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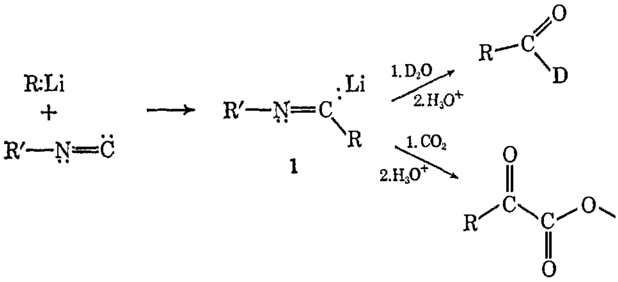
Lithium Aldimines. A New Synthetic Intermediate[1]

Sir:

The recent reports by Meyers[2] on his elegant syntheses of aldehydes and ketones prompts us to report our findings on the simple synthesis of lithium aldimines (1), which we have used as precursors for the preparation of aldehydes, 1-deuterio aldehydes, and α-keto acids.[3]



The lithium aldimine (1) reagent is prepared by the addition of an organolithium reagent to the appropriate isonitrile, which in this case is 1,1,3,3-tetramethylbutylisonitrile[4] (TMBI). For example, when 1 equiv of *sec*-butyllithium and TMBI were combined, treated with D_2O, and then hydrolyzed, 1-deuterio-2-methylbutanal was isolated in 92% yield.[5] This is, in our opinion, the cheapest and most convenient synthesis of C-1 labeled aldehydes yet reported.[2,6] Moreover, carbonation of the intermediate lithium aldimine (1) yields, after hydrolysis, the corresponding α-keto acid in 80% yield.

Various types of α additions to isonitriles have been observed originally by Ugi and coworkers[7] and later by Saegusa and coworkers,[8] but our work represents the first successful 1:1 addition by an organometallic to an isonitrile.[9] Table I lists the reactions carried out to date and the isolated yields of pure products.

Table I. Aldehydes and α-Keto Acids from Organolithium and 1,1,3,3-Tetramethylbutylisonitrile (TMBI)

RiLi	% crude 1	% overall yield Aldehyde[b]	 α-Keto acid[b]
sec-Butyl	100[a]	96	80
	100[c]	92[c]	
n-Butyl	100[a]	93	56
Phenyl	67	55	52

[a] Reaction solvent was pentane. [b] All aldehydes and α-keto acids gave 2,4-dinitrophenylhydrazones which compared with the literature values. [c] Represents yield of 1-deuterio derivative.

The following is an experimental procedure which shows the simplicity of the synthesis. To a stirred solution of 3.76 g (0.027 mol) of TMBI[10] dissolved in 27 ml of ether at 0° under a nitrogen atmosphere is added rapidly 0.027 mol of *sec*-butyllithium in hexane to yield a solution of **1**.

(a) After 10 min, 1.6 ml (0.08 mol) of D_2O was added and stirring continued for an additional 10 min. The reaction mixture was filtered and the solvent evaporated to yield 5.45 g (quantitative crude yield) of aldimine. Steam distillation of the crude aldimine from 0.027 mol of oxalic acid yielded 2.16 g (0.025 mol 92%) of 1-deuterio-2-methylbutanal, bp 92°. Nmr analysis showed >97% deuterium incorporated.

(b) After 10 min, the solution of **1** was added dropwise to an ether slurry of Dry Ice. The solvent was evaporated and the carbonated imine was refluxed in an oxalic acid solution (7.5 g of oxalic acid in 60 ml of water) for 15 min. Extraction with methylene chloride, followed by evaporation of solvent, gave 2.8 g (80% yield) of 2-oxo-3-methylpentanoic acid which gave a 2,4-DNP derivative, mp 169–170°.

The scope and limitations of this[11] and related reactions are under current investigation.

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[1] The support of this work by grants from the National Science Foundation and Public Service Research Grant No. 04065 from the National Cancer Institute is gratefully acknowledged.

[2] A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzes, *J. Amer. Chem. Soc.*, **91**, 763 (1969); A. I. Meyers, *et al.*, *ibid.*, **91**, 764, 765 (1969); A. I. Meyers and A. C. Kovelesky, *ibid.*, **91**, 5887 (1969).

[3] It should be recognized that lithium aldimines (1) have the potential use as intermediates for the preparations of ketones, α-amino acids, and acyloins, just to name a few. We are in the process of exploring this potential.

[4] The reason for the choice of this particular isonitrile will be discussed in our full paper.

[5] Isotopic purity is greater than 97% by nmr analysis.

[6] E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1075, 1077 (1966); D. Seebach, B. Erickson, and G. R. Singh, *J. Org. Chem.*, 31, 4303 (1966); J. C. Craig, *ibid.*, 33, 781 (1968); R. A. Olafson and P. M. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 5058 (1967); D. J. Bennett, *Chem. Commun.*, 218 (1967).

[7] (a) I. Ugi, *Angew. Chem. Intern. Ed. Engl.*, 1, 8 (1962); (b) I. Ugi, K. Rosendahl, and F. Bodesheim, *Ann.*, **666**, 54 (1963); (c) I. Ugi and E. Boettner, *ibid.*, **670**, 74 (1963); (d) I. Ugi and K. Offermann, *Ber.*, **97**, 2276 (1964); (e) I. Ugi, W. Betz, and K. Offermann, *ibid.*, **97**, 3008 (1964).

[8] (a) T. Saegusa, Y. Ito, S. Hobayashi, and K. Hirota, *Tetrahedron Lett.*, 521 (1967); (b) T. Saegusa, Y. Ito, S. Kobayaski, N. Takeda, and K. Hirota, *ibid.*, 1273 (1967); (c) T. Saegusa, Y. Ito, S. Kobayashi, and K. Hirota, *J. Amer. Chem. Soc.*, **89**, 2240 (1967); (d) T. Saegusa, S. Kobayashi, K. Hirota, Y. Okumura, and Y. Ito, *Bull. Chem. Soc. Jap.*, **41**, 1638 (1968); T. Saegusa, Y. Ito, S. Hobayashi, K. Hirota, and N. Takeda, *Can. J. Chem.*, **47**, 1271 (1969).

[9] I. Ugi and U. Fetzer, *Ber.*, **94**, 2239 (1961), found that phenylmagnesium bromide did not undergo a simple addition to cyclohexylisonitrile, but rather several dimeric forms were isolated from the complex reaction mixture.

[10] Prepared in 93% yield from commercially available 1,1,3,3-tetramethylbutylamine by converting the amine to the formamide with formic acid and dehydrating the amide with thionyl chloride in N,N-dimethylformamide. The experimental procedure will be provided upon request. Available from Columbia Organic Chemicals.

[11] The use of different isonitriles and organometallics is now being investigated.

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Photodetachment Energies of Negative Ions by Ion Cyclotron Resonance Spectroscopy. Electron Affinities of Neutral Radicals

Sir:

The electron affinities of free radicals remain some of the most elusive quantities of chemical interest. Because of the great difficulty in obtaining gas-phase electron affinities and consequent lack of available data, knowledge of heats of formation of negatively charged ionic species is very limited, and construction of many thermodynamic cycles thus is impossible. Consequently, except for a small number of reactions, one cannot estimate the energetics required for ionic reactions (for example, acid dissociation) in the gas phase. It is apparent that a convenient method for determining electron affinities of free radicals would be of great value.

In this communication we report preliminary results of our work in determining the energies required for photodetachment of electrons from negative ions in the gas phase, eq 1, by ion cyclotron resonance (icr) techniques.

$$A^- + h\nu \longrightarrow A + e^- \qquad (1)$$

niques. This method is unusually promising in that it is applicable to many ions, as well as being very convenient. To the extent that photodetachment energies approximate, or can be used to obtain, electron affinities, the icr technique may prove to be the method of choice in determining these previously inaccessible quantities. The technique involves measuring the concentrations of ions in the icr spectrometer as a function of the frequency of light which is directed into the resonance cell.

The ion cyclotron resonance spectrometer with modifications for multiple-resonance experiments has been described previously.[1] One additional modification was needed to study photodetachment: the small stainless steel vacuum flange was replaced with a flange containing a glass viewing port. The light source was a 500-W Sylvania DAK bulb housed in a conventional slide projector.[2]

In the ion cyclotron resonance experiment the ions formed in the source region of the resonance cell are drifted by crossed electric and magnetic fields into the analyzer region, where they are detected by measuring their radiofrequency power absorption with a marginal oscillator. This detection scheme is particularly suited to the study of photodetachment not only because of the sensitivity of the instrument but especially because of the long residence times of the ions (greater than 5 msec as opposed to microseconds in other types of experiments). As a result, many of the difficulties inherent in the early photodetachment experiments[3] are obviated. The negative ions can be generated with relative ease.[4] There is no need to detect the light after it has passed through the beam of negative ions,[5] and there is no need to generate high negative ion fluxes. In addition, observation of the negative ions provides direct confirmation of the detachment process while at the same time eliminating the problems associated with measuring the concentration of detached electrons.

The incorporation of the glass window allows the light beam to enter the resonance cell along its longitudinal axis.[6] Since this is the same axis along which the ions move, the probability for photodetachment is maximized, as can be seen in eq 2, where P is the probability for photodetachment,[7] t is the time the ion spends in the beam,[8] f is the geometrical overlap factor between the light beam and the ion beam, $\sigma(\lambda)$ is the cross section for photodetachment, and $\rho(\lambda)$ is the photon flux; the integration is over wavelength.

$$P = tf\int \sigma(\lambda)\rho(\lambda)\, d\lambda \qquad (2)$$

The experiments performed thus far have employed only single resonance with field modulation.[9] Upon irradiation of the resonance cell with light, a decrease in signal intensity indicates that photodetachment is occurring. For OH^-,[10] irradiation with all of the light from the 500-W lamp resulted in a substantial decrease in signal intensity. A set of long-wavelength pass filters was then utilized,[11] with the results displayed in Figure 1. Since the greatest decrease corresponds to the largest probability for photodetachment, it can be seen that photodetachment increases as more and more visible light is allowed to irradiate the OH^- ions. (The fact that little

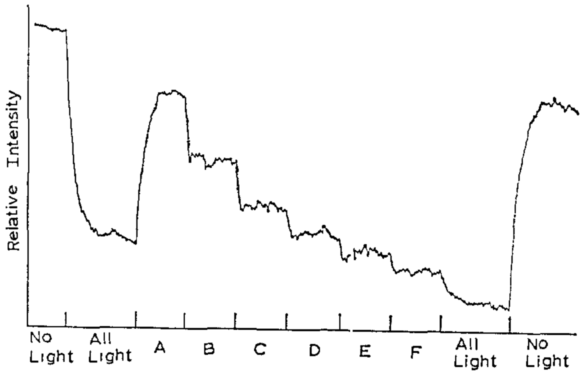

Figure 1. Photodetachment from OH^- using a 500-W tungsten light source and long-wavelength pass filters. "All Light" refers to the incident light beam without filtering; A, B, C, D, E, F refer to the six filters whose 80% transmission cutoff wavelengths are 6400, 5840, 5370, 4970, 4510, and 4100 Å, respectively. High filtering and long scan times were employed; total time is about 17 min. Relative intensities should be interpreted in terms of a slowly decreasing base line.

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(1) Spectra were obtained using a Varian V-5900 icr spectrometer; see J. L. Beauchamp, L. R. Anders, and J. D. Baldeschwieler, *J. Amer. Chem. Soc.*, **89**, 4569 (1967); and J. D. Baldeschwieler, *Science*, **159**, 263 (1968).

(2) It should be noted that the relative spectral intensity curve for an incandescent tungsten bulb exhibits the maximum in the near-ir and decreases sharply toward the near-uv.

(3) L. M. Branscomb in "Atomic and Molecular Processes," D. R. Bates, Ed., Academic Press, New York, N. Y., 1962, pp 100–140.

(4) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **90**, 5636, 6561 (1968); **91**, 2126 (1969).

(5) In more refined future experiments the intensity of the source will be monitored as a function of wavelength. This calibration can be performed separately from the photodetachment experiments.

(6) Cell dimensions are 2.54 × 2.54 × 12.7 cm with the usual open-ended design.

(7) If we let I_0 be the initial concentration of ions formed in the source region and $I(t)$ be the concentration of ions as they drift down the cell in the light beam, then

$$I(t) = I_0 \exp(-tf\textstyle\int\sigma(\lambda)\rho(\lambda)\, d\lambda) = I_0 \exp(-P)$$

In the ion cyclotron resonance experiments the observed signal decrease represents an average of $I(t)$ over the analyzer region. This average $I(t)$ can be related to P at a given time and so to $\sigma(\lambda)$.

(8) Residence times of the ions in the cell have been so long that phase-sensitive detection utilizing light modulation (chopping) has succeeded only at low frequencies (5–10 cps). Different cell geometries which would lower residence times and thus decrease the probability for photodetachment would be expected to increase sensitivity for phase-sensitive detection at higher frequencies (30–40 cps).

(9) The negative ion power absorption is thus displayed as a derivative signal. In the experiments described here, the maximum side of the peak was tuned up for greatest possible sensitivity.

(10) Maximum intensities for OH^- were obtained with an electron beam energy of 6.5–7.0 eV (uncorrected). The principal negative ion formed on electron impact with H_2O has been shown to be H^- (dissociative attachment, peak maximum 6.5 eV), and the principal negative ion–molecule reaction is the proton transfer from H_2O to H^-. See R. N. Compton and L. G. Christophorou, *Phys. Rev.*, **154**, 110 (1967), and references cited therein.

(11) Optics Technology, Set No. 60. Each filter transmits all light of wavelength longer than a specified cutoff out to 2.5 μ. The set of six filters covers the visible region in nominal 500-Å intervals.

photodetachment occurs with light of wavelength longer than 6400 Å indicates[3,10] that photodetachment from H^- is not being observed on a scale comparable with that of OH^-.) During the experiment, f and t in eq 2 remain constant, while the wavelength range is changing. Since the relative spectral intensity of the tungsten bulb decreases at shorter wavelengths,[2] it is evident that the relative photodetachment cross-section curve for OH^- does not fluctuate markedly in the range 6000–4000 Å. This behavior agrees qualitatively with the photodetachment cross section determined by Branscomb.[12] An order of magnitude calculation of the absolute magnitude of the maximum for the cross section is also in accord with Branscomb's value.[12]

A similar study was performed using SH^-.[13] In this case photodetachment was not observed for light of wavelength longer than 5840 Å (filters A and B of Figure 1), and photodetachment was observed for more energetic radiation. The results of using the same set of long-wavelength pass filters as before allow a quantitative estimate of the vertical detachment energy of SH^- of 2.28 ± 0.15 eV.[14] Since the vibronic ground-state structures of the negative ion SH^- and the neutral free radical $SH\cdot$ are similar,[15] the threshold for the photodetachment of SH^- occurs at the energy corresponding to the electron affinity[16] of $SH\cdot$. The value found above agrees within experimental error with that of Steiner, 2.319 ± 0.010 eV.[15] Finally, no photodetachment has been observed with the tungsten light source for Cl^-, consistent with its known electron affinity of 3.613 ± 0.003 eV.[17]

It is now apparent that with beam collimation, more intense light sources, and monochromatic radiation, it should be possible to carry out determinations of photodetachment energies with ease and convenience for a wide variety of negative ions. In favorable cases, this energy can be related directly to the electron affinity, and structural parameters of the ions can be deduced. We expect to report on such determinations shortly.

Acknowledgment. We thank Drs. J. D. Baldeschwieler and S. W. Benson for helpful discussions and J. V. Garcia for technical assistance. We gratefully acknowledge support from the National Science Foundation (GP-4924-X; GP-10621), the National Institutes of Health (GP-145752-02), the donors of the Petroleum Research Fund administered by the American Chemical Society (2917-A4), the National Aeronautics and Space Administration (NGR-05-020-250), and the Center for Materials Research, Stanford University.

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Received October 18, 1969

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(12) L. M. Branscomb, *Phys. Rev.*, 148, 11 (1966).

(13) Maximum intensities for SH^- from H_2S were obtained with an electron beam energy of 2.6 eV (uncorrected).

(14) This estimate is made by assuming that the threshold for photodetachment lies at an energy less than that corresponding to the 10% transmission value of filter C (5130 Å, 2.42 eV) and at an energy greater than that corresponding to the 80% transmission value of filter B (5840 Å, 2.13 eV).

(15) B. Steiner, *J. Chem. Phys.*, **49**, 5097 (1968).

(16) This is true in the case where there is no vibrational excitation and the effects of rotational heating are neglected.

(17) R. S. Berry, C. W. Reimann, and G. N. Spokes, *J. Chem. Phys.*, 37, 2278 (1962).

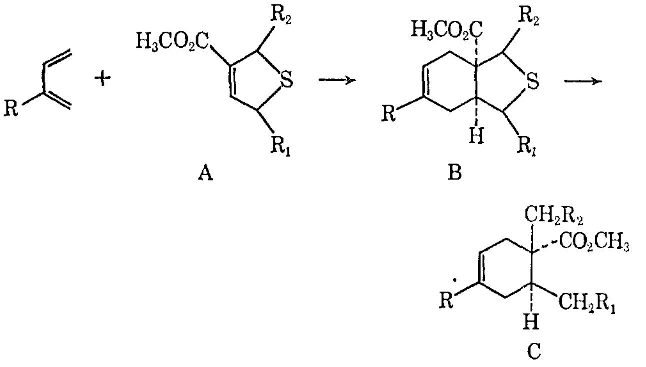
(18) Alfred P. Sloan Fellow 1968–1970.

A New Approach to the Stereospecific Synthesis of Angularly Substituted Polycyclic Systems

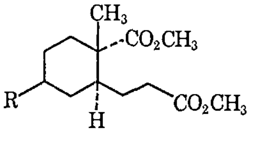
Sir:

The construction of *trans*-fused bicyclic systems has been the object of much effort over the years, especially since the recognition of that structural feature in the C/D hydrindan system of the steroids.[1]

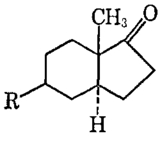
We have devised a new approach of some generality for the solution of this synthetic problem. The approach is schematized by the conversion A → C, and it is obvious that when the substituent R_1 is capable of participating in ring formation with the carbalkoxy group (or a function derivable from it) an angularly substituted *trans* bicyclic system would result, with complete stereospecificity.[2,3] For instance, should the particular dihydrothiophene be A, $R_1 = CH_2CO_2CH_3$, $R_2 = H$, product C would yield after hydrogenation and saponification a (*trans*-2-carboxy)-2-methylcyclohexanepropionic acid (D), the cyclization of which is well known to lead to the 8-methyl-1-hydrindanone system (E).



A B C



D



E

We now detail the synthesis of the dihydrothiophene A, $R_1 = CH_2CO_2CH_3$, $R_2 = H$, and its further transformations along the lines indicated above.

The readily available β-keto ester **1**,[4] from the addition of methyl β-mercaptopropionate and dimethyl maleate followed by cyclization, was reduced most effectively by treatment of its methanol solution with an excess of morpholine–borane[5] at room temperature until a ferric chloride test became negative (*ca.* 3 hr). Addition of 1.1 equiv of sodium methoxide, removal of solvent, and washing with ether gave the sodium salt of 2,5-dihydro-4-carbomethoxy-2-thiopheneacetic acid, from which was isolated the free acid **2**, mp 109.5–110.5° (from ether), $\lambda_{max}^{CHCl_3}$ 3–4, 5.82, 6.02 μ. Esteri-

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(1) *Cf.* W. S. Johnson, *J. Amer. Chem. Soc.*, **66**, 215 (1944).

(2) The obvious possibility of using homologs of tiglic esters in the Diels–Alder reaction is not feasible because such additions are either unsuccessful or give very low yields.

(3) Clearly, when the groups CH_2R_1 and CH_2R_2 are capable of ring formation a stereospecific construction of *cis* polycyclic systems with an angular carboxyl group would result.

(4) B. R. Baker, M. V. Querry, and A. F. Kadish, *J. Org. Chem.*, **13**, 123 (1948).

(5) From Alfa Inorganics, Inc.