of ice–water containing zinc dust (8 g) and stirred while the temperature was allowed to rise to room temperature. Periodic tests[13] showed the absence of peroxide during the hydrolysis. The ethereal phase was separated, and the aqueous phase was extracted with several portions of ether. Evaporation of the combined and dried ether solutions gave dark red crystals which showed only one major spot corresponding to ferrocenecarboxaldehyde on a thin layer chromatogram. The material was column chromatographed [benzene–ether, 1:1 (v/v)] to give 32 mg (32% yield) of pure ferrocenecarboxaldehyde (**3**): mp 124–125° (lit.[14] mp 124.5°); infrared and nmr spectra identical with those obtained from authentic material.

In a third run, trimethyl phosphite (91 mg, 0.73 mmol) was added to the cold (−78°) ozonization mixture of vinylferrocene (100 mg, 0.472 mmol), which was obtained as described above. During the addition the temperature of the reaction mixture rose to −20°, and after the addition was complete the mixture was allowed to come to room temperature. The ethereal solution was washed with several small portions of water, dried, and evaporated to a brown oil which was column chromatographed. Elution with benzene provided ferrocenecarboxaldehyde (**3**), identified by its infrared and nmr spectra (86 mg, 85% yield).

Ozonation of 1-Ferrocenyl-1-phenylethene (4).—1-Ferrocenyl-1-phenylethene (200 mg, 0.694 mmol), dissolved in 20 ml of anhydrous ether and cooled to −78°, was treated with the appropriate amount of standardized ethereal ozone solution in the usual way. During the addition the color changed from deep red to orange, and, after 30 min at −78°, the reaction mixture was allowed to warm to room temperature before it was added to a stirred suspension of lithium aluminum hydride (80 mg, 2.1 mmol) in 100 ml of ether. After the excess hydride was destroyed with ethyl acetate and the mixture hydrolyzed with saturated aqueous ammonium chloride solution, the aqueous phase was separated and extracted with several portions of ether. Evaporation of the combined and dried ether solutions left ferrocenylphenylcarbinol (**5**) [103 mg, 50.9% yield; mp 81–82° (lit.[7] mp 81–82°)] which gave rise to the infrared and nmr spectra superimposable upon those determined from authentic[7] ferrocenylphenylcarbinol.

The cold (−78°) ozonation mixture, prepared in the usual way from 1-ferrocenyl-1-phenylethene, was poured into 100 ml of ice–water containing zinc dust (8.0 g) and stirred for 1 hr, during which time periodic tests[13] for the presence of peroxide were negative. After the separated ether layer was washed with water and dried, it was evaporated to leave a residue of deep red cyrstals which was column chromatographed. Elution with benzene gave rise to pure 84 mg (42% yield) of benzoylferrocene mp 111–112° (lit.[15] mp 111–112°), whose identity was confirmed by comparison of its infrared and nmr spectra with those obtained from authentic benzoylferrocene.

Trimethyl phosphite (114 mg, 0.919 mmol) was added to the cold ozonization mixture prepared from 1-ferrocenyl-1-phenylethene (200 mg, 0.694 mmol), giving an exothermic reaction. The ethereal solution was washed with several small portions of water, dried, and evaporated to a brown oil which was column chromatographed. Elution of the prominent red band with benzene gave 91 mg (45% yield) of benzoylferrocene, mp 111–112°. Both admixture melting with authentic benzoylferrocene and comparison of infrared spectra were used to establish the identity.

Ozonization of Cinnamoylferrocene (7).—An ethereal solution (20 ml) of cinnamoylferrocene (157 mg, 0.497 mmol) was cooled to −78° and treated with an equivalent amount of ozone contained in cold (−78°) ether. The original orange color persisted while the mixture was kept at −78° during 30 min. At that time the cold solution was added to a stirred suspension of lithium aluminum hydride (80 mg, 2.1 mmol) in 100 ml of ether. After 30 min of stirring the excess hydride was destroyed by addition of ethyl acetate, and the reaction mixture was hydrolyzed with saturated aqueous ammonium chloride solution. The ether extracts of the aqueous phase were combined with the original ethereal phase, and the whole was dried and evaporated to give an orange gum which was carefully placed onto a silica gel column. Elution of the major band (orange) gave a substance whose spectral properties were found to be consistent with 1-ferrocenyl-1,2-dihydroxyethane (**8**): 44 mg, 36% yield; ir (CCl$_4$), 3560 (O-H), 3100 (Fc-H), 2950, 2925 (C-H), 1095 and 1000 cm^{-1} (unsubstituted Fc ring); nmr (CDCl$_3$), δ 4.21 (complex, 12), 3.42 (s, 1) and 1.23 (s, 1).

The cinnamoylferrocene ozonization mixture prepared as described above was poured into a stirred mixture of ice–water and zinc dust. As usual periodic spot tests for the presence of peroxide were negative. However, no ferrocene compounds could be found in the ethereal phase or extracts of the hydrolysate, and only some intractable tar was obtained from the aqueous portion.

Treatment of 1-Ferrocenylcyclopentene (11) with Ozone.—1-Ferrocenylcyclopentene (130 mg, 0.516 mmol) was dissolved in 20 ml of anhydrous ether and cooled at −78° while an equivalent of ozone (0.516 mmol) was slowly added *via* the usual standardized ethereal solution. The reaction mixture became brown-black immediately. After it was allowed to warm to room temperature the dark reaction mixture was added slowly to a stirred suspension of lithium aluminum hydride (60 mg, 1.6 mmol) in 100 ml of ether. The stirring was continued for an additional hour before the excess hydride was destroyed (ethyl acetate) and the mixture was hydrolyzed (saturated ammonium chloride). The only material detected and isolated from the ethereal phase and extracts was the starting compound 1-ferrocenylcyclopentene (13 mg, 10% recovery).

Registry No.—**8**, 12269-77-1.

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[13] F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., New York, 1960, p 535.

[14] P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson, and G. M. Whitman, *J. Amer. Chem. Soc.*, **79**, 3416 (1957).

[15] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).

The Reaction of Phenylacetylene with Nickel Carbonyl and Lithium Dimethylamide

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It has been known that lithium aroyl, or lithium acyl metal carbonylates Li[RCOM(CO)$_x$] (R = alkyl or aryl) are formed from the reaction of organolithium compounds with mononuclear metal carbonyls.[1] Previously, it was reported from our laboratory that lithium aroylnickel carbonylate, one of these unstable complexes, gave ketone or α-diketone by thermal decomposition and acyloin by hydrolysis.[1c] Furthermore, as this complex has a carbon–transition metal σ bond, it undergoes reaction with acetylenic compounds very easily to give 1,4-diketones in high yields.[2]

Analogous to the formation of lithium aroylnickel carbonylate, the formation of lithium carbamoylnickel carbonylate (I), Li[RR′NCONi(CO)$_3$], from the reaction of lithium amide with nickel carbonyl is predicted. In fact, the formation of I (R = R′ = CH$_3$) was confirmed by the infrared spectrum of the reaction mixture of lithium dimethylamide and nickel carbonyl. This carbamoyl complex also has a carbon–metal σ bond; so it is expected that the complex undergoes reaction with acetylenic compounds to give succinic acid amide derivatives directly. In the case of lith-

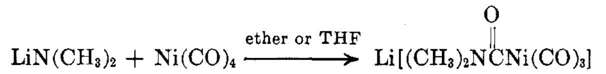
[1] (a) M. Ryang, I. Rhee, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **37**, 341 (1964). (b) E. O. Fischer and A. Maasböl, *Angew. Chem.*, **76**, 645 (1964); German Patent 1,214,233 (1966); *Chem. Ber.*, **100**, 2445 (1967). (c) M. Ryang, Song K-M, Y. Sawa, and S. Tsutsumi, *J. Organometal. Chem.*, **5**, 305 (1966).

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

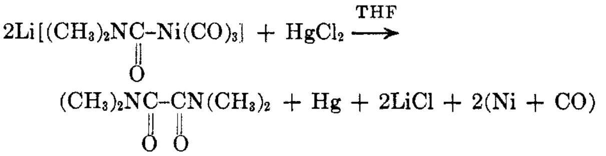
ium dimethylcarbamoylnickel carbonylate and phenylacetylene, 2-phenyl-N,N,N′,N′-tetramethylsuccinamide (40.7%) and N,N-dimethylcinnamamide (0.6%) were obtained from the reaction in ether at 20°. From acetylenic compounds and nickel carbonyl, acrylic acid derivatives can be obtained by the Reppe reaction,[3] but succinic acid derivatives cannot be obtained. Natta and Albanesi[4] have reported that succinic acid was obtained by the reaction of acetylene with carbon monoxide (250 atm) using $Co_2(CO)_8$ at 110°. On the other hand the succinamide derivative is easily obtained under mild conditions by the present reaction.

Results and Discussion

Treatment of Lithium Dimethylamide with Nickel Carbonyl.—The infrared spectrum of nickel carbonyl shows only one peak at 2057 cm^{-1} in ether or tetrahydrofuran (THF), but when nickel carbonyl is added to the ether (or THF) solution of lithium dimethylamide, the infrared spectrum shows new peaks at 1978 (s), 1958 (m) (terminal metal carbonyls), and 1560 cm^{-1} (broad) in addition to the original peak at 2057 cm^{-1}. As the peak at 1560 cm^{-1} is thought to be due to the carbonyl stretching vibration of the carbamoyl group bonding to nickel atom directly,[5] it is reasonable to consider that nickel carbonyl underwent reaction with lithium dimethylamide to give a carbamoylnickel complex with high electron density on the nickel atom (eq 1). This complex reacts with mercuric chloride in THF to give N,N,N′,N′-tetramethyloxamide [30.1 % based on used $LiN(CH_3)_2$], N,N,N′,N′-tetramethylurea (0.2%), and metallic mercury (eq 2).



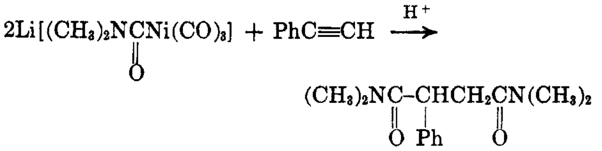
$$\mathrm{LiN(CH_3)_2 + Ni(CO)_4 \xrightarrow{\text{ether or THF}} Li[(CH_3)_2N\overset{O}{\overset{\|}{C}}Ni(CO)_3]} \quad (1)$$



$$\mathrm{2Li[(CH_3)_2N\underset{\overset{\|}{O}}{C}\text{-}Ni(CO)_3] + HgCl_2 \xrightarrow{THF}}$$
$$\mathrm{(CH_3)_2N\underset{\overset{\|}{O}}{C}\text{-}\underset{\overset{\|}{O}}{C}N(CH_3)_2 + Hg + 2LiCl + 2(Ni + CO)} \quad (2)$$

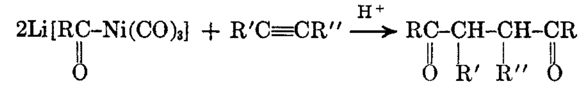
The carbamoylnickel complex is remarkably different from lithium aroylnickel carbonylate in thermal stability and decomposition behavior. That is, lithium aroylnickel carbonylate gives ketone or α-diketone by its decomposition at room temperature, and gives acyloin by hydrolysis at low temperature.[2] On the other hand, the carbamoyl complex is moderately stable at room temperature in solution and does not give a compound corresponding to acyloin or dimethylformamide by hydrolysis with diluted hydrochloric acid but gives only dimethylamine hydrochloride (62%).

Treatment of Phenylacetylene with Lithium Dimethylcarbamoylnickel Carbonylate.—Phenylacetylene undergoes reation with lithium dimethylcarbamoylnickel carbonylate in ether or THF to give 2-phenyl-N,N,N′,N′-tetramethylsuccinamide as a main product and N,N-dimethylcinnamamide as a minor product (eq 3).

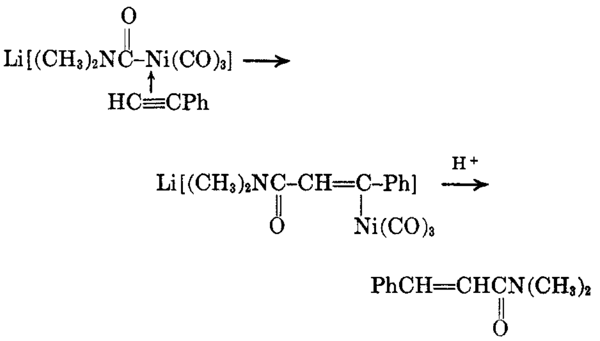


$$\mathrm{2Li[(CH_3)_2N\underset{\overset{\|}{O}}{C}Ni(CO)_3] + PhC{\equiv}CH \xrightarrow{H^+}}$$
$$\mathrm{(CH_3)_2N\underset{\overset{\|}{O}}{C}\text{-}\underset{Ph}{\underset{|}{C}}HCH_2\underset{\overset{\|}{O}}{C}N(CH_3)_2} \quad (3)$$

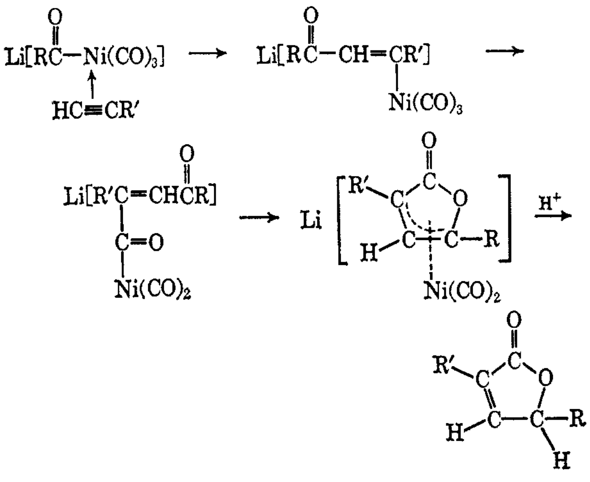
This reaction is analogous to the reaction of lithiumacyl nickel carbonylate with acetylenic compounds[2] (eq 4). The mechanism of the formation of 2-phenyl-N,N,N′,N′-tetramethylsuccinamide and 1,4-diketone are not clear. But the mechanism of the formation of N,N-dimethylcinnamamide and unsaturated five-membered-ring lactone, minor products of eq [3 and 4, respectively, are thought to be as shown in eq 5 and 6.



$$\mathrm{2Li[R\underset{\overset{\|}{O}}{C}\text{-}Ni(CO)_3] + R'C{\equiv}CR'' \xrightarrow{H^+} R\underset{\overset{\|}{O}}{C}\text{-}\underset{R'}{\underset{|}{C}}H\text{-}\underset{R''}{\underset{|}{C}}H\text{-}\underset{\overset{\|}{O}}{C}R} \quad (4)$$



$$\mathrm{Li[(CH_3)_2N\overset{O}{\overset{\|}{C}}\text{-}Ni(CO)_3] \longrightarrow}$$
$$\mathrm{\uparrow HC{\equiv}CPh}$$
$$\mathrm{Li[(CH_3)_2N\underset{\overset{\|}{O}}{C}\text{-}CH{=}\underset{Ni(CO)_3}{\underset{|}{C}}\text{-}Ph] \xrightarrow{H^+}}$$
$$\mathrm{PhCH{=}CH\underset{\overset{\|}{O}}{C}N(CH_3)_2} \quad (5)$$



(6)

Compared with the Reppe reaction the formation of N,N-dimethylcinnamamide in this reaction is interesting. In the Reppe reaction, monosubstituted acetylenes react with nickel carbonyl and hydrochloric acid in the presence of water, or an alcohol, or an amine to give compounds of the type RC(COY) = CH_2 (Y = OH, OR, NR′R″). In the above reaction it was thought that a proton of the hydronickel carbonyl adds to the terminal carbon atom of the monosubstituted acetylenes and nickel adds to the inner carbon atom to give an alkylnickel complex and the insertion of carbon monoxide into the carbon–nickel bond occurs, followed by hydrolysis, alcoholysis, or aminolysis,[6] but in an acyl–metal complex with a carbon–metal σ

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[3] W. Reppe, *Ann. Chem.*, **582**, 1 (1953).

[4] G. Natta and G. Albanesi, *Chim. Ind.* (Milan), **48**, 1157 (1966).

[5] π-Cyclopentadienyl dialkylcarbamoyliron dicarbonyl prepared by R. B. King shows a $\nu_{C=O}$ peak at 1535 ± 10 cm^{-1}: *J. Amer. Chem. Soc.*, **85**, 1918 (1963).

[6] P. L. Pauson, *Proc. Chem. Soc.*, 297 (1960).

bond, the acyl group generally tends to add to the terminal carbon of the monosubstituted acetylenes. In fact, in the case of the reaction of phenylacetylene with a carbamoyl nickel complex, cinnamamide was obtained, and atropic acid amide (product of the Reppe reaction) was not detected.

Experimental Section

All reactions were carried out under nitrogen. Yields were calculated based on the used lithium dimethylamide.

Reaction of Lithium Dimethylamide with Nickel Carbonyl.—*n*-Butyllithium (0.025 mol) was added dropwise to dimethylamine (0.1 mol) dried with potassium hydroxide, and then excess dimethylamine was removed at 40°. The ether (or THF) (20 ml) solution of nickel carbonyl (0.025 mol) was added dropwise to the ether (or THF) solution of lithium dimethylamide at −70°. Then the solution was stirred 5–10 hr at 20°. The infrared spectrum of the orange-red colored reaction mixture showed peaks at 2057 (s) ($\nu_{C\equiv O}$ of nickel carbonyl), 1978 (s) and 1958 (m) ($\nu_{C=O}$ of terminal carbonyl of the anionic complex), and 1560 cm^{-1} (broad) ($\nu_{C=O}$ of carbamoyl group directly bonded to nickel). When the solvent was removed from this solution under reduced pressure, an orange-red powder was obtained. This powder was unstable in air and spontaneous ignition occurred. This complex was not isolated pure, but was treated with mercuric chloride (0.01 mol) in THF at −40° (5 hr) to give N,N,N′,N′-tetramethyloxamide 0.055 g (30.1%) and N,N,N′,N′-tetramethylurea 0.002 g (0.2%) as organic products. Mercury and lithium chloride were also obtained as inorganic products. Organic products were confirmed by gas chromatography (column: SE 30, 2.25 *M*, 120–200°; He 7.5 cc/min). When the carbamoyl solution was hydrolyzed by 25 ml of 3 *N* hydrochloric acid, 1.01 g (62%) of dimethylamine hydrochloride was obtained and no compounds resulting from carbon monoxide insertion were obtained.

Reaction of Phenylacetylene with Lithium Dimethylcarbamoylnickel Carbonylate.—Phenylacetylene (5.1 g, 0.05 mol) was added to the ether solution of lithium dimethylcarbamoylnickel carbonylate (0.05 mol) and the mixture was stirred for 4 hr at 20°. After ether and remaining nickel carbonyl were removed under reduced pressure, benzene (150 ml) was added and then 2 *N* hydrochloric acid (80 ml) was added with cooling. From the water-soluble part, 0.50 g (12.4%) of dimethylamine hydrochloride was obtained. The benzene-soluble part was distilled under reduced pressure after removal of benzene to give fractions (1) bp 100–150° (0.6 mm) and (2) bp 150–200° (0.6 mm) in yields of 2.23 g and 0.55 g, respectively. A part of these fractions was separated by column chromatography [silica gel, petroleum ether (bp 35–65°)] to give triphenylbenzene (mixture of 1,3,5- and 1,2,4-) [mp 108–112°; white crystals; nmr, τ 2.5–3.0 (multiplet)] and all-*trans*-1,4-diphenylbutadiene [mp 147.5–149° (white needles)] which were confirmed by a comparison of the infrared spectrum and a mixture melting point determination with an authentic sample prepared by a Wittig reaction of cinnamyl bromide with benzaldehyde. By the recrystallization of these fractions using petroleum ether–benzene, 2-phenyl-N,N,-N′,N′-tetramethylsuccinamide, and N,N-dimethylcinnamamide were obtained. A gas chromatographic analysis (column: SE 30, 2.25 *M*, 200°; He 7.5 cc/min) of fractions 1 and 2 showed that these fractions consisted of 2-phenyl-N,N,N′,N′-tetramethylsuccinamide (2.52 g, 40.7%), N,N-dimethylcinnamamide (0.05 g, 0.6%), a trace of triphenylbenzene, and a trace of all-*trans*-1,4-diphenylbutadiene. 2-Phenyl-N,N,N′,N′-tetramethylsuccinamide had mp 93.1–93.8° (white crystals); the infrared absorptions (KBr) appeared at 3025 (w), 2980 (w), 2810 (m), 1645 (sh), 1630 (vs), 1620 (sh), 1590 (m), 1495 (m) 1458 (m), 1415 (m), 1390 (s), 1268 (s), 1130 (s), 765 (s), 725 (m), and 703 (s) cm^{-1}. The nmr spectrum showed peaks (in τ) at 7.6 (multiplet, 1 H), 7.1 (singlet, 12 H), 6.6 (multiplet, 1 H), 5.6 (multiplet, 1 H), and 2.8 (singlet, 5 H).

Anal. Calcd for $C_{14}H_{20}N_2O_2$: C, 67.71; H, 8.12; N, 11.28; mol wt, 248. Found: C, 67.60; H, 8.20; N, 11.27; mol wt, 258 (osmometer in benzene, 25°).

The structure of N,N-dimethylcinnamamide, mp 100.6–101.5° (white needles), was confirmed by mixture melting point determination and infrared and nmr spectral comparison with an authentic sample.

The same reaction was carried out under different conditions. The results are listed in Table I.

TABLE I

YIELDS OF PRODUCTS

			% yield		
Solvent	Temp, °C	Time, hr	PhCHCON$(CH_3)_2$ | CH_2CON$(CH_3)_2$	PhCH ‖ HCCON$(CH_3)_2$	$(CH_3)_2$-NHHCl
Et_2O	20	4	40.7	0.6	12.4
Et_2O	−70	33	7.5	4.5	28.8
THF	20	4	14.1	0.2	10.1
THF	−70	33	6.0	0.8	20.8

Registry No.—Phenylacetylene, 536-74-3; nickel carbonyl, 13463-39-3; lithium dimethylamide, 3585-33-9; 2-phenyl-N,N,N′,N′-tetramethylsuccinamide, 16607-43-5.

Reaction of ω-Chloro Ketones with Methylenetriphenylphosphorane[1]

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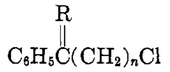
In another investigation we required a series of homologous chloro olefins of structure 1 (R = CH_2). As a series of chloro ketones (1, R = O) was available from a previous investigation,[3] we investigated the possibility of direct conversion of the chloro ketones into the chloro olefins utilizing methylenetriphenylphosphorane.



$$C_6H_5\overset{\overset{R}{\|}}{C}(CH_2)_nCl$$

1

It appears that relatively few investigations of the action of Wittig reagents on halo ketones have been carried out.[4] Siemiatycki and Strzelecka[5] have reported that the reaction of phenacyl bromide with phenacylidenetriphenylphosphorane produced *trans*-dibenzoylethylene (50%), *trans*-1,2,3-tribenzoylcyclopropane (7%), and a nearly quantitative yield of phenacyltriphenylphosphonium bromide. The authors proposed a mechanism for product formation involving phenacyl carbene. Surprisingly, carrying out the reaction in the presence of *cis*-dibenzoylethylene did not result in an increase in the yield of the cyclopropane derivative.[5] Maercker[4] has suggested that the cyclopropane derivative is formed by a Micheal addition of the ylide to dibenzoylethylene followed by ring closure involving an intramolecular displacement.

Bestmann and Schulz[6] have reported that the reaction of phenacyl bromide with carbomethoxymethylenetriphenylphosphorane produced benzoylcarbome-

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[2] (a) Alfred P. Sloan Research Fellow, 1967–1969; (b) NASA Predoctoral Trainee.

[3] D. J. Pasto and M. P. Serve, *J. Amer. Chem. Soc.*, **87**, 1515 (1965).

[4] For a recent review, see A. Maercker, *Org. Reactions*, **14**, 270 (1965).

[5] M. Siemiatycki and H. Strzelecka, *Compt. Rend.*, **250**, 3489(1960).

[6] H. J. Bestmann and H. Schulz, *Angew. Chem.*, **73**, 620 (1961).