volved some methyl radicals generated in its photolysis was dismissed since vpc analysis revealed negligible formation of products arising from acetone.[11]

The sharp increase in Φ(HCl) with acetone dilution (Figure 2) points to the *monomer* form of the $[n,\pi^*]^1$ state as the effective photosensitizer.[19a] Thus, for example, just as the acetone monomer fluorescence yield is approximately doubled in going from 1.1×10^{-2} to 2.7×10^{-3} *M* in hexane,[9] also is Φ(HCl) doubled for the same concentrations. However, at [acetone] $\gtrsim$ 0.1 *M*, the $[n,\pi^*]^1$ state is mainly in the excimer form, so that Φ(HCl) will reflect the concentration of singlet monomer in equilibrium with its excimer.[19b] In fact, according to the kinetics of energy transfer involving successive excimer formation and dissociation,[20] the energy-transfer efficiency, and hence Φ(HCl), should be independent of the sensitizer concentration (*i.e.*, independent of isooctane dilution) at a given concentration of 1,4-DCB, so long as [acetone] $\gtrsim$ 0.1 *M*. As Figure 1 shows, this is indeed the case, as is also the expected linearity of this plot.[21]

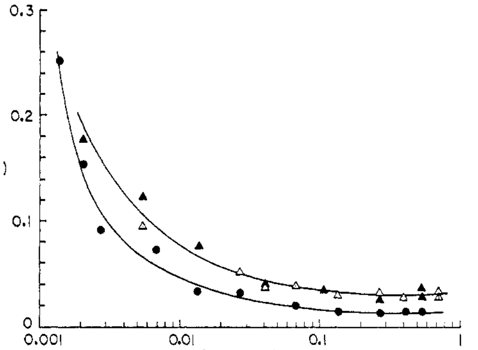

Figure 2. Effect of acetone concentration on the quantum yield of hydrogen chloride at 3130 Å. The circles correspond to 1,4-DCB–acetone–isooctane solutions at constant 1,4-DCB concentration (5.1 *M*) irradiated in Pyrex, while the triangles have the same significance as in Figure 1.

The mechanism for HCl formation, as well as rearrangement to 1,3-DCB, ensuant on sensitized C–Cl cleavage in 1,4-DCB, is presumed to be that depicted for the analogous processes in the photolysis and radiolysis of *n*-propyl chloride.[22]

Further work on sensitizing the photolysis of 1,4-DCB[23] using various excimer-forming compounds besides acetone is currently in progress.

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(19) (a) Sensitization presumably entails collisional deactivation by 1,4-DCB, the energy of the monomer $[n,\pi^*]^1$ state ($\gtrsim$92 kcal/mole) being ample to promote rupture of the C–Cl bond (bond strength $\simeq$ 80 kcal/mole). (b) Dissociation of 1,4-DCB through collisional deactivation of the excimer is probably unimportant since the excimer energy ($\sim$71 kcal/mole)[9] is less than the C–Cl bond strength.

(20) J. B. Birks, J. M. de C. Conte, and G. Walker, *IEEE Trans. Nucl. Sci.*, *NS*, **13,** 148 (1966); J. B. Birks and J. C. Conte, *Proc. Roy. Soc.*, **A303,** 85 (1968), and references cited therein.

(21) In view of the low quantum yields, and hence high rates of competing decay processes.[20]

(22) H. L. Benson, Jr., and J. E. Willard, *J. Am. Chem. Soc.*, **83,** 4672 (1961); **88,** 5689 (1966).

(23) Preliminary data indicate that toluene and benzophenone are two other singlet sensitizers for this reaction.

Acknowledgment. The author is indebted to Drs. John A. Parker and Thomas H. Anderson for their support and helpful discussions throughout this study.

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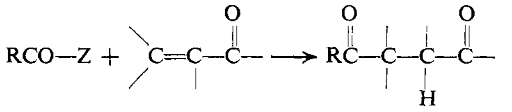
A Method for 1,4 Addition of Acyl Groups to Conjugated Enones

Sir:

This communication reports a new reaction which leads to the formation of a 1,4-dicarbonyl unit by the combination of acyl and conjugated enone moieties as depicted in eq 1. The direct formation of such 1,4-dicarbonyl structures by *intermolecular* coupling is not possible using classical synthetic reactions,[1] and consequently indirect approaches have been required, *e.g.*, a sequence employing the conjugate addition of nitro-stabilized carbanions to enones.[2] The reaction of conjugated enones with 2-lithio-1,3-dithianes, which are synthetically equivalent to C-nucleophilic carbonyl groups,[3] leads only to 1,2 addition to the enone system,[4] and other potentially useful and general reagents (*e.g.*, acetylide anions[5]) suffer from the same limitation.



$$\mathrm{RCO{-}Z} + \;\rangle\mathrm{C{=}\underset{|}{C}{-}\overset{\overset{\textstyle O}{\|}}{C}{-}} \longrightarrow \mathrm{R\overset{\overset{\textstyle O}{\|}}{C}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{\underset{\textstyle H}{|}}{C}}{-}\overset{\overset{\textstyle O}{\|}}{C}{-}} \qquad (1)$$

We chose to investigate the unstable intermediates formed by the reaction of metal carbonyls with organolithium reagents[6-9] as potential nucleophilic acyl equivalents. Complexes from nickel carbonyl[8] seemed especially promising in view of the recently discovered alkoxy- and aminocarbonylation reactions of halides.[10] Three reasonable mechanistic pathways by which conjugate addition of acyl could occur from such complexes are outlined in eq 2. Path a involves preliminary electron transfer, path b, direct acyl anion transfer, and path c, cycloaddition of acyl anion as though it were an

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(1) The cyclization of 4-methyl-4-(β-ethoxycarbonylethyl)-2-cyclohexenone to *cis*-9-methylindene-1,6-dione by lithium–ammonia reagent, an *intramolecular* enone acylation, has been reported recently by R. G. Carlson and R. G. Blecke, *Chem. Commun.*, 93 (1969); see also M. Tanabe, J. W. Chamberlin, and P. Nishiura, *Tetrahedron Lett.*, 601 (1961); B. J. Majerlein and J. A. Hogg, *J. Am. Chem. Soc.*, **80,** 2220 (1958).

(2) See E. J. Corey, I. Vlattas, N. H. Andersen, and K. Harding, *ibid.*, **90,** 3247 (1968), for an illustration.

(3) E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4,** 1075, 1077 (1965).

(4) E. J. Corey and D. Crouse, *J. Org. Chem.*, **33,** 298 (1968); N. H. Andersen, unpublished work in these laboratories.

(5) For the synthesis of 1,4-dicarbonyl compounds from γ,δ-acetylenic ketones, see G. Stork and R. Borch, *J. Am. Chem. Soc.*, **86,** 935 (1964).

(6) M. Ryang, I. Rhee, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **37,** 341 (1964).

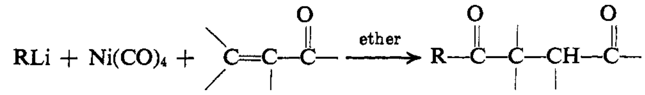
(7) S. Kwang-Myeong, Y. Sawa, M. Ryang, and S. Tsutsumi, *ibid.*, **38,** 330 (1965).

(8) M. Ryang, S. Kwang-Myeong, Y. Sawa, and S. Tsutsumi, *J. Organometal. Chem.*, **5,** 305 (1966).

(9) E. O. Fischer and A. Maasböl, *Chem. Ber.*, **100,** 2445 (1967), and references cited therein.

(10) E. J. Corey and L. S. Hegedus, *J. Am. Chem. Soc.*, **91,** 1233 (1969).

Table I. Conjugate Addition of Acyl Groups to α,β-Carbonyl Compounds



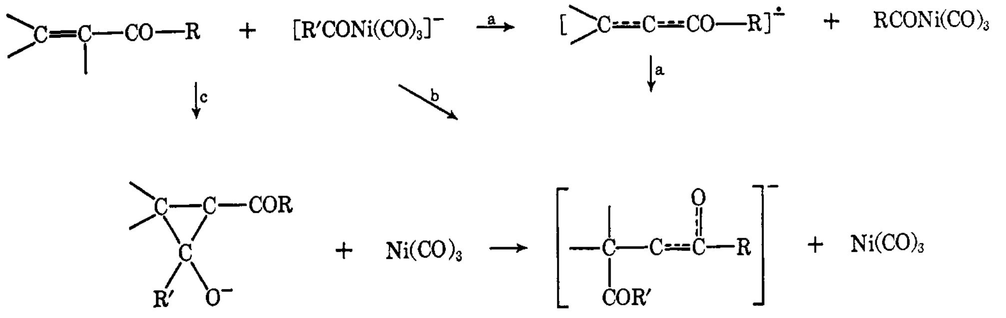
$$\mathrm{RLi + Ni(CO)_4 + {>}C{=}C{-}C({=}O){-} \xrightarrow{\text{ether}} R{-}C({=}O){-}C{-}CH{-}C({=}O){-}}$$

R	Substrate	Ratio, RLi:Ni(CO)$_4$: substrate	Reaction time, hr, and temp, °C	Product,[a] % yield[b]
CH_3	Benzalacetone	4:4:3	5, −78	3-Phenyl-2,5-hexanedione, 82
n-C_4H_9	Benzalacetone	4:4:3	20, −78 4, −50	4-Phenyl-2,5-nonanedione, 92
C_6H_5	Benzalacetone	5:5:3	24, −50 3.5, −25	1,2-Diphenyl-1,4-pentanedione, 42[c]
CH_3	Methyl cinnamate	2:2:1	8, −30	Methyl 3-phenyl-4-oxopentanoate, 71
n-C_4H_9	Methyl cinnamate	4:4:3	12, −50	Methyl 3-phenyl-4-oxooctanoate, 59
CH_3	2-Cyclohexenone	4:4:3	12, −50	3-Acetylcyclohexanone, 35[c]
n-C_4H_9	2-Cyclohexenone	4:4:3	12, −50	3-n-Valerylcyclohexanone, 64
CH_3	3-Methyl-3-penten-2-one	4:4:3	7.5, −50	3,4-Dimethyl-2,5-hexadione, 50
n-C_4H_9	3-Methyl-3-penten-2-one	4:4:3	7, −50	3,4-Dimethyl-2,5-nonanedione, 64
CH_3	Mesityl oxide	5:5:3	16, −50	4,4-Dimethyl-2,5-hexanedione, 60
n-C_4H_9	Mesityl oxide	5:5:3	16, −50	4,4-Dimethyl-2,5-nonanedione, 89
n-C_4H_9	3-Buten-2-one	5:5:3	5, −50	2,5-Nonanedione, 64
CH_3	Methyl crotonate	4:4:3	4.5, −50	Methyl 3-methyl-4-oxopentanoate, 49
n-C_4H_9	Methyl crotonate	4:4:3	4.5, −50	Methyl 3-methyl-4-oxooctanoate, 76

[a] Products were identified by infrared, nuclear magnetic resonance, and mass spectra and C and H analyses. [b] Yields refer to purified product, isolated by distillation or preparative layer chromatography. [c] Several by-products were noted in this reaction.

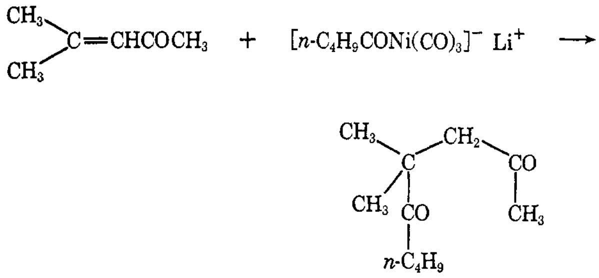
alkoxycarbene; in each case the fairly stable nickel tricarbonyl fragment serves as the leaving group.

In fact the complexes of nickel carbonyl with organolithium reagents, generated at −50°, react smoothly with a variety of α,β-unsaturated carbonyl compounds in the desired manner to form 1,4-dicarbonyl derivatives.



(2)

For example, from mesityl oxide and the reagent prepared from equimolar amounts of n-butyllithium and nickel carbonyl, 4,4-dimethyl-2,5-nonanedione was obtained in 89% yield (eq 3) using the following experimental procedure.

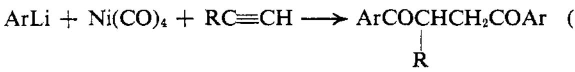


(3)

(*All reactions involving nickel carbonyl should be carried out in a well-ventilated hood.*) To 10 ml of dry, argon-saturated ether in a 100-ml flask fitted with a side arm and three-way stopcock opened to an argon-filled balloon was added nickel carbonyl (5.0 mmol, 0.65 ml). The mixture was cooled to −50° (Dry Ice–technical grade acetonitrile), and n-butyllithium (5.0 mmol, 3.85 ml of 1.3 *M* solution in pentane) was added slowly. The mixture was stirred for 2 hr at −50°. Mesityl oxide (3.0 mmol, 0.294 g) was added slowly, and the mixture was stirred at −50° for 16 hr, quenched at −50° by addition of 10 ml of aqueous ammonium chloride, and then allowed to warm to room temperature. Excess nickel carbonyl and nickel complexes were decomposed by careful addition of iodine in ether (*care! carbon monoxide is evolved and the reaction foams*) until the brown color of iodine remained. The mixture was poured into a separatory funnel containing 50 ml of ether and 10 ml of saturated sodium chloride solution and was shaken. The aqueous phase was washed with 25 ml of ether, and the combined ether extracts were washed with 10 ml of saturated sodium chloride containing sodium sulfite until colorless, dried over anhydrous magnesium sulfate, and concentrated. The diketone product was separated from impurities (including those derived from the reagent butyllithium and minor amounts of side products) by preparative thin layer chromatography to give 0.49 g (89%) of 4,4-dimethyl-2,5-nonanedione, homogeneous by vapor phase and thin layer chromatography and having infrared and nuclear magnetic resonance spectra and elemental analyses in accord with the assigned structure.

The generality of the reaction between lithium acylcarbonylnickelate reagents and α,β-unsaturated carbonyl compounds is apparent from the results summarized in Table I which covers 12 examples. The utility of the new process becomes clear when a comparison is made with other synthetic routes to the 1,4-dicarbonyl compounds which are listed in the table. In addition, simple approaches to other types of structures, *e.g.*, furan, pyrrole, and 2-cyclopentenone derivatives, are now possible based on acylnickel reagents.

During the course of this work it was reported that the reaction of aryllithium reagents with nickel carbonyl in the presence of certain acetylenes produces 1,4-dicarbonyl derivatives according to eq 4.[11] Since it is unclear whether this reaction involves enone intermediates, the relationship with the conjugate addition described above is uncertain at present.



$$\mathrm{ArLi} + \mathrm{Ni(CO)_4} + \mathrm{RC{\equiv}CH} \longrightarrow \mathrm{ArCO}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C}}\mathrm{HCH_2COAr} \qquad (4)$$

Work is continuing on these and related synthetic applications of lithium acylcarbonylnickelate reagents.[12]

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

(12) This work was supported by the National Science Foundation.

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Nuclear Polarization in the Products of Chemical Reactions Occurring in the Absence of a Magnetic Field

Sir:

The initial reports of the observation of chemically induced dynamic nuclear polarization (CIDNP) resulting from rapid free-radical reactions[1] have been followed by a number of examples[2] of this phenomenon in diverse chemical systems. To date all of these experiments have had the common characteristic that the reactions were carried out with the sample totally immersed in a static magnetic field. We here report that enhanced nmr signals can be observed from the protons in the products of reactions conducted in the absence of a magnetic field and introduced into the spectrometer only after the reactions are complete or have ceased.

A typical example of this phenomenon is presented in Figure 1. The spectra are of H-1 of 1-chloro-1-phenylpropane formed as a radical coupling product in the reaction between ethyllithium and α,α-dichlorotoluene[3] in benzene. Experimental conditions for recording the spectra in Figure 1 differ only in the time which has elapsed between mixing the reactants and placing the sample in the spectrometer field. Estimates of the rate of the reaction obtained by calorimetry indicate that the reaction proceeds to greater than 95% completion in 5–6 sec.[4] Because of this rapid rate, the reaction for Figure 1A was carried out by mixing the reactants in the probe of the A-60A nmr spectrometer. Figure 1B was taken of samples introduced into the probe 12 sec after mixing. The time constant for decay of the nmr signal in all cases is the $\sim$8-sec longitudinal relaxation time,[5] T_1, for the nuclei at 60 MHz. Failure of the enhanced signal to recover following radiofrequency saturation confirms that the reaction is essentially complete before observation of the spectrum. If the sample is allowed to remain outside of the spectrometer field for a time much longer than T_1, the observed signal is only the weak triplet absorption expected for the $\sim$25% yield of the product.

The observed effects seem to depend *solely* on whether the reaction was run in or out of a high magnetic field. Variables which have negligible effects on the spectra include: (i) order of mixing of reactants, (ii) temperature of the reaction mixture, (iii) thermal equilibration of the reactant nuclear spin states in the field before mixing, and (iv) shielding from the earth's magnetic field of the samples run outside of the probe.

The experiments described above illustrate the conversion by a magnetic field of negative to positive enhancement in multiplets exhibiting net magnetization.[6] We have also found that the magnetic field may lead to a superposition of the "multiplet effect"[6] on lines exhibiting net magnetization. The thermal decomposi-

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(1) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967); R. G. Lawler, *ibid.*, **89**, 5519 (1967); J. Bargon, H. Fischer, and U. Johnsen, *Z. Naturforsch.*, **22a**, 1551 (1967); J. Bargon and H. Fischer, *ibid.*, **22a**, 1556 (1967).

(2) (a) H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969), and references therein; (b) H. R. Ward, R. G. Lawler, and H. Y. Loken, *J. Amer. Chem. Soc.*, **90**, 7359 (1968); (c) H. R. Ward, R. G. Lawler, and R. A. Cooper, *Tetrahedron Letters*, 527 (1969); (d) H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Amer. Chem. Soc.*, **91**, 746 (1969); A. R. Lepley and R. L. Landau, *ibid.*, **91**, 748 (1969); A. R. Lepley, *ibid.*, **91**, 749 (1969); A. R. Lepley, *Chem. Commun.*, 64 (1969); A. R. Lepley, *J. Amer. Chem. Soc.*, **91**, 1237 (1969); J. E. Baldwin and J. E. Brown, *ibid.*, **91**, 3647 (1969).

(3) (a) The radical nature of the reaction of another *gem*-dichloride with alkyllithiums has been reported.[2b] (b) Other products of this reaction also exhibit proton polarization: α-chlorotoluene (δ 4.2, enhanced absorption) and 1,2-dichloro-1,2-diphenylethane (an emission doublet, *meso* at δ 5.11, *dl* at δ 5.16). The observed polarization for these compounds is the same for reactions run internal and external to the magnetic field.

(4) The reaction was carried out with volumes and vessel shape approximating those of the nmr experiments, and the temperature of the reaction mixture was monitored with a thermocouple. The temperature reached its maximum in $\sim$6 sec, and then slowly decreased as the vessel and solution approached thermal equilibrium. A similar cooling curve was observed when benzene, at the maximum temperature reached by the reacting solution, was introduced into the same reaction vessel. The conclusion is that the heat evolution of the highly exothermic reaction is essentially complete in <7 sec.

(5) Estimated by progressive saturation of the resonance in a nonreacting sample of the product (see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 82).

(6) It is possible to classify the nuclear polarization effects resulting from chemical reactions as (a) those in which the value of the total z magnetization averaged over all of the transitions for a single set of equivalent nuclei is equal to the equilibrium magnetization, and (b) those in which there is a net increase or decrease in magnetization of a set of nuclei. The former of these phenomena has been called the "multiplet effect"[2a] while the latter is analogous to the enhancement usually observed in electromagnetically pumped dynamic nuclear polarization experiments [K. H. Hausser and D. Stehlik, *Advan. Mag. Resonance*, **3**, 79 (1968)].