(H-2) which is *cis* oriented with respect to H-3 and H-3′.[7-9] The τ 8.33 signal reflects the deshielding effect of the proximate cyano groups on these cyclopropyl hydrogens (H-3, H-3′). Both the location and the shape of the τ 5.77 signal are consistent with the bridgehead (H-4, H-4′) assignment. The decoupling data (Table I) provide dramatically convincing evidence for the central location of the hydrogens producing this signal. Finally, the τ 3.77 signal is unexceptional and is assigned to the olefinic hydrogens (H-5, H-5′).

Registry No.—II, 16118-23-3.

[7] It is tempting to estimate the angles in the cyclopropyl ring by application of the Karplus[8] and Gutowsky, Karplus, Grant[9] correlations of *J* with vicinal dihedral and geminal angles, respectively. Since there are no polar groups directly attached to the three-membered ring, such a treatment may be reasonable. The values obtained (H_1–C–C–H_3 = 118°; H_2–C–C–H_3 = 30°; H_1–C–H_2 = 116°) agree well with predictions based on models.

[8] N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 49–50, and references cited therein.

[9] H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959); see also, R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, **7**, 335 (1966).

Synthesis of 1,4-Diketones by the Reaction of Lithium Aroyltricarbonylnickelates with Acetylenes

Yoshihiko Sawa, Isao Hashimoto, Membo Ryang, and
Shigeru Tsutsumi

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

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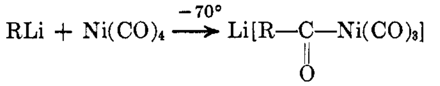
We have reported that aryllithiums reacted with nickel carbonyl at low temperature (−70°) in ether solution to give lithium aroyltricarbonylnickelates (I).[1]



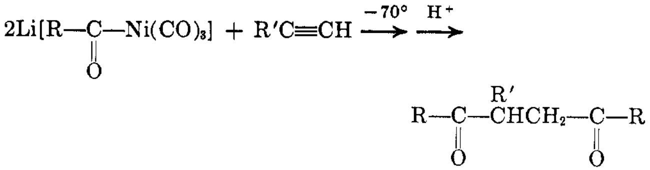
$$\mathrm{RLi} + \mathrm{Ni(CO)_4} \xrightarrow{-70^\circ} \mathrm{Li[R{-}\underset{\underset{O}{\|}}{C}{-}Ni(CO)_3]}$$

I

Fischer and Maasböl also described the formation of lithium benzoylpentacarbonyltungstate by the reaction of phenyllithium with tungsten hexacarbonyl,[2a] and they furthermore reported the formation of several lithium acyl- or aroylcarbonylmetalates.[2b]

Although an attempt to isolate the pure complexes of these metalates was unsuccessful, their synthetic applications were investigated since lithium aroyltricarbonylnickelates showed useful reactivity. For example, these complexes were reactive toward organic halides[1b] and toward unsaturated compounds[3] such as styrene because of their carbon–nickel σ bond.

Now we have investigated the reaction of lithium aroyltricarbonylnickelates with acetylenes and found that 2 mol of these complexes added to 1 mol of acetylenes at −70° to give 1,4-diketones (II) in yields of 47–74%, and γ-lactones were produced as by-products in yields of 2–24% when the reaction was carried out at higher temperature (−30°).



$$\mathrm{2Li[R{-}\underset{\underset{O}{\|}}{C}{-}Ni(CO)_3]} + \mathrm{R'C{\equiv}CH} \xrightarrow{-70^\circ} \xrightarrow{H^+} \mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}\overset{R'}{C}HCH_2{-}\underset{\underset{O}{\|}}{C}{-}R}$$

II (main product)

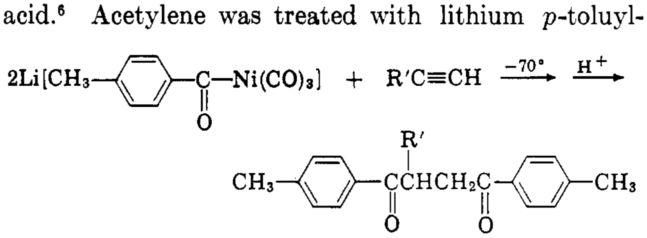
Several workers have reported that acetylenes insert between the acyl and metal carbonyl groups in acyl metal carbonyls. Heck isolated 2,3-diethyl-π-(2,4)-penteno-4-lactonylcobalt tricarbonyl in the reaction of acetylcobalt tetracarbonyl with 3-hexyne.[4] Cassar and Chiusoli reported that allylic halides react with nickel carbonyl in acetone solution containing small amounts of water in the presence of carbon monoxide and acetylene to produce γ-lactone derivatives.[5]

Thus, it was found to be probable that acetylenes insert into the bond between the acyl and metal carbonyl group to form acylvinylmetal carbonyls which may undergo CO insertion and cyclization to give unsaturated γ-lactones. However, in the reaction of lithium aroyltricarbonylnickelates with acetylenes main products are not lactones but 1,4-diketones.

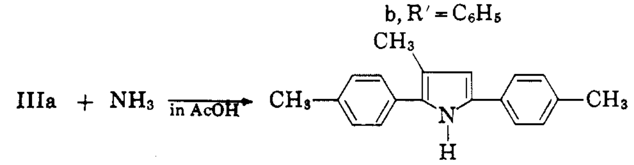
In this paper, we would report the reaction of lithium aroyl- and acyltricarbonylnickelates with acetylenes which promises to be of general use for the synthesis of 1,4-diketones.

Results and Discussion

The reaction between lithium *p*-toluyltricarbonylnickelate and methylacetylene followed by hydrolysis gave 1,2-di-*p*-toluylpropane (69%), and a similar reaction with phenylacetylene gave 1,2-di-*p*-toluyl-1-phenylethane (47%). The structures of these products were confirmed by ir and nmr spectroscopy. Furthermore, the structure of 1,2-di-*p*-toluylpropane was confirmed from the formation of 2,5-di-*p*-tolyl-4-methylpyrrole by the action of ammonia in acetic acid.[6] Acetylene was treated with lithium *p*-toluyltricarbonylnickelate at −70° to give 1,2-di-*p*-toluylethane in a yield of 56%. This compound was too insoluble for nmr study, but from the chemical data and by analogy with the previous reactions this com-



IIIa, $R' = CH_3$
b, $R' = C_6H_5$



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[1] (a) K.-M. Song, Y. Sawa, M. Ryang, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **38**, 330 (1965); (b) M. Ryang, K.-M. Song, Y. Sawa, and S. Tsutsumi, *J. Organometal. Chem.*, **5**, 305 (1966); (c) M. Ryang, I. Rhee, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **37**, 341 (1964)

[2] (a) E. O. Fischer and A. Maasböl, *Angew. Chem.*, **76**, 645 (1964); (b) E. O. Fischer and A. Maasböl, German Patent 1,214,233 (1966).

[3] M. Ryang, K.-M. Song, Y. Sawa, and S. Tsutsumi, unpublished work.

[4] R. F. Heck, *J. Amer. Chem. Soc.*, **86**, 2819 (1964).

[5] L. Cassar and G. P. Chiusoli, *Tetrahedron Lett.*, 3295 (1965).

[6] W. S. Bishop, *J. Amer. Chem. Soc.*, **67**, 2261 (1945).

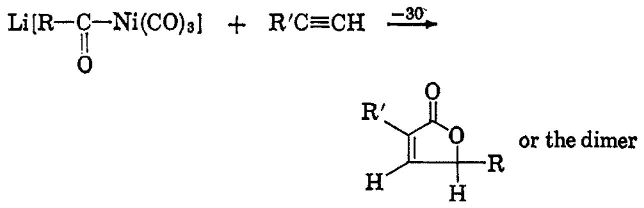
TABLE I

$RC(=O)CHR'CH_2C(=O)R$ BY THE REACTION OF $Li[RC(=O)Ni(CO)_3]$ AND $R'C\equiv CH$ AT −70°

R	R′	Registry no.	Yield, %	$\nu_{C=O}$, cm^{-1}	Nmr, τ
C_6H_5	C_6H_5	4441-01-4	74	1680	
C_6H_5	CH_3	15982-59-9	44	1685	8.69 (d, 3 H), 6.50 (m, 3 H), 1.9, 2.8 (m, 10 H)
C_6H_5	H	495-71-6	50.4	1683	
p-$CH_3C_6H_4$	C_6H_5	15982-61-3	47	1670	7.71 (s, 3 H), 7.67 (s, 3 H), 6.95 (q, H), 5.97 (q, H), 4.82 (q, H), 2.1, 3.1 (m, 13 H)
p-$CH_3C_6H_4$	CH_3	15982-62-4	69	1690	8.75 (d, 3 H), 7.62 (s, 6 H), 6.0, 7.3 (m, 3 H), 2.81 (m, 4 H), 2.13 (m, 4 H)
p-$CH_3C_6H_4$	H	13145-56-7	56	1680	
p-$CH_3OC_6H_4$	H	15982-64-6	31	1678	6.58 (s, 4 H), 6.10 (s, 6 H), 3.05 (d, 4 H), 1.98 (d, 4 H)
n-C_4H_9	H	15982-65-7	24	1705	

pound was determined to be the correct structure. Lithium benzoyltricarbonylnickelate, when also treated with acetylene, gave 1,2-dibenzoylethane (50.4%), when treated with methylacetylene, gave 1,2-dibenzoylpropane (44%), and when treated with phenylacetylene gave 1,2-dibenzoyl-1-phenylethane (74%). Lithium p-anisoyltricarbonylnickelate gave 1,2-di-p-anisoylethane (31%) from the reaction with acetylene. Furthermore, lithium valeryltricarbonylnickelate gave n-dodeca-5,8-dione (24%).

Thus, the treatment of lithium aroyl- or acyltricarbonylnickelates with several acetylenes at −70° gave 1,4-diketones in good yields. But when the same reactions were carried out at higher temperature (−30°), γ-butenyllactone derivatives were produced as by-products in yields of 2–24% in addition to the above 1,4-diketones. Structures of these lactones were assumed by the elemental analyses, molecular weight determinations, and ir and nmr spectra. (For spectral data, see Table I.)


$$Li[R-\underset{\underset{O}{\|}}{C}-Ni(CO)_3] + R'C\equiv CH \xrightarrow{-30^\circ}$$

To elucidate the roles of the nickel and lithium atoms in lithium aroyltricarbonylnickelates for the 1,4-diketone formation, the reaction of lithium p-toluyltetracarbonylferrate[1c] with phenylacetylene was investigated at −30°. In this reaction, however, p-tolualdehyde was isolated as a sole product in a yield of 70.5% and the products resulting from phenylacetylene insertion into carbon–iron σ bond were not obtained.

The same type of complex was prepared at 0° from p-tolylmagnesium bromide and nickel carbonyl,[1b] and the reaction of this complex with phenylacetylene was carried out at room temperature. However, the formation of 1,4-diketone was not observed, and 4,4′-dimethylbenzil and 1,3,5-triphenylbenzene were isolated in yields of 72 and 41%, respectively.

Although we cannot make a definite decision owing to the absence of other data, it seems probable that both the lithium and nickel atoms are playing important roles in the steps leading to formation of 1,4-diketones.

As to the mechanism, the following results seem to be suggestive, that is, the hydrolysis of lithium aroyltricarbonylnickelates gave acyloins in good yields, while the hydrolysis of other lithium aroyl- or acylcarbonylmetalates (Fe,[1c] W,[2a], Cr,[2b] Mo[2b]) gave aldehydes in good yields. These results indicate that the aroyltricarbonylnickelates are mainly dimeric in solution, whereas the other acylarbonylmetalates are monomeric. Therefore, it is considered to be probable that the dimeric aroyltricarbonyl nickelates react with acetylenes at −70° to give 1,4-diketones after hydrolysis, but the minor component, monomeric aroyltricarbonylnickelates, can react with acetylenes at somewhat higher temperature (−30°) to give the minor products, γ-lactones, after hydrolysis.

However, the precise mechanism of the 1,4-diketone formation is now under investigation and detailed description of the mechanism and further application of this reaction will be reported shortly.

Experimental Section

Bromobenzene, p-bromotoluene, p-bromoanisole, n-butyl bromide, and phenylacetylene were used after purification of commercial reagents by fractional distillation. Acetylene was passed through a sodium bisulfite solution and dried with sulfuric acid, and methylacetylene was used without purification. Diethyl ether was dried over sodium wire, and all the reactions were carried out under a dry argon atmosphere.

Molecular weight measurements were made with a Mechrolab vapor pressure osmometer in dimethylformamide or benzene. Melting points were taken on a Yanagimoto micro melting point apparatus and were uncorrected. Infrared spectra were run on a Shimazu IR-27, and nmr spectra were determined with a JOEL LNM-3H-60 spectrometer using tetramethylsilane as an internal standard.

Lithium aroyl- or acyltricarbonylnickelates were prepared from the aryl- or alkyllithium and nickel carbonyl in ether at −70°.[1a]

1,2-Di-p-toluylpropane.—Methylacetylene (2.0 g, 0.05 mol) was added to the ether solution of lithium p-toluyltricarbonylnickelate (0.05 mol), prepared from the p-tolyllithium and nickel carbonyl, and was stirred for 5 hr at −70°. Then the reaction mixture was hydrolyzed with 50 ml of 4 N HCl and subsequently warmed up to room temperature slowly. The separated organic layer was treated with three succesive 30-ml portions of 5% sodium hydroxide solution and divided into an organic layer and aqueous solution. The organic layer was washed with water and was dried over anhydrous magnesium sulfate. After removal of solvent, the residual oil was distilled under reduced pressure to give the following fractions: (1) bp 70–100° (1.1 mm) 0.3 g and (2) bp 130–195° (1.0 mm), 5.3 g. Fraction 2 crystallized on standing and these crystals were recrystallized from ethanol to give 4.8 g of white needles of pure 1,2-di-p-toluylpropane, mp 118–119°.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19; mol wt, 280.4. Found: C, 81.09; H, 7.35; mol wt, 279.

An acetic acid solution of these crystals and ammonium acetate was refluxed for a few minutes, and white needles of 2,5-di-p-

tolyl-4-methylpyrrole were obtained after recrystallization of the resulting solid from ethanol-water,[6] mp 90–91°; ν_{N-H}, 3420 cm^{-1}. Test of this pyrrole with *p*-dimethylaminobenzaldehyde was positive.[7]

When the same reaction was carried out at −30°, 1.2 g of 1,2-di-*p*-toluylpropane was obtained; 2.2 g of pale yellow liquid (bp 130–140° (2.1 mm)) also was obtained after column chromatography on silica gel. This liquid showed the presence of a carbonyl group at 1770 cm^{-1} in the ir spectrum (characteristic of γ-lactones) and was assumed to be 2-methyl-4-*p*-tolyl-γ-butenyl lactone by analogy with another reaction described later and from ir and nmr spectra (crude yield, 17%).

The nmr spectrum showed peaks at τ 8.27 (d, 3 H), 7.76 (s, 3 H), 4.60 (d, H), 4.40 (m, H), 3.07 (s, 4 H).

1,2-Di-*p*-toluyl-1-phenylethane.—Phenylacetylene (5.1 g, 0.05 mol) was added into the ether solution of lithium *p*-toluyltricarbonylnickelate (0.05 mol) and stirring was continued for 5 hr at −70°. After the same treatment, white crystals (3.9 g, recrystallized from ethanol) were obtained, mp 129°, and were identified as 1,2-di-*p*-toluyl-1-phenylethane from results of nmr analysis (Table I), testing with $FeCl_3$ solution (negative), and analytical data.

Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47; mol wt, 342.4. Found: C, 84.17; H, 6.30; mol wt, 344.

When the same reaction was carried out at −30°, 3.8 g of 1,2-di-*p*-toluyl-1-phenylethane and 2.0 g of white crystals (mp 110.5–111°, after recrystallization from petroleum ether) were obtained. The latter crystals were assumed to be 2-phenyl-4-*p*-tolyl-γ-butenyl lactone from results of ir spectroscopy and analytical data, $\nu_{C=O}$ 1750 cm^{-1} (15.7% yield).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64; mol wt, 250.3. Found: C, 81.76; H, 5.81; mol wt, 254.

Furthermore, an ether-insoluble solid was obtained and recrystallized from benzene to give white needles which were assummed to be the dimer of the γ-butenyllactone: mp 270–271° dec; $\nu_{C=O}$ 1750 cm^{-1}.

Anal. Calcd for $C_{34}H_{26}O_4$: C, 81.91; H, 5.26; mol wt, 498. Found: C, 82.02; H, 5.41; mol wt, 493 (Rast method in camphor).

1,2-Di-*p*-toluylethane.—Acetylene (*ca.* 1.2 l.) was bubbled into the lithium *p*-toluyltricarbonylnickelate solution at −70° and was stirred for 5 hr. After similar treatment, white crystals of 1,2-di-*p*-toluylethane were obtained, mp 159°. These crystals were too insoluble for nmr study.

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81; mol wt, 266.3. Found: C, 81.12; H, 6.75; mol wt, 266.

These crystals were treated with ammonia in acetic acid solution to give 2,5-di-*p*-tolylpyrrole: mp 198–199°; ν_{N-H} 3460 cm^{-1}. Furthermore, the reduction of these crystals with lithium aluminium hydride in ether solution gave white neeldes of 1,4-di-*p*-tolylbutane-1,4-diol: mp 139.5°; ν_{O-H} 3340 and 3390 cm^{-1}.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.23; H, 8.13.

1,2-Dibenzoyl-1-phenylethane.—Phenylacetylene (5.1 g, 0.05 mol) was added to the lithium benzoyltricarbonylnickelate solution at −70° and was stirred for 5 hr. After hydrolysis with 50 ml of 4 *N* HCl, the reaction mixture was treated as described above. A fraction of bp 220–225° (2.3 mm) gave white crystals after recrystallization from ethanol, mp 127°, and these crystals were identified as 1,2-dibenzoyl-1-phenylethane from results of nmr spectroscopy and analytical data.

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 84.10; H, 5.85.

These crystals were treated with ammonia in acetic acid to give 2,4,5-triphenylpyrrole: mp 139–140° (recrystallized from ethanol); ν_{N-H} 3420 cm^{-1}.

Anal. Calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.48; H, 5.83; N, 4.61.

1,2-Dibenzoylpropane.—Methylacetyene (2.0 g, 0.05 mol) was added into the lithium benzoyltricarbonylnickelate solution (0.05 mol) at −70° and stirring was continued for 5 hr. After treatment as described above, white crystals of 1,2-dibenzoylpropane were obtained, mp 105° (recrystallized from ethanol).

Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39; mol wt, 252.3. Found: C, 81.19; H, 6.11; mol wt, 253.

The dioxime of these crystals had mp 163° dec.

Anal. Calcd for $C_{17}H_{18}O_2N_2$: C, 72.32; H, 6.43. Found: C, 72.49; H, 6.65.

1,2-Dibenzoylethane.—Acetylene (*ca.* 1.2 l.) was bubbled into the lithium benzoyltricarbonylnickelate (0.05 mol) at −70° and was stirred for 5 hr. After the above treatment, white crystals of 1,2-dibenzoylethane were obtained, mp 146° (recrystallized from ethanol). These crystals were too insoluble for nmr study, but the melting point of these crystals was not depressed by admixture with authentic sample.[8]

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.92; H, 5.67.

1,2-Di-*p*-anisoylethane.—Acetylene (*ca.* 1.2 l.) was bubbled into the lithium *p*-anisoyltricarbonylnickelate solution (0.05 mol) at −70° and stirring was continued for 5 hr. After similar treatment, white crystals of 1,2-di-*p*-anisoylethane were obtained, mp 154° (recrystallized from ethanol).

Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.35; H, 6.04.

***n*-Dodeca-5,8-dione.**—Acetylene (*ca.* 1.2 l.) was bubbled into the lithium valeryltricarbonylnickelate solution (0.05 mol) at −70° and was stirred for 5 hr. After similar treatment, white leaflets of *n*-dodeca-5,8-dione were obtained, mp 53° (recrystallized from petroleum ether (40–60°).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18; mol wt, 198.3. Found: C, 72.64; H, 11.26; mol wt, 202.

Registry No.—$C_{17}H_{14}O_2$, 15982-66-8; dimer of $C_{17}H_{14}O_2$, 16059-92-0; $C_{18}H_{22}O_2$, 15982-67-9; $C_{22}H_{17}N$, 3274-61-1; $C_{17}H_{18}O_2N_2$, 15982-69-1.

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[7] F. Feigl, "Spot Tests in Organic Analysis," 5th ed, Elsevier Publishing Co., Amsterdam, 1956, p 278.

[8] P. S. Bailey and R. E. Lutz, *J. Amer. Chem. Soc.*, **70**, 2412 (1948).

Elimination Reaction of Hydrogen Chloride from 1,1,2-Trichloroethane on Ion-Exchanged Molecular Sieves

ISAO MOCHIDA AND YUKIO YONEDA

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

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It has been reported in a previous paper[1] that the catalytic elimination reaction of hydrogen chloride from 1,1,2-trichloroethane proceeded with different selectivities on solid bases, solid acids, and alumina. The product distributions were 1,1-dichloroethylene > *trans*-1,2-dichloroethylene > *cis*-1,2-dichloroethylene on solid bases, and *cis* > *trans* > 1,1 on solid acids, and *cis* > 1,1 > *trans* on alumina. The reactivity order of five reactants in Table I on solid acids such as silica–alumina and alumina–boria was satisfactorily explained by the relative stability of a hypothetical E2

TABLE I

REAGENTS AND THEIR REACTION PRODUCTS

Reagent[a]	Reaction and products	
1,1-Dichloroethane (75-34-3)	a	$CHCl{=}CH_2$
1,2-Dichloroethane (107-06-2)	b	$CHCl{=}CH_2$
1,1,1-Trichloroethane (71-55-6)	c	$CCl_2{=}CH_2$
1,1,2-Trichloroethane (79-00-5)	d	$CCl_2{=}CH_2$
	e	*trans*-$CHCl{=}CHCl$ and *cis*-$CHCl{=}CHCl$
1,1,2,2-Tetrachloroethane (79-34-5)	f	$CCl_2{=}CHCl$

[a] Registry numbers appear in parentheses.

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[1] I. Mochida, J. Take, Y. Saito, and Y. Yoneda, *J. Org. Chem.*, **32**, 3894 (1967).