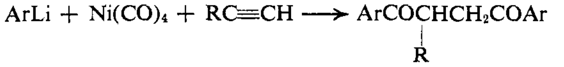
tion and was shaken. The aqueous phase was washed with 25 ml of ether, and the combined ether extracts were washed with 10 ml of saturated sodium chloride containing sodium sulfite until colorless, dried over anhydrous magnesium sulfate, and concentrated. The diketone product was separated from impurities (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.



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

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

[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 ~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 ~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 ~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)].

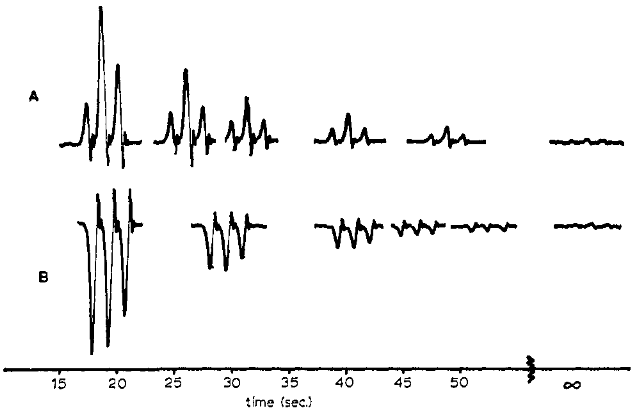

Figure 1. Nmr spectra (δ 4.4–4.8) of H-1 of the 1-chloro-1-phenylpropane produced from the reaction of α,α-dichlorotoluene (0.5 *M*) with ethyllithium (0.6 *M*) in benzene. The time axis indicates the number of seconds after the reagents were mixed; the infinity spectra were taken at times greater than 150 sec. (A) Reagents were mixed in the spectrometer probe. (B) Reagents were mixed outside the spectrometer field, and placed in the probe 12 sec after mixing.

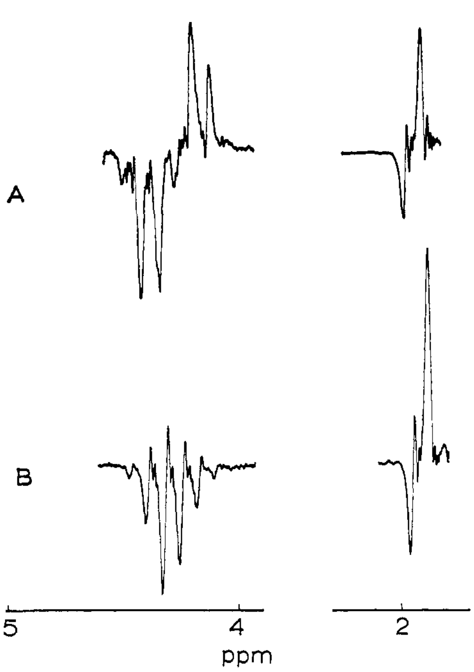

Figure 2. Nmr spectra of 2-iodopropane (1.48 *M*) in *o*-dichlorobenzene solution containing 0.61 *M* benzoyl peroxide. (A) Spectrum taken at 140° during decomposition of the benzoyl peroxide. (B) Spectrum taken approximately 5 sec after quenching the thermal decomposition, which was conducted at 140° outside the spectrometer field.

tion of acyl peroxides in the presence of alkyl iodides gives rise to polarization in the protons of both reagent and product iodides.[2c] Such reactions provide an attractive test system for zero field polarization, since they can be thermally initiated and then quenched by cooling, before the sample is introduced into the spectrometer. Figure 2 shows the effect of a magnetic field on the nmr spectrum of 2-iodopropane in *o*-dichlorobenzene taken during (Figure 2A) or following (Figure 2B) the thermal decomposition of benzoyl peroxide in the same solution. In this case also the observed effects are insensitive to temperature and depend only on whether the product was formed in or out of the magnetic field. It should be noted that in this example the methyl protons of 2-iodopropane seem to be unaffected by the magnetic field, and appear in both instances as a doublet with positive and negative enhancements of the high- and low-field lines, respectively.

Although these results bear some resemblance to polarization effects obtained in flowing liquids[7] and in solids subjected to magnetic field changes,[8] the analogy cannot be exact. We have been unable to produce any approximation to these effects in nonreacting samples or in rapid ionic reactions by simply transferring the sample to and from the nmr probe. Possible time-dependent interactions available to a system undergoing a free-radical reaction in zero field include the electron–electron and electron–nuclear scalar and dipolar couplings. Effective operation of these interactions to produce transitions does not require the presence of a magnetic field, although the efficacy of exchange of energy within the spin system and between the spin system and the lattice is, in general, modified by a field. It is therefore at least plausible that transient nonequilibrium populations of the zero-field spin levels arising from electron–electron and electron–nuclear interactions may occur during a free-radical reaction in solution. The mechanisms by which these zero-field relaxation processes can affect spin level populations after quantization in the field of the spectrometer have yet to be detailed.

Zero-field polarization has been observed in every rapid radical reaction (*i.e.*, reactions complete in times less than T_1 of the products) that we have examined.[9] If it proves to be a general phenomenon, it may be utilized beneficially in CIDNP investigations of reaction mechanisms. Radical reactions can be conducted outside the spectrometer field, thus facilitating the introduction of energy (as light or heat, for example) into the sample. Experiments providing examples of such applications are in progress.

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(8) R. V. Pound and E. M. Purcell, *Phys. Rev.*, **81**, 279 (1951); A. Abragam and W. G. Proctor, *ibid.*, **109**, 1441 (1958).

(9) H. Fischer has observed a field effect on the polarization in the products of peroxide pyrolysis and photolysis (personal communication).

(10) National Center for Air Pollution Control Special Fellow (predoctoral).

(11) National Defense Education Act Trainee, 1967–1968.

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Electron Spin Resonance of the Cation of Ferrocene

Sir:

The chemical bonding in ferrocene ($FeCp_2$) has attracted much theoretical interest.[1-3] Although in checking bonding theories esr data are very useful, it is only for a few sandwich complexes that the esr spectra have been measured, and for the cation of ferrocene

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(3) R. Prins and J. D. W. van Voorst, *J. Chem. Phys.*, **49**, 4665 (1968).