(SiOSi). *Anal.* Calcd for $Si_2C_{10}H_{22}O_3$: Si, 22.8; C, 48.7; H, 8.98. Found: Si, 21.7; C, 48.7; H, 9.16.

The 2,4-dinitrophenylhydrazone had mp 185–186°. *Anal.* Calcd for $Si_2C_{22}H_{30}N_8O_9$: Si, 9.26; N, 18.4. Found: Si, 9.20; N, 17.9.

The residue, 8.0 g, was similar to that obtained from the hydrolysis with hydrochloric acid.

Hydrolysis of a Mixture of 6 and 7.—A mixture of 1 l. of 0.36 *N* sulfuric acid and 113.9 g (0.336 mol) of **6** and **7** was refluxed for 6 hr. After cooling, the hydrolysate was extracted with ether and the ethereal solution was dried over sodium sulfate and filtered, and the ether was removed *in vacuo*. A cold trap at −80° was used to collect the volatiles. Treatment of these volatiles with 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of propionaldehyde, mp 148–152°, mixture melting point undepressed. The resulting 81.5 g (98%) of crude material contained two major components, **5** and hexamethyltrisiloxane-1,5-dipropanal in a ratio of 2:1, as well as several other components by glc analysis. The trisiloxane was separated from **5** by two successive fractional distillations: bp 104° (0.15 mm); $n^{25}D$ 1.4394; d^{25}_4 1.000; RD 0.263 (calcd 0.268); 2,4-dinitrophenylhydrazone, mp 172–173°. *Anal.* Calcd for $Si_3C_{24}H_{36}N_8O_{10}$(2,4-dinitrophenylhydrazone): Si, 12.4; C, 42.4; H, 5.31; N, 16.45. Found: Si, 12.5; C, 42.7; H, 5.40; N, 16.2.

Acidic Aldol Condensation of 5.—A mixture of 1.0 g (4 mmol) of **5** and 100 ml of 2.4 *N* hydrochloric acid was refluxed for 4 hr. After cooling the hydrolysate was worked up as described above. The 700 mg (75%) of product was >95% **8** by glc analysis.

Basic Aldol Condensation of 5.—A mixture of 5.0 g (20 mmol) of **5** and 22 ml of 1.0 *N* sodium hydroxide was refluxed for 1 hr. After work-up as described above, 3.5 g (93%) of material was obtained which was a mixture of **8** and **5** in a ratio of 4:1. There were a few additional peaks corresponding to higher boiling products which accounted for *ca.* 5% of the product.

***sym*-Bis(3,3-dimethylaminopropyl)tetramethyldisiloxane.**—To 25.8 g (0.105 mol) of **5** in 25 ml of methanol cooled in an ice-water bath was added 61.0 g of 36% dimethylamine in cold methanol (0.49 mol). To this mixture was added 200 mg of 10% palladium on carbon. The mixture was immediately hydrogenated on a Parr apparatus at 39 psig. A pressure decrease to 25.5 psig was noted within 1 hr with no additional pressure decrease in the next 2 hr. The catalyst was removed by filtration. The methanol was removed *in vacuo*. The residue was distilled to give 24.8 g (78%) of *sym*-bis(3,3-dimethylaminopropyl)tetramethyldisiloxane: bp 77–79° (0.05 mm); $n^{25}D$ 1.4351; neut equiv 164.5 (calcd 152.3); ir (CCl_4) 2770 (NMe_2), 1250 (SiMe), 1060 cm^{-1} (SiOSi). There was a small nearby peak in the glc chromatogram which integrated for about 10%, presumably 1-(3′-hydroxypropyl)-3-(3′-dimethylaminopropyl)tetramethyldisiloxane.

3,3-(Dimethoxypropyl)trimethoxysilane.—To 34.1 g (0.33 mol) of **1** at 75° containing 10^{-3} mol of chloroplatinic acid was added slowly 55.0 g of 75% trimethoxysilane (0.33 mol). No reaction was observed for some time after which the silane was added at a rate sufficient to maintain vigorous reflux. The mixture was then heated for an additional hour at 90°. Distillation gave 58 g (77%) of 3,3-dimethoxypropyltrimethoxysilane: bp 77–81° (6 mm); $n^{25}D$ 1.4090; d^{25}_4 1.030; RD 0.240 (calcd 0.244); ir (CCl_4) 2840 cm^{-1} (OCH_3); ir (CS_2) 1090 and 1190 cm^{-1} ($SiOCH_3$).

Dimethylchlorosilane and 1.—To 34.1 g (0.33 mol) of refluxing **1** that contained 10^{-3} mol of chloroplatinic acid was slowly added 31 g (0.33 mol) of dimethylchlorosilane. The catalyst was increased to 10^{-2} mol and the solution refluxed for 20 hr. The mixture did not show a peak in the glc above the peak corresponding to **1**; however, there was a new peak with a shoulder between dimethylchlorosilane and **1**. Distillation gave 10.5 g of this material: bp 68–72°; $n^{25}D$ 1.3808; ir (CCl_4) 2840 cm^{-1} $(OCH_3)_3$; ir (CS_2) 1257 and 803 ($SiCH_3$), 1190 and 1090 ($SiOCH_3$), 480 cm^{-1} (SiCl). The nmr (CCl_4) had peaks at τ 9.58 $(CH_3)_2Si(OMe)Cl$ and 9.91 $(CH_3)_2Si(OMe)_2$ in a ratio of 1.6:1. The material boiling below 68° was a mixture of at least seven compounds and presumably contained methyl propenyl ether.

***sym*-Bis(3-hydroxypropyl)tetramethyldisiloxane.**—To 1.0 g (20 mmol) of lithium aluminum hydride in 30 ml of ether was slowly added 3.0 g (12 mmol) of **5**. The excess lithium aluminum hydride was decomposed with methanol and 3 *N* hydrochloric acid after the evolution of hydrogen ceased. The organic layer was separated and dried over sodium sulfate and then the ether was removed *in vacuo* to give 2.8 g of *sym*-bis(3-hydroxypropyl)tetramethyldisiloxane, $n^{25}D$ 1.4495 (lit.[8] $n^{25}D$ 1.4472).

Registry No.—**2,** 26542-45-0; **4,** 26542-46-1; **5,** 26542-47-2; **5** (2,4-DNP), 26599-12-2; **6,** 26542-48-3; **8,** 26542-49-4; **8** (2,4-DNP), 26542-50-7; **8** (oxime), 26542-51-8; 1-methoxy-3-(3′,3′-dimethoxypropyl)tetramethyldisiloxane, 26542-52-9; hexamethyltrisiloxane-1,5-dipropanol, 26542-53-0; hexamethyltrisiloxane-1,5-dipropanol (2,4-DNP), 26542-54-1; *sym*-bis(3,3-dimethylaminopropyl)tetramethylsiloxane, 26-526 97-6; 3,3-dimethoxypropyltrimethoxysilane, 25760-57-0; *sym*-bis(3-hydroxypropyl)tetramethyldisiloxane, 18001-97-3.

[8] J. L. Speier, M. P. David, and B. A. Eynon, *J. Org. Chem.*, **25**, 1637 (1960).

The Reaction of Lithium Acyl Carbonyl Metalates with Organic Halides

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Reaction of lithium acyl tetracarbonylferrates with benzyl halides or acid halides in ether yielded unsymmetrical ketones, while lithium acyl tricarbonylnickelates gave α-benzylacyloins or stilbenediol diesters by reaction with benzyl halides or acid halides, respectively. A dinuclear structure was suggested for lithium acyl tricarbonylnickelates based on the chemical behaviors of the complexes and the results of an infrared study, and furthermore an allusion to alkoxy- or acyloxycarbene metal complexes as precursors to unsymmetrical ketones, α-benzylacyloins, and stilbenediol diesters was made.

Organolithium compounds are reactive toward carbonyl metals and add reductively to the metals even at low temperature to form rather stable anionic metal complexes. Two different aspects of such reactions with organolithium compounds have received recent attention: (1) the synthesis of carbene–transition metal complexes using hexacarbonyls of chromium, molybdenum, and tungsten;[1] (2) the organic synthesis by means of pentacarbonyliron[2,3] and tetracarbonylnickel.[4,5] The carbonyls of iron or nickel are the most reactive toward organolithium compounds. Especially, reactions of alkyl- or aryllithiums with tetracarbonylnickel proceed exothermically even at −70° to

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(1) E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100**, 2445 (1967); E. O. Fischer and A. Riedel, *ibid.*, **101**, 156 (1968).

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(3) Y. Sawa, M. Ryang, and S. Tsutsumi, *Tetrahedron Lett.*, 5189 (1969).

(4) M. Ryang, K.-M. Song, Y. Sawa, and S. Tsutsumi, *J. Organometal. Chem.*, **5**, 305 (1966).

(5) Y. Sawa, I. Hashimoto, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **33** 2159 (1968).

form lithium acyl tricarbonylnickelates. These anionic complexes are not stable enough for the structural study. Nevertheless, they have been found to be useful reagents for organic synthesis because of the tendency to facile decomposition even under mild conditions to organic compounds and because of the versatile reactivities in organic reactions. Thus, aldehydes,[2] acyloins,[4] α diketones,[4] and 1,4 diketones[5] have been synthesized in good yields by means of these metalate complexes.

In recent years, a variety of anionic organometallic complexes have been shown to be excellent nucleophilic reagents in various synthetic reactions, *e.g.*, lithium dialkylcuprate,[6,7] sodium dicyanocuprate,[8] potassium hexacyanodinickelate (1),[9,10] and reagents[9] from tetracarbonylnickel and alkali metal alkoxides. Lithium acyl carbonyl metalate is one of these type reagents, admitting acyl group to add nucleophilically to carbon of organic halides.

We have reported previously that lithium acyl tetracarbonylferrates react with benzyl halides or acid halides to produce unsymmetrical ketones in rather good yields.[3] During the course of our study, it was reported that lithium acyl tricarbonylnickelates react with α,β-unsaturated carbonyl compounds to give 1,4-dicarbonyl compounds in excellent yields.[11]

This report deals with the syntheses of unsymmetrical ketones, α-benzylacyloins, and stilbenediol diesters by using acyl carbonyl metalates as nucleophilic acylating reagent to benzyl halides or acid halides, reactions which offer a useful method for the preparation of the above type compounds. Furthermore, the mechanism of the reaction was discussed on the basis of reaction products and the results of ir study of acyl carbonyl metalates. In this report, we wish to propose that the formation of alkoxy- or acyloxycarbene–metal complexes is antecedent to unsymmetrical ketones, α-benzylacyloins, and stilbenediol diesters.

Results and Discussion

A. Syntheses of Unsymmetrical Ketones by the Reactions of Lithium Acyl Tetracarbonylferrates with Benzyl Halides or Acid Halides.—Into the ethereal solution of lithium acyl tetracarbonylferrate, prepared by the reaction between equimolar amounts of organolithium compound and pentacarbonyliron, was added benzyl halide at −50°, and then the reaction mixture was warmed to the reflux temperature of ether or ether–benzene. After hydrolysis, corresponding benzyl ketones were isolated in moderate yields. The results are listed in Table I.

Unsymmetrical ketones could not be isolated from the reactions with ethyl bromide, bromobenzene, and 1,2-dibromoethane. When acid chlorides were used instead of benzyl halides, unsymmetrical ketones were formed as main products and α diketones as by-products (Table II). These yields are not very good at present, but we think that they will become higher if the reaction is carried out under more suitable reaction conditions.

TABLE I

$$\mathrm{Li[RCOFe(CO)_4] + C_6H_5CH_2X \longrightarrow RCOCH_2C_6H_5}$$

R	$C_6H_5CH_2X$	Product	Yield, %[a]
C_6H_5	$C_6H_5CH_2Br$	$C_6H_5COCH_2C_6H_5$	73
p-$CH_3C_6H_4$	$C_6H_5CH_2Br$	p-$CH_3C_6H_4COCH_2C_6H_5$	67
n-C_4H_9	$C_6H_5CH_2I$	n-$C_4H_9COCH_2C_6H_5$	50

[a] Yields were calculated on the basis of the amount of benzyl halides used.

TABLE II

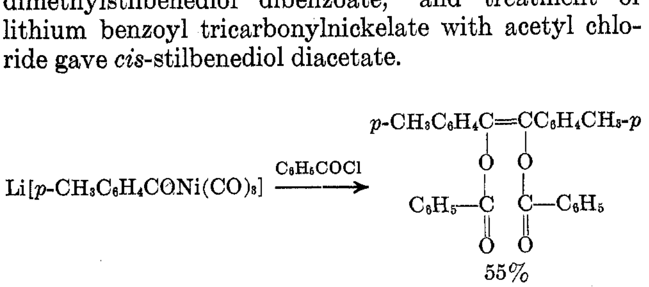
$$\mathrm{Li[RCOFe(CO)_4] + R'COX \longrightarrow RCOR' + RCOCOR'}$$

R	R'COX	Product	Yield, %[a]
C_6H_5	C_6H_5COCl	$C_6H_5COC_6H_5$	22
		$C_6H_5COCOC_6H_5$	10
C_6H_5	CH_3COCl	$C_6H_5COCH_3$	54
		$C_6H_5COCOCH_3$	Trace
C_6H_5	$C_6H_5CH{=}CHCOCl$	$C_6H_5COCH{=}CHC_6H_5$	22
p-$CH_3C_6H_4$	C_6H_5COCl	p-$CH_3C_6H_4COC_6H_5$	21
		p-$CH_3C_6H_4COCOC_6H_5$	Trace
n-C_4H_9	C_6H_5COCl	n-$C_4H_9COC_6H_5$	36

[a] Yields were calculated on the basis of the amount of acid halides used.

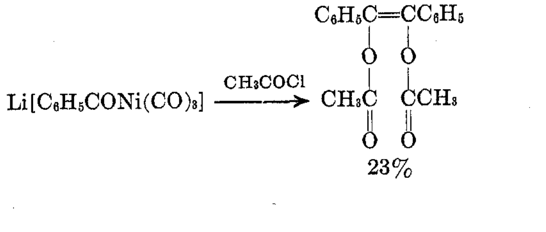
B. Formation of α-Benzylacyloins by the Reaction of Lithium Acyl Tricarbonylnickelates with Benzyl Halides.—Contrary to the formation of benzyl alkyl (or aryl) ketones in the case of lithium acyl tetracarbonylferrates, treatment of lithium acyl tricarbonylnickelates with benzyl halides resulted in the formation of α-benzylacyloins, and no benzyl ketones were obtained in significant amounts. Some other alkyl halides such as ethyl bromide or methyl chloride failed to yield detectable amounts of the products formed by the nucleophilic displacement of halogen. The results are listed in Table III.

C. Formation of Stilbenediol Diesters by the Reaction of Lithium Aroyl Tricarbonylnickelates with Acid Halides.—Nucleophilic displacement of halogen in acid halides with lithium aroyl tricarbonylnickelates led to the formation of stilbenediol diesters instead of the unsymmetrical ketones in the case of lithium acyl tetracarbonylferrates; the reaction of lithium p-toluyl tricarbonylnickelate with benzoyl chloride yielded 4,4'-dimethylstilbenediol dibenzoate,[4] and treatment of lithium benzoyl tricarbonylnickelate with acetyl chloride gave *cis*-stilbenediol diacetate.



$$\mathrm{Li[\mathit{p}\text{-}CH_3C_6H_4CONi(CO)_3] \xrightarrow{C_6H_5COCl} \mathit{p}\text{-}CH_3C_6H_4C(OCOC_6H_5){=}C(OCOC_6H_5)C_6H_4CH_3\text{-}\mathit{p}}$$

55%



$$\mathrm{Li[C_6H_5CONi(CO)_3] \xrightarrow{CH_3COCl} C_6H_5C(OCOCH_3){=}C(OCOCH_3)C_6H_5}$$

23%

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[6] E. J. Corey and G. H. Posner, *Tetrahedron Lett.*, 315 (1970), and references cited therein.

[7] G. M. Whitesides, W. F. Fischer, Jr., J. S. Filippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969).

[8] H. O. House and W. F. Fischer, Jr., *J. Org. Chem.*, **34**, 3626 (1969).

[9] E. J. Corey and L. S. Hegdeus, *J. Amer. Chem. Soc.*, **91**, 1233 (1969).

[10] I. Hashimoto, M. Ryang, and S. Tsutsumi, *Tetrahedron Lett.*, 3291 (1969).

[11] E. J. Corey and I. S. Hegedus, *J. Amer. Chem. Soc.*, **91**, 4926 (1969).

TABLE III

$Li[RCONi(CO)_3] + C_6H_5CH_2X \longrightarrow RCOC(CH_2C_6H_5)(OH)R$

R	$C_6H_5CH_2X$	Product	Yield,[a] %
C_6H_5	$C_6H_5CH_2Br$	$C_6H_5COC(CH_2C_6H_5)(OH)C_6H_5$	41
$p\text{-}CH_3C_6H_4$	$C_6H_5CH_2Cl$	$p\text{-}CH_3C_6H_4COC(CH_2C_6H_5)(OH)C_6H_4CH_3\text{-}p$	73[b]
$n\text{-}C_4H_9$	$C_6H_5CH_2Br$	$n\text{-}C_4H_9COC(CH_2C_6H_5)(OH)C_4H_9\text{-}n$	58

[a] Yields were calculated on the basis of the amount of organolithium used. [b] From ref 4.

D. Structure of Lithium Acyl Carbonyl Metalates.—The above results show a remarkable difference in reaction behavior between the complexes from tetracarbonylnickel and those from pentacarbonyliron. That is, the products from nickel complexes always contain two organic groups from the original complexes, while in the case of iron complexes only one organic group is introduced. This tendency coincides well with the previously reported results; lithium acyl tricarbonylnickelates give acyloins[4] by hydrolysis, α diketones[4] by thermal decomposition, and 1,4 diketones[5] by the reaction with acetylenes, while lithium acyl tetracarbonylferrates[2] and pentacarbonyl metalates[1] of chromium, molybdenum, and tungsten give aldehydes by hydrolysis, but does not yield 1,4 diketone from the reaction with acetylenes.

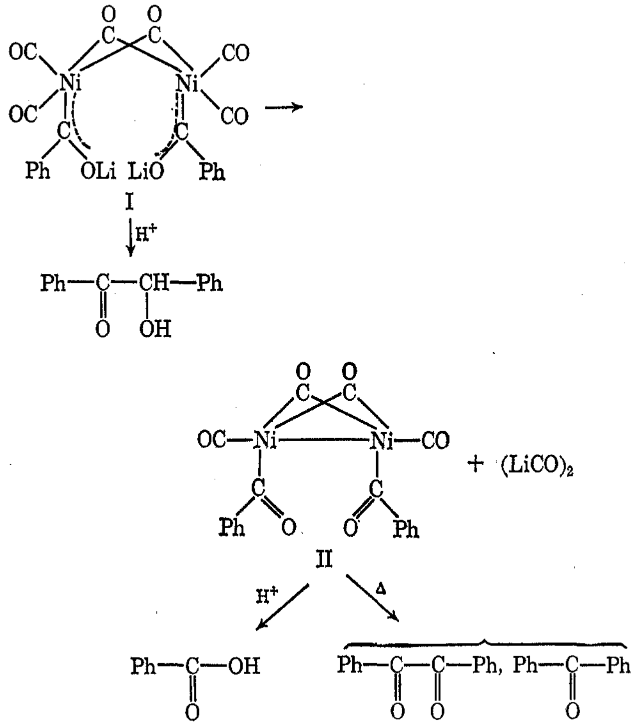
The structure of the acyl carbonyl metalates derived from the carbonyls of iron,[12] chromium,[1] molybdenum,[1] and tungsten[1] have been studied by Fischer and coworkers and found to be monomeric carbene complexes.

Furthermore, it is well known that the mononuclear carbonylferrate anion exists, but no monomeric carbonylnickelate anion has been known. These results provide one suggestion regarding the dinuclear nature of the present nickelate complexes, although the relation between the structure of metal complexes and the decomposition products has not yet been established.

So to ascertain the dinuclear nature of the nickelate complex, the infrared spectrum of the reaction mixture from phenyllithium and tetracarbonylnickel in ether was measured at room temperature.

Absorption frequencies at 1550–2300 cm^{-1} are as follows: 1585 (w), 1590 (w), 1595 (m), 1640 (w), 1660 (w) 1690 (w), 1745 (w), 1855 (m), 1915 (s, broad), 1962 (vs), 2010 (w), 2130 (w), 2190 (w), and 2225 cm^{-1} (w) (vs = very strong, s = strong, m = medium, w = weak intensity). Although unequivocal assignment of the above absorption is rather difficult because of the complexity, the following assignments were considered to be probable by referring to the so far known absorption spectra[13] of carbonyl metals and their derivatives. The main absorptions at 1962, 1915, 1855, and 1745 cm^{-1} would be due to lithium benzoyl tricarbonylnickelate. The absorptions at 1962, 1915, and 1855 cm^{-1} were assigned to the stretching of terminal carbonyl of anionic nickel complex (I in Scheme I), 1745 cm^{-1} to its bridged carbonyl, and 1595 cm^{-1} to the carbonyl of the benzoyl group, which has decreased bond order due to the anionic nature. Herein, the presence of bridged carbonyl provides spectral proof for the dinuclear nature of the carbonylnickelate complex. The remaining weak absorptions were considered to be due to the decomposition products of the carbonylnickelate complex: 2010 cm^{-1} to the terminal carbonyl of neutral benzoyl carbonylnickel (II in Scheme I), 1640 cm^{-1} to carbonyl of benzoyl group bonded to nickel(II), 2225, 2190, 2130, 1590, and 1585 cm^{-1} to the so-called lithium carbonyl,[14] and 1690 and 1660 cm^{-1} to the carbonyl of bibenzoyl and benzophenone, respectively.

SCHEME I



So it was considered to be probable that the ethereal solution of lithium benzoyl tricarbonylnickelate at room temperature consists of the complex I (main), the complex II, lithium carbonyl, bibenzoyl, and benzophenone as shown in Scheme I.

In accordance with this proposal, the hydrolysis of the reaction mixture at room temperature gave benzoin (72%), bibenzoyl (7.8%), benzophenone (7.9%), benzyl phenyl ketone (2%), biphenyl (3%), and benzoic acid (4%). Herein, benzoin corresponds to the anionic complex (I) and its good yield suggests that the complex I is rather stable in ether solution even at room temperature. The formation of benzoic acid is chemical evidence for the presence of the neutral benzoyl carbonylnickel complex (II). Thus, the structure and decomposition scheme of the nickelate complex may be described as shown in Scheme I, which are compatible with the available data.

On the other hand, the infrared spectra of the ether solution of the carbonylferrate complexes, prepared by

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(12) E. O. Fischer, V. Kiener, and R. D. Fischer, *J. Organometal. Chem.*, **16**, 60 (1969).

(13) F. Calderazzo, R. Ercoli, and G. Natta, in "Organic Synthesis *via* Metal Carbonyls," I. Wender and P. Pino, Ed., Wiley, New York, N. Y., 1968, p 241.

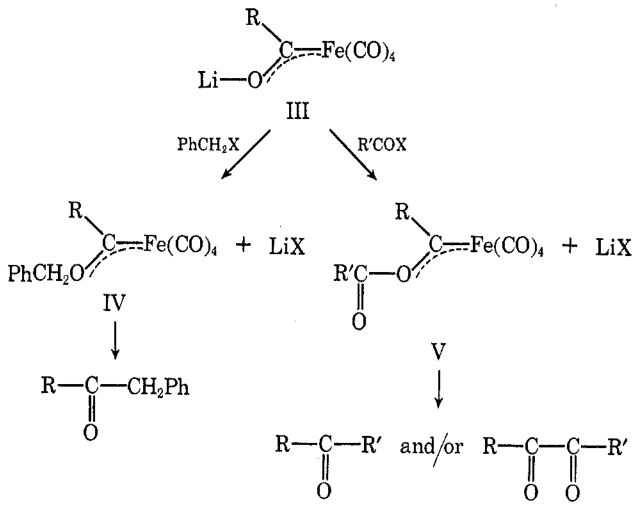
(14) W. Büchner, *Helv. Chim. Acta*, **46**, 2111 (1963).

the reaction of phenyllithium and pentacarbonyliron, show absorptions at 1945, 1940, 1900, and 1860 cm^{-1} due to terminal carbonyl and 1595 cm^{-1} due to the carbonyl of the benzoyl group bonded to iron ($\overset{\text{Ph}}{\underset{\text{Fe}}{\geqslant}}$=OLi) but no absorption due to bridged carbonyl in accordance with its monomeric chemical properties.

E. Precursors to Unsymmetrical Ketones, α-Benzylacyloins, and Olefin Diol-Diesters.—Although there is as yet no clearcut evidence for the structure of lithium acyl carbonyl metalates, the results discussed above suggest that the nucleophilic attack of the acyl carbonyl metalates to the carbon of benzyl halides or acid halides would provide carbene iron or nickel carbonyl complexes, which are precursors to unsymmetrical ketones, α-benzylacyloins, and stilbenediol diesters.

Thus the scheme for the formation of unsymmetrical ketones from the reactions of lithium acyl carbonylferrates with benzyl halides or acid halides may be described (Scheme II). As described in the Experimental Section, in the course of the reaction between lithium benzoyl tetracarbonylferrate and acetyl chloride at the reflux point of ether, lithium chloride was precipitated and the ether soluble part, after removal of ether and pentacarbonyliron, showed the following absorptions in its infrared spectrum: 2050 (s), 1994 (vs), 1982 (vs), 1770 (m), 1218 (s), 740 (vs), and 700 cm^{-1}.

SCHEME II

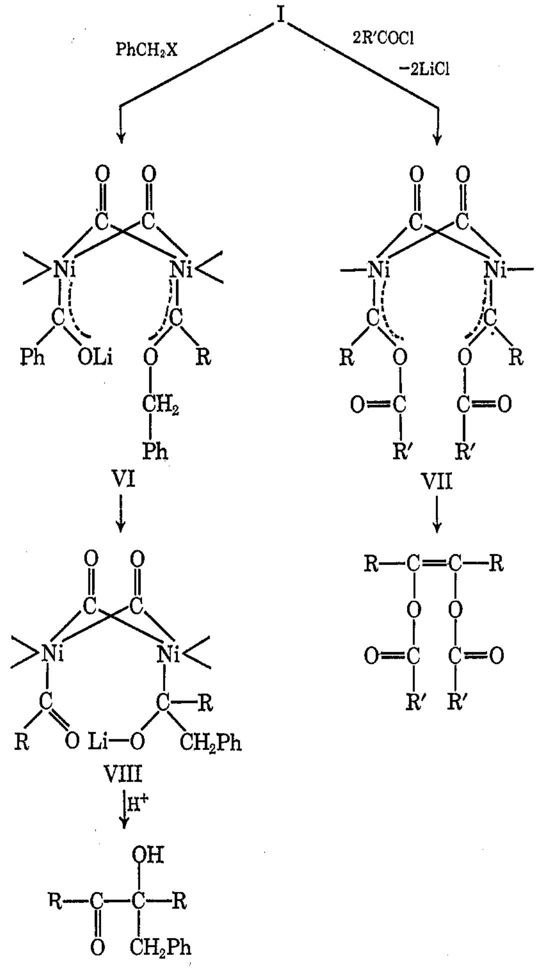


Absorptions at 2050, 1994, and 1982 cm^{-1} were assigned to stretching of terminal carbonyl of complex V, 1770 cm^{-1} to carbonyl stretching of acetoxy group, 1218 cm^{-1} to CO– stretching of acetoxycarbene group, and 740, 700 cm^{-1} to phenyl group. Distillation of this ether soluble part gave acetophenone in 54% yield. So phenyl acetoxycarbene–iron complex (V) seems to be the precursor to acetophenone with confidence.

Similarly, the ether soluble part, obtained by the reaction between lithium benzoyl tetracarbonylferrate and benzyl bromide, shows the presence of phenyl benzyloxycarbene–iron complexes (IV) in the infrared spectrum and distillation gave benzyl phenyl ketone.

In the case of lithium acyl tricarbonylnickelate (I), the intermediate complexes, formed by the reaction with organic halides, are unstable and decompose readily at room temperature to α-benzylacyloins or stilbenediol diesters, so infrared spectra of the intermediate complexes were not measured. Nevertheless, by analogy with the reaction of lithium acyl tetracarbonylferrates, it was considered to be probable that a nucleophilic attack of lithium acyl tricarbonylnickelate (I) to carbon of organic halide would lead to dinuclear alkoxy- or acyloxycarbene–nickel complexes (VI, VII). As shown in Scheme III, coupling of two of the acyloxycarbenes in VII results in the formation of stilbenediol diester. When benzyl halides were used, the benzyl group in benzyloxycarbene complex (VI) would migrate from oxygen to carbon, providing complex VIII, which decomposes to give α-benzylacyloins.

SCHEME III



Further work both on the applications of these lithium acyl carbonyl metalates to the organic synthesis and the structural study is currently underway and will be the subject of future reports.

Experimental Section

Phenyllithium and *p*-tolyllithium were prepared from bromobenzene or *p*-bromotoluene and lithium in anhydrous diethyl ether. *n*-Butyllithium and pentacarbonyliron were obtained commercially, and tetracarbonylnickel was prepared from nickel chloride and carbon monoxide by the method reported by Chiusoli and Mandelli.[15] All the reactions were carried out under a nitrogen atmosphere freed of oxygen by passing through active copper and molecular sieves 5A. Infrared spectra were run on a Shimazu IR-27 in the case of KBr disks, or Hitachi 225 in the case of solutions of the reaction mixtures.

The Reaction of Phenyllithium with $Ni(CO)_4$.—Into a 500-ml four-necked flask equipped with a mechanical stirrer, a thermometer, a reflux condenser attached to a gas bubbler with liquid paraffin, a dropping funnel, and a gas inlet was placed 15 g (0.0875 mol) of $Ni(CO)_4$ in 50 ml of anhydrous diethyl ether. The mixture was cooled to −70° (Dry Ice–trichloroethylene), and 100 ml of an ethereal solution of phenyllithium (0.0875 mol) was added slowly maintaining the temperature at −70 to −65°. The reaction mixture was stirred for 2 hr at −70° and then warmed to 18°. After the mixture was stirred for 3 hr at 18°, 1 ml of the reaction mixture was sucked in a hypodermic syringe and an ir spectrum was measured with a liquid cell of 0.1 mm thickness. The remaining mixture was hydrolyzed with 50 ml of 4 *N* HCl and 300 ml of benzene was added. After the mixture was separated into an organic phase and an aqueous phase, the aqueous phase was washed with 100 ml of benzene and the combined organic phase was washed with 50 ml of saturated $NaHCO_3$ solution and 50 ml of saturated NaCl and dried ($MgSO_4$). After removal of solvent, the residue crystallized spontaneously on cooling, and these crystals were recrystallized from benzene to give 6.68 g of benzoin, mp and mmp 134°. The filtrate was distilled under reduced pressure to give 2.06 g of the fraction, bp 50 (15 mm) to 188° (0.2 mm). The fraction was separated and identified by a preparative glc and ir spectra; it contained bibenzoyl (0.72 g), benzyl phenyl ketone (0.18 g), benzophenone (0.63 g), and biphenyl (0.2 g). The combined aqueous $NaHCO_3$ and NaCl phase was neutralized with 2 *N* HCl, saturated with NaCl, and extracted with 100 ml of ether. The ether phase was dried ($MgSO_4$) and concentrated. The residue (0.42 g) crystallized on standing, and the crystals were identified as benzoic acid after recrystallization from ethanol.

Reaction of Lithium Acyl Tricarbonylnickelates with Organic Halides. A. Formation of α-Benzylbenzoin.—Into a solution of lithium benzoyl tricarbonylnickelate (0.0216 mol), prepared as described above, was added benzyl bromide (3.8 g, 0.0216 mol) in 10 ml of ether with stirring at −70°. The mixture was stirred for 1 hr at −70° and slowly warmed to 20°. After the stirring was continued for 5 hr, the mixture was hydrolyzed with 50 ml of 4 *N* HCl and separated into an ethereal phase and an aqueous phase. The ethereal extracts were dried ($MgSO_4$), concentrated, and distilled giving 1.33 g of α-benzylbenzoin: mp 118.5–119.5°; ir 3500 (OH), 1680 cm^{-1} (C=O); nmr ($CDCl_3$) τ 2.2–3.1 (m, broad, 15), 6.33 (dd, 2), 6.33 (s, broad, 1, disappeared on adding D_2O).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00; mol wt, 302. Found: C, 83.21; H, 6.13; mol wt (vapor pressure osmometer, benzene), 298.

Oxidation of this material by using lead tetraacetate in 90% aqueous acetic acid gave benzyl phenyl ketone and benzoic acid.

B. Formation of 5-Benzyl-5-hydroxy-4-decanone.—A solution of lithium valeryl tricarbonylnickelate was prepared from reaction of *n*-butyllithium (19.2 ml, 1.56 *M* in *n*-hexane) and $Ni(CO)_4$ (5.1 g, 0.03 mol) in 50 ml of ether at −70° for 5 hr. Benzyl bromide (5.1 g, 0.03 mol) in 20 ml of ether was added to the solution at −70°, after which the reaction mixture was kept at −70° for 3 hr. The mixture was slowly warmed to 13° and stirred for 5 hr. After treatment of the mixture carried out as mentioned above, 5-benzyl-5-hydroxy-4-decanone (2.9 g) was obtained, which was purified by glc (79% purity): ir 3500 (OH), 1720 cm^{-1} (C=O); nmr ($CDCl_3$) τ 2.8 (s, 5), 6.58 (s, 1, OH), 7.07 (s, 2), 7.5–8.13 (m, complex, 18).

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99; mol wt, 262.38. Found: C, 77.66; H, 10.22; mol wt (mass spectrum), 262.

C. Formation of α,α′-Stilbenediol Diacetate.—From a similar reaction of lithium benzoyl tricarbonylnickelate (0.0127 mol) with acetyl bromide (1.5 g, 0.0127 mol), there was obtained 0.43 g of *cis*-α,α′-stilbenediol diacetate: mp 118–119° (lit.[16] 119°); ir 1770 (C=O), 1250 cm^{-1} (COC); nmr ($CDCl_3$) τ 2.8 (s, 10), 7.8 (s, 6).

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 73.23; H, 5.46.

Reaction of Lithium Acyl Tetracarbonylferrates with Organic Halides. A. Formation of Acetophenone.—To 20 ml of ether in a similar apparatus to the reaction of lithium acyl nickel complexes was added 5.9 g of $Fe(CO)_5$ (0.03 mol). The mixture was cooled to −50°, and phenyllithium (0.03 mol, 34 ml of 0.9 *M* solution in ether) was added maintaining the temperature at −50 to −40°. The mixture was stirred for 2 hr at −40°, warmed to 18°, and stirred for 2 hr. The mixture (1 ml) was sucked in a hypodermic syringe and the ir spectrum was measured. The remaining mixture was again cooled at −30° and acetyl chloride (2.3 g, 0.03 mol) was added slowly. After 100 ml of benzene had been added, the mixture was slowly warmed to 60° and stirred for 1.5 hr. After filtration, the filtrate was concentrated with a rotary evaporator giving a dark brown residue. A little of the residue was submitted to ir spectrum measurement and the remaining material was distilled giving acetophenone (1.95 g) and acetylbenzyl (trace). Analysis and identifications were made by glc.

B. Formation of Benzyl Phenyl Ketone.—Into a solution of lithium benzoyl tetracarbonylferrate (0.03 mol) was added benzyl bromide (5.1 g, 0.03 mol) and 100 ml of benzene at −30°. Then the reaction mixture was kept at 60° for 5 hr with stirring. After filtering the mixture, a filtrate was freed of solvent and the ir spectrum of the residue was measured: ir 2050, 1990, 1980, 1690, 1205, 757, 730, 698, 690 cm^{-1}. Absorptions at 2050, 1990, 1980, 1205, 730, and 690 cm^{-1} would be due to the carbonyliron complex IV and at 1690, 757, and 698 cm^{-1} to benzyl phenyl ketone.

The remaining residue was distilled, yielding 4.27 g of benzyl phenyl ketone as crude product. The glc analyses showed 8% impurity in the crude product. Recrystallization from petroleum ether (40–60°) gave the ketone as white crystals, mp and mmp 56–57°, ir 1690 cm^{-1} (C=O).

C. Formation of Benzal Acetophenone.—From a similar reaction of lithium benzoyltetracarbonylferrate (0.03 mol) with cinnamoyl chloride (5 g, 0.03 mol) was obtained 1.4 g of benzal acetophenone. Ir and glc analysis were identical with those of authentic sample, ir 1675 cm^{-1} (C=O).

D. Formation of Benzophenone.—From the reaction of lithium benzoyl tetracarbonylferrate (0.05 mol) with benzoyl chloride (7.1 g, 0.05 mol) was obtained 3.1 g of crude product. Glc analyses showed it to contain benzophenone (2.0 g) and bibenzoyl (1.1 g).

E. Formation of Benzyl *p*-Tolyl Ketone.—From the reaction of lithium *p*-toluyl tetracarbonylferrate, prepared from the reaction of *p*-tolyllithium (0.05 mol) and $Fe(CO)_5$ in 100 ml of ether with benzyl bromide (8.6 g, 0.05 mol), was obtained 7.1 g of benzyl *p*-tolyl ketone, mp and mmp 109–110.5°.

F. Formation of Benzyl *n*-Butyl Ketone.—Into a solution of lithium valeryl tetracarbonylferrate (0.045 mol) prepared from the reaction of *n*-butyllithium and $Fe(CO)_5$ was added benzyl iodide (9.8 g, 0.045 mol) and the reaction mixture was treated as mentioned above, giving benzyl *n*-butyl ketone as a crude product. The yield was determined to be 4 g of the ketone by glc, and the crude product was purified by column chromatography: ir 1720 cm^{-1} (C=O); nmr ($CDCl_3$) τ 2.79 (s, 5), 6.35 (s, 2), 7.58 (t, 2), 8.60 (m, broad, 4), 9.15 (t, 3).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 81.77; H, 9.15. Found: C, 81.59; H, 8.86.

G. Reaction of Lithium *p*-Toluyl Tetracarbonylferrate with Benzoyl Chloride.—From reaction of lithium *p*-toluyl tetracarbonylferrate (0.05 mol) with benzoyl chloride (7.1 g, 0.05 mol) was obtained 2.1 g of 4-methylbenzophenone and 0.2 g of 4-methylbibenzoyl, which were determined by glc. Authentic samples of 4-methylbenzophenone and 4-methylbibenzoyl were prepared by oxidizing phenyl *p*-tolyl carbinol or 4-methylbenzyl phenyl ketone, respectively.

H. Reaction of Lithium Valeryl Tetracarbonylferrate with Benzoyl Chloride.—From reaction of lithium valeryl tetracarbonylferrate (0.045 mol) with benzoyl chloride (6.3 g, 0.045 mol) was obtained 2.6 g of *n*-butyl phenyl ketone, determined by glc comparison with an authentic sample prepared by oxidizing *n*-butyl phenyl carbinol.

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(15) G. Chiusoli and G. Mandelli, Italian Patent 652,138; *Chem. Abstr.*, **61**, 2763*g* (1964).

(16) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1957, p 176.

Registry No.—2-Benzylbenzoin, 7540-93-4; 5-benzyl-5-hydroxy-4-decanone, 26431-42-5; *cis*-α,α'-stilbenediol diacetate, 26431-43-6; benzyl *n*-butyl ketone, 25870-62-6; Li[$PhCOFe(CO)_4$], 26402-46-0; Li[*p*-$CH_3C_6H_4COFe(CO)_4$], 26402-47-1; Li[*n*-$C_4H_9COFe(CO)_4$], 26402-48-2; $C_6H_5CH_2Br$, 100-39-0; $C_6H_5CH_2I$, 620-05-3; C_6H_5COCl, 98-88-4; CH_3COCl, 75-36-5; $C_6H_5CH{=}CHCOCl$, 102-92-1; Li[$PhCONi(CO)_3$], 26402-49-3; Li[*p*-$CH_3C_6H_4CONi(CO)_3$], 26402-50-6; Li[*n*-$C_4H_6CONi(CO)_3$], 26402-51-7; $C_6H_5CH_2Cl$, 100-44-7.

Synthesis of Long-Chain *tert*-Alkylbenzenes by the Grignard–Wurtz Reaction

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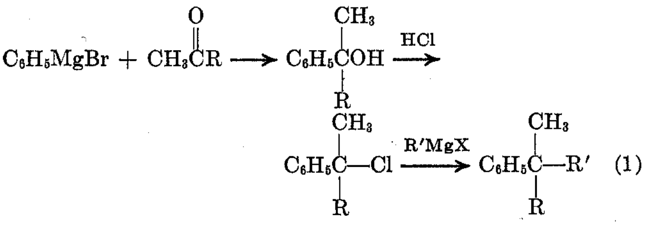
The Grignard–Wurtz reaction was extended to the synthesis of eleven long-chain mono- and di-*tert*-alkylbenzenes. In this reaction nonpolar media, such as *n*-hexane or *n*-heptane, gave yields double those obtained in diethyl ether. In nonpolar media the major side reaction was substitution of halogen by hydrogen in the starting benzylic halides. This reduction apparently does not proceed by functional exchange.

The synthesis of high-molecular-weight hydrocarbons of good purity is of continuing interest for the elucidation of structure–property relationships.[1] In our own laboratories we were interested in *tert*-alkylbenzenes, particularly di-*tert*-alkylbenzenes. Only 25 mono-*tert*-alkylbenzenes have been prepared[2] by routes not likely to lead to rearranged side chains and in none of these did the *tert*-alkyl group have more than 12 carbon atoms. We could find no example, other than *p*-di-*tert*-butylbenzene, of a di-*tert*-alkylbenzene of unquestionable structure. In this paper we report 11 new *tert*-alkylbenzenes, four of which have a *p*-di-*tert*-alkyl structure.

Two general routes to *tert*-alkylbenzenes have been described in the literature: an eight-step sequence developed by Rabjohn involving as the key step the 1,4 addition of Grignard reagents to alkylidenecyanoacetates,[2j,3] and the Grignard–Wurtz reaction.[2a,c,k]

In contrast to the alkylidenecyanoacetate route, the Grignard–Wurtz route involves only three steps: preparation of a tertiary alcohol by the familiar Grignard–ketone condensation, conversion of the alcohol to a tertiary chloride by means of anhydrous hydrogen chloride, and coupling of the tertiary chloride with a second Grignard reagent. Because of its apparent simplicity, this route seemed more suitable for extension to the synthesis of long-chain *tert*-alkylbenzenes and especially di-*tert*-alkylbenzenes.

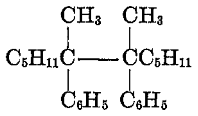


$$C_6H_5MgBr + CH_3\overset{O}{\overset{\|}{C}}R \longrightarrow C_6H_5\underset{R}{\overset{CH_3}{C}}OH \xrightarrow{HCl} C_6H_5\underset{R}{\overset{CH_3}{C}}{-}Cl \xrightarrow{R'MgX} C_6H_5\underset{R}{\overset{CH_3}{C}}{-}R' \quad (1)$$

1

a, R = pentyl; R′ = decyl
b, R = hexyl; R′ = octyl
c, R = pentyl; R′ = butyl

We first investigated this scheme for the synthesis of 6-methyl-6-phenylhexadecane (**1a**) by the coupling of decylmagnesium bromide with 2-chloro-2-phenylheptane. This reaction yielded 1-decane, 1-decene, 2-phenylheptane, a mixture of isomeric 2-phenylheptenes, eicosane, and a high-boiling solid residue in addition to the desired **1a**. The high-boiling solid residue consisted predominantly of 6,7-dimethyl-6,7-diphenyldodecane (**2**), a dimeric coupling product derived from 2-chloro-2-phenylheptane.[4] No chlorodecane and only small amounts, <2%, of 1-bromodecane could be detected in the product mixture by gas chromatography.



$$C_5H_{11}\underset{C_6H_5}{\overset{CH_3}{C}}{-}\underset{C_6H_5}{\overset{CH_3}{C}}C_5H_{11}$$

2

The product distribution, shown in Table I, was strongly influenced by changes in the reaction medium. Thus, the amount of **1a** in the product mixture, expressed as gas chromatography area %, increased from 7.5% in tetrahydrofuran at 60–80°, to 22% in refluxing ether, to 46% in *n*-hexane at 70–75°. The concentration of 2-phenylheptane remained relatively constant at 14–16% of the product mixture. On the other hand, polar media favored the formation of 1-decene, decane, and 2-phenyl-2(1)-heptene.[5]

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[2] (a) A. D. Petrov and E. P. Zakharov, *J. Gen. Chem. USSR*, **27**, 3019 (1957); (b) A. D. Petrov, G. I. Nikishin, and V. D. Vorobiev, *ibid.*, **28**, 1809 (1958); (c) M. S. Malinovskii and A. A. Yavorovskii, *ibid.*, **25**, 2169 (1955); (d) A. D. Petrov, G. I. Nikishin, and V. D. Vorobiev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 717 (1960); (e) A. D. Petrov, O. M. Nefedov, and Yu. N. Ogibin, *ibid.*, 1004 (1957); (f) K. Ziegler, H. Grimm, and R. Willer, *Justus Liebigs Ann. Chem.*, **542**, 90 (1940); (g) V. N. Gramenitskaya, G. I. Nikishin, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **128**, 548 (1959); (h) M. S. Malinovskii and A. A. Yavorovskii, *Ukr. Khim. Zh.*, **21**, 723 (1955); *Chem. Abstr.*, **50**, 11961 (1956); (i) G. M. K. Hughes, *J. Chem. Soc.*, 3703 (1958); (j) E. R. Lynch and E. B. McCall, *ibid.*, 1254 (1960); (k) M. Inatome, J. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Amer. Chem. Soc.*, **74**, 292 (1952); (l) F. W. Gray and K. J. Krems, *J. Org. Chem.*, **26**, 209 (1961); (m) L. V. Bugrova and I. P. Tsukervanik, *Zh. Org. Khim.*, **1**, 714 (1965); (n) H. S. Block, U. S. Patent 3,268,610 (1966).

[3] (a) N. Rabjohn, L. V. Phillips, and R. J. DeFeo, *J. Org. Chem.*, **24**, 1964 (1959); (b) G. Desgrandchamps, A. Deluzarche, and A. Maillard, *Bull. Soc. Chim. Fr.*, 264 (1961).

[4] The structure of this product was assigned on the basis of elemental and nmr analyses and its facile thermal cleavage to a 1:1 mixture of 2-phenylheptane and 2-phenyl-2(1)-heptene.

[5] Under the conditions of gas chromatographic analysis, compound **2** which was also formed in the reaction underwent partial cleavage to give an equimolar mixture of 2-phenylheptane and 2-phenyl-2(1)-heptene. Therefore, the amounts of 2-phenylheptane and 2-phenyl-2(1)-heptene shown in Table I are the sums of the amounts produced directly as well as by the cleavage reaction.