give the following fractions: (1) b.p. 120-135°/1 mm Hg, 0.8 g; (2) b.p. 155-155°/1 mm Hg, 1.6 g; and (3) b.p. 180-190°/1 mm Hg, 0.3 g. The fraction (1) showed the presence of carbonyl group (1660 cm⁻¹) in IR and was identified as benzophenone (yield 15 %) by mixed melting point measurement of its 2,4-dinitrophenyl-

hydrazone (m.p. 232–233°, from ethyl acetate). Fraction (2) was recrystallized from ethanol to give yellow prisms, m.p. 95°, and was identified as benzil by mixed melting point (yield 25 %).

*The reaction of lithium *p*-toluoylnickel carbonylate with benzyl chloride*

Lithium *p*-toluoylnickel carbonylate (6 g), the air-sensitive black powder obtained by procedure (B), was added to the benzene solution of 12.5 g (0.1 mole) of benzyl chloride, and the reaction was carried out at 80° for 3 h. After hydrolysis, the neutral part was distilled under reduced pressure to give the following fractions: (1) b.p. 90–110°/1.5 mm Hg, 0.3 g; (2) b.p. 110–160°/1.5 mm Hg, 0.2 g; and (3) b.p. 220–235°/0.15 mm Hg, 4.1 g. Fraction (2) crystallized on standing and was recrystallized from petroleum ether to give white crystals (m.p. 109–109.5) and identified as *p*-tolyl benzyl ketone by the mixed melting point with an authentic sample. The fraction (3) was recrystallized from ethanol to give white needles, m.p. 147.5–148.5°. The infrared spectrum showed the presence of a carbonyl group (1665 cm⁻¹) and a hydroxyl group (3500 cm⁻¹). (Found: C, 83.60; H, 6.71; mol. wt. in benzene, 336. C₂₃H₂₂O₂ calcd.: C, 83.43; H, 6.71 %; mol. wt., 340.)

Oxidation of this material by using lead tetraacetate in 90 % aqueous acetic acid gave *p*-tolyl benzyl ketone (m.p. 109–109.5°) and *p*-toluic acid (m.p. 178°). Thus this material was identified as α -benzyl-*p*-toluoin (yield 73 %).

*The reaction of lithium *p*-toluoylnickel carbonylate with benzoyl chloride*

Lithium *p*-toluoylnickel carbonylate (8 g) reacted smoothly with 4.2 g of benzoyl chloride in 50 ml of benzene at room temperature to give 4.1 g of α,α' -dibenzoyloxy-4,4'-dimethylstilbene (yield 55 %); b.p. 220–235°/0.15 mm Hg, m.p. 142–143° (recrystallized from ethanol), IR 1745 cm⁻¹ (C=O), 1270, 1240, and 1085 cm⁻¹ (-C-O-C-). (Found: C, 80.76; H, 5.39 %. C₂₀H₂₄O₄ calcd.: C, 80.33; H, 5.39 %.) Hydrolysis with potassium hydroxide/methanol gave benzoic acid and *p*-tolil.

SUMMARY

The reaction of aryllithiums with nickel carbonyl is described.

The formation of lithium arylnickel carbonylates is considered to be antecedent to both ketones and acyloins, and further, the mechanism of the decomposition reaction of lithium arylnickel carbonylates is discussed and their chemical behavior examined.

REFERENCES

- 1 SONG KWANG-MYEONG, Y. SAWA, M. RYANG AND S. TSUTSUMI, *Bull. Chem. Soc. Japan*, 38 (1965) 330.
- 2 M. RYANG, Y. SAWA, H. MASADA AND S. TSUTSUMI, *Kogyo Kagaku Zasshi*, 66 (1963) 1080; M. RYANG, I. KHEE AND S. TSUTSUMI, *Bull. Chem. Soc. Japan*, 37 (1964) 341.
- 3 E. O. FISCHER AND A. MAASBÖL, *Angew. Chem.*, 76 (1964) 645.
- 4 M. RYANG AND S. TSUTSUMI, *Bull. Chem. Soc. Japan*, 35 (1962) 1121.
- 5 W. HIEBER, O. VOHLER AND G. BRAUN, *Z. Naturforsch.*, 131 (1958) 192; W. HIEBER, W. BECK AND E. LINDNER, *Z. Naturforsch.*, 166 (1961) 229.
- 6 G. N. SCHRAUZER, *J. Am. Chem. Soc.*, 81 (1959) 5307.
- 7 G. BOOTH AND J. CHATT, *Proc. Chem. Soc.*, (1961) 67.
- 8 J. A. BERTRAND, C. L. ALDRIDGE, S. HUSEBYE AND H. B. JONASSEN, *J. Org. Chem.* 29 (1964) 790.
- 9 N. L. BAULD, *Tetrahedron Letters*, (1963) 1814.
- 10 F. L. BENTON, SR. M. CONSOLATA VOSS AND P. A. MCCUSKER, *J. Am. Chem. Soc.*, 67 (1945) 82.