a moderate peak at m/e 52, but the intensity of this peak is very small for arsabenzene. The decreasing abundance of the $(M - HCX)^+$ peak might be understandable in terms of decreasing stability of the eliminated HCX molecules.

The uv spectrum of pyridine shows a weak peak at 270 mμ (ε 450) assigned to the $n \rightarrow \pi^*$ transition and three more intense peaks at 250 (ε 2000), 192 (ε 6300), and 175 mμ (ε 80,000), due to $\pi \rightarrow \pi^*$ transitions.[10] The spectra of **2** and **3** were taken in cyclohexane. Each shows two intense bands: at 213 (ε 19,000) and 246 mμ (ε 8500) for **2** and at 219 (ε 15,000) and 268 mμ (ε 11,000) for **3**. Each has a shoulder on the high-wavelength side of these peaks: at 290 mμ (ε 250) for **2** and 305 mμ (ε 350) for **3**. This low-intensity shoulder can probably be assigned to an $n \rightarrow \pi^*$ transition.

The infrared spectrum of pyridine has been subject to a complete analysis.[11] The ir spectra of **2** and **3** in CCl_4 grossly resemble that of **1**. Although there is some uncertainty in the assignment of bands for **2** and **3**, there appears to be a progressive shift to lower frequency of corresponding bands in the series **1**, **2**, and **3**. This shift is rather small from C-H bands: **1** has bands at 3083, 3054, and 3036 cm^{-1}, **2** at 3080, 3045, and 3015 cm^{-1}, and **3** at 3065, 3020, and 2995 cm^{-1}. The shift becomes rather larger for the ring modes. For example, pyridine shows two intense peaks at 1572 and 1439 cm^{-1}. **2** shows bands at 1515 and 1395 cm^{-1}, while **3** shows them at 1505 and 1375 cm^{-1}. Such shifts are in the expected direction for vibrations which involve much displacement of the heavy heteroatom. A similar shift of bands has been noted between furan and thiophene.[12]

Preliminary examination of **1**, **2**, and **3** shows considerable similarity in their spectra. Whether **2** and **3** do show other "aromatic properties" must await an elucidation of their chemistry now in progress.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant No. 5241-AC3-4) and also the National Science Foundation for a grant (GP-8345) to the University of Michigan for the purchase of an MS-9 mass spectrometer.

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(11) C. H. Kline, Jr., and J. Turkevich, *J. Chem. Phys.*, 12, 300 (1944); L. Corrsin, B. J. Fox, and R. C. Lond, *ibid.*, 21, 1170 (1953); J. K. Wilmshurst and H. J. Bernstein, *Can. J. Chem.*, 35, 1183 (1957).

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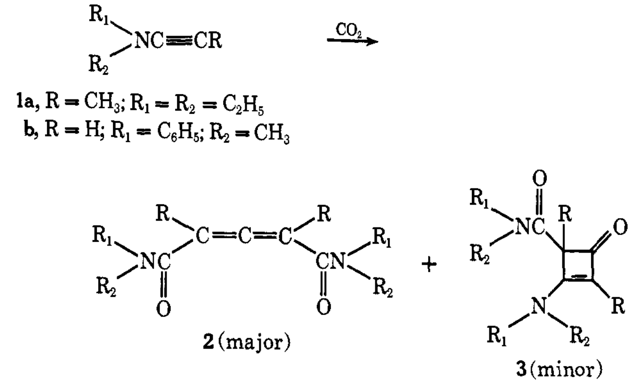
Cycloaddition of Ynamines with Carbon Dioxide. A Route to Diamides of Allene-1,3-dicarboxylic Acids

Sir:

The literature records only a very small number of cycloadditions involving carbon dioxide.[1] We have now observed that ynamines react with great facility with this very simple heterocumulene, and describe here the first results we have obtained on interesting cycloadditions which lead from 2 mol of ynamines (**1**) and 1 mol of carbon dioxide to allenic derivatives of type **2** accompanied by small quantities of aminocyclobutenones of type **3** (Scheme I).

Scheme I



The reaction involving diethylaminopropyne, $(Et)_2NC{\equiv}CCH_3$,[2] is especially fast; its reaction with a saturated solution of carbon dioxide in acetonitrile–ether is exothermic and is complete in 1 hr at −60° or 15 min at room temperature. The reaction is even more rapid under carbon dioxide pressure. Under any of these conditions the yield of the allenic diamide **2a** (ir (film) 1965, 1630 cm^{-1}; nmr[3] (CCl_4) 1.1 (t, 12 H), 1.9 (s, 6 H), 3.4 ppm (q, 8 H)) is practically quantitative. A small amount (less than 5%, not detectable by nmr) of aminocyclobutenone **3a** can be detected by the presence of a very weak absorption band at 1750 cm^{-1} in the reaction product.

The same aminocyclobutenone **3a** (bp 120° (0.005 mm); ir (film) 1750, 1640, 1590 cm^{-1}; nmr (CCl_4) δ 1.45 (s, 3 H), 1.65 ppm (s, 3 H)) is produced, however, in 24% yield, together with 76% of the allenic diamide **2a**, by the use of a less polar solvent, such as hexane (under pressure of carbon dioxide).

N-Methyl-*N*-phenylaminoacetylene (**1b**),[2a] a less reactive ynamine than diethylaminopropyne, reacts slowly with carbon dioxide in hexane, but at ordinary temperature in acetonitrile under 35 atm of carbon dioxide it gives a 40% yield of the *N*-methyl-*N*-phenyldiamide of pentadiene-2,3-dicarboxylic acid (**2b**): mp 173°; ir ($CHCl_3$) 1970, 1640 cm^{-1}; nmr ($CDCl_3$) δ 3.3 (s, 6 H), 5.7 (s, 2 H), 7.2 ppm (m, 10 H). No aminocyclobutenone can be detected in this instance.

The allenic structure of the adducts **2**, which was strongly suggested by their infrared spectra, was confirmed by chemical means: catalytic hydrogenation of the *N*-methyl-*N*-phenyldiamide of allene-1,3-dicarboxylic acid (**2b**) (platinum in acetic acid) gives an 85% yield of the *N*-methyl-*N*-phenyldiamide of glutaric acid (mp 92°) identified by comparison with an authentic sample prepared from the reaction of *N*-methylaniline with dichloroglutaric acid (mp 92°).

(1) (a) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, p 267. (b) In a recent review on cycloaddition (R. Gompper, *Angew. Chem., Int. Ed. Engl.*, 312 (1969)) Gompper refers to unpublished work on the reactivity of aminothioketene ketals.

(2) (a) J. Ficini and C. Barbara, *Bull. Soc. Chim. Fr.*, 2787 (1965); (b) H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, 6, 767 (1967); (c) also obtainable from Fluka Lab., Switzerland.

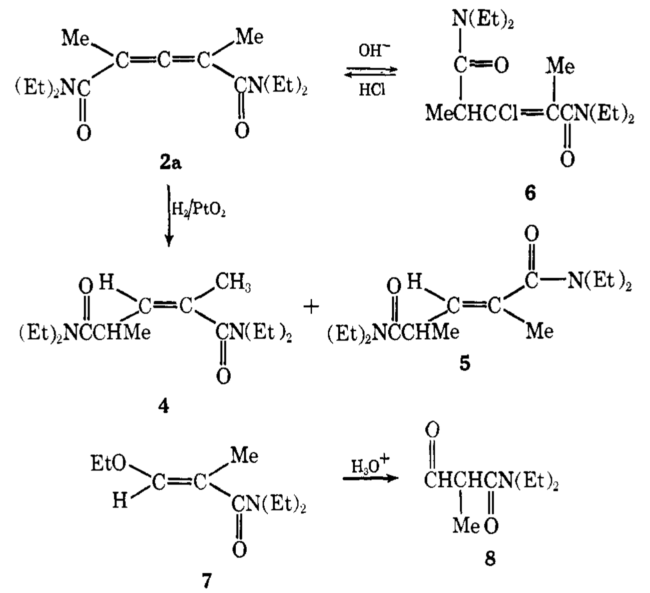
(3) Nmr spectra were recorded on a Varian T-60 with internal TMS reference, or on a Varian A-60.

The allenic *N*,*N*-diethyldiamide **2a** absorbed only 1 mol of hydrogen (platinum in alcohol, 40 atm of hydrogen) to give a quantitative yield of the *N*,*N*-diethyldiamide of 2,4-dimethylglutaconic acid, which is a mixture (correct elemental analysis) of the cis (**4**)[4] (80%) and trans (**5**) (20%) isomers: bp 115–125° (0.05 mm); ir (film) 1640 cm^{-1}. The authentic trans isomer **5** (bp 113° (0.005 mm); ir (film) 1640 cm^{-1}; nmr (C_6D_6) δ 1.8 (d, vinylic methyl, J = 1.6 Hz), 5.75 ppm (d of q, vinylic H, J_d = 10 Hz, J_q = 1.6 Hz)) was prepared (35% yield) by the reaction of diethylaminopropyne (**1a**) with the mixed amide–aldehyde **8** (bp 73–74° (0.08 mm); ir (film) 1730–1640 cm^{-1}; nmr (CCl_4) δ 9.2 ppm (1 H)) obtained (90% yield) *via* hydrolysis in acidic conditions of the adduct **7** (bp 89° (0.05 mm); ir (film) 1650, 1620 cm^{-1}; nmr (CCl_4) δ 1.65 (3 H), 6.2 ppm (1 H)), which is formed (40% yield) by the reaction of *N*,*N*-diethylaminopropyne with ethyl formate.[5]

The mass spectrum[6] of the trans isomer **5** ((70 eV) *m/e* (relative intensity) 268 (M^+, 2) 196 (8), 168 (20), 140 (15), 129 (21), 100 (100), 96 (8), 72 (69), 67 (9), 58 (51)) and the mass spectrum of the mixture of cis (**4**) and trans (**5**) isomers (obtained *via* catalytic semihydrogenation of **2a**) (268 (M^+, 2), 196 (12), 168 (20), 140 (23), 129 (19), 100 (90), 96 (15), 72 (100), 67 (21), 58 (11)) show the same fragmentation.

The allenic diamide **2a** also adds 1 mol of hydrogen chloride to form the *N*,*N*-diethyldiamide of 3-dichloro-2,4-dimethylglutaconic acid (**6**) (mixture of cis and trans isomers: mp 31°; ir (CCl_4) 1640, 1650 cm^{-1}; nmr ($CDCl_3$) δ 1.9 (s, vinylic methyl), 2 ppm (s, vinylic methyl)), which leads to the allenic diamide **2a** upon treatment with a cold solution of 2 *N* sodium hydroxide (Scheme II).

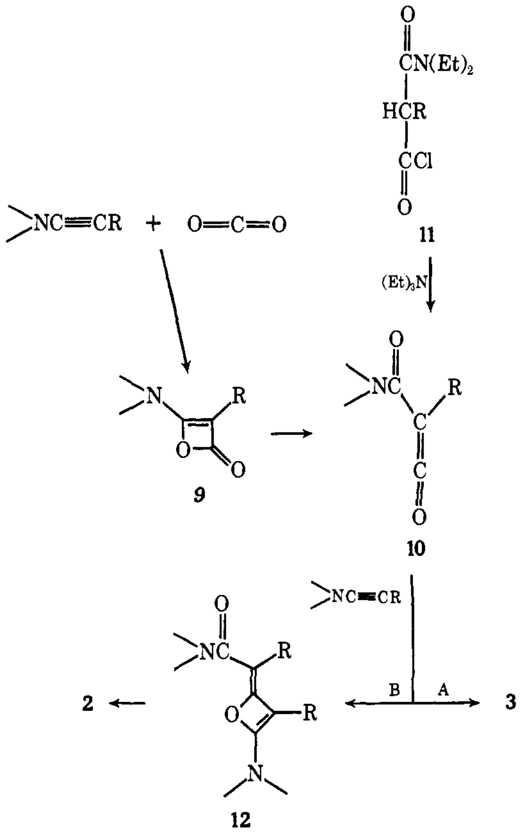
Scheme II



To our knowledge allenic diacids and their derivatives of type **2** are unknown, with the exception of allene-1,3-dicarboxylic acid,[7] the preparation of which is rather laborious. The easy cycloaddition of ynamines with carbon dioxide represents, therefore, a particularly attractive route to these allenic systems.

We would like to suggest that initial cycloaddition of the ynamine and carbon dioxide produces the four-membered enol lactone **9** which then rearranges to the intermediary ketene **10**. The latter would be expected[8] to react with the initial ynamine in two different manners: cycloaddition to the carbon–carbon double bond (path A) leads to aminocyclobutenone **3**, whereas addition to the carbon–oxygen bond (path B) produces the allenedicarboxylic acid diamide **2**, presumably *via* the intermediary oxetene **12** (Scheme III). Strong support for the suggested mechanism was obtained by examining the reaction of diethylaminopropyne (**1a**) with ketene **10** (R = CH_3) (prepared *in situ* by the reaction of triethylamine with the diethylamide–acid chloride from methylmalonic acid **11**). The reaction led, in hexane solution, to a mixture of 80% of the allenic diamide **2a** and 20% of the cyclobutenone **3a**. These are the same yields that were obtained in the reaction of that same ynamine directly with carbon dioxide in hexane.

Scheme III



We conclude that ketenes of type **10** can be intermediates in the cycloaddition of ynamines with carbon dioxide and experiments are in progress to see whether

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(8) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4406 (1968). M. Delannois and L. Ghosez, *Angew. Chem.*, **81**, 33 (1969); W. E. Truce, R. H. Bavry, and P. S. Bailey, Jr., *Tetrahedro Lett.*, **54**, 5651 (1968).

these intermediates might be trapped by other reagents than the starting ynamines.

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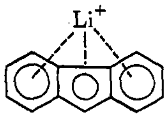
A ^{7}Li Nuclear Magnetic Resonance Investigation of the Structure of Some Aromatic Ion Pairs

Sir:

In a previous investigation[1] of the proton and lithium-7 nmr spectra of fluorenyllithium in diethyl ether, a relatively large upfield shift[2] ($\sim$6 ppm) was observed for the lithium resonance as compared to an aqueous lithium chloride reference. This result was rationalized by suggesting that the lithium cation was located directly above the plane of the aromatic carbanion and in the shielding region of the diamagnetic ring current in the aromatic ion. Subsequently[3] it was shown that the effect of solvent itself on the ^{7}Li chemical shifts of LiBr and $LiClO_4$ can be of the same magnitude ($\sim$6 ppm). Since a change in the ^{7}Li chemical shift of 3.2 ppm on changing the solvent from ether to benzene was observed for fluorenyllithium,[1] there remains the question of whether this change in chemical shift observed for fluorenyllithium is a result of a solvent effect or a change in the structure of the ion pair.



We wish to report some studies of the ^{7}Li nmr spectra of aromatic carbanion systems which strongly suggest that the lithium cation is located above the π cloud of certain planar aromatic anions. The ^{7}Li chemical shifts observed for these anions are determined largely by the distance separating the lithium cation and aromatic anion and to a lesser extent by the degree of delocalization of the negative charge in the anion.

The ^{7}Li chemical shifts obtained from four aromatic carbanions[4] in various solvents are given in Table I. Changes in the ^{7}Li shifts over the concentration range of 0.1–0.4 M are less than 0.2 ppm. In all cases, the chemical shifts are upfield from that of the reference, external aqueous 1.0 M lithium chloride. The ^{7}Li chemical shifts for cyclopentadienyllithium (I) and indenyllithium (II) are considerably upfield from those of 1-phenylallyllithium (III). Since the relative chemical shifts of I–III are approximately the same for a given solvent (either THF or DME), the range of ^{7}Li chemical shifts observed for I–III is most likely due to structural differences of the ion pairs.

Table I. ^{7}Li Chemical Shifts for Some Aromatic Anion Systems

Anion[a]/solvent	δ,[b] ppm
Cyclopentadienyl/THF	8.37
Cyclopentadienyl/DME	8.66
Cyclopentadienyl/p-dioxane	8.68
Indenyl/THF	6.17
Indenyl/DME	6.62
Phenylallyl/THF	0.61
Phenylallyl/DME	0.96
Fluorenyl/Et_2O	6.95
Fluorenyl/DME	3.04
Fluorenyl/THF	2.07
Fluorenyl/HMPA	0.73

[a] Concentration is 0.4 M. [b] In parts per million upfield relative to external, aqueous 1.0 M LiCl.

Evidence from the effect of cation, solvent, and temperature on the proton chemical shifts of I, II,[6] and III[7] suggests that these systems exist in solution as contact or tight ion pairs. Furthermore, proton nmr data on III[7] and a substituted phenylallyl carbanion[8] suggest that the cation is coordinated with the allyl part of the molecule and not directly associated with the π cloud of the phenyl ring. Therefore, the differences in the ^{7}Li chemical shifts of I, II, and III can be accounted for if the lithium cation is located above the π cloud of I and II in the shielding region of the induced diamagnetic ring current of these anions and coordinated with the allyl part of III. The smaller upfield shift of II compared to I with respect to the reference could possibly be due to a combination of two factors: (1) either the ring current in II is not as intense as in I or (2) the contact ion pair formed by II is not as tight an ion pair as that formed by I, resulting in smaller coulombic attractions between anion and cation. Either of these factors would result in a downfield shift of II compared to I with the lithium cation coordinated with the π cloud of these anions.

The data for fluorenyllithium IV (Table I) do not appear to support the above conclusions since the effect of solvent on the ^{7}Li chemical shifts of IV is almost as large as the range of shifts observed for I–III. The suggestion[1] that the lithium cation is coordinated with the π cloud of the aromatic anion would account for the shift in diethyl ether but does not appear to account for the $\sim$6-ppm variation in the ^{7}Li shift with the other solvents. However, IV is a unique system compared to I–III in that IV forms[9,10] both contact and solvent-separated ion pairs in solution depending upon the solvent. In ether, only contact ion pairs are formed, whereas with THF, DME, and hexamethylphosphoric amide (HMPA), essentially all of the ions are in the

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[1] J. A. Dixon, P. A. Gwinner, and D. C. Lini, *J. Amer. Chem. Soc.*, **87**, 1379 (1965).

[2] The ^{7}Li chemical shifts of lithium alkyls are usually found from 1 to 2 ppm downfield from external aqueous lithium bromide reference: T. L. Brown, *Accounts Chem. Res.*, **1**, 23 (1968).

[3] G. E. Maciel, J. K. Hancock, L. F. Lafferty, P. A. Mueller, and W. K. Musker, *Inorg. Chem.*, **5**, 554 (1966).

[4] All spectra were obtained on a Varian Associates HA-100 spectrometer operating at 38.8 MHz in the HR mode. Reported values of the chemical shifts are the average of either alternate upfield and downfield scans calibrated by the side-band technique. Samples were prepared either by using a glove bag with an argon atmosphere and/or high vacuum techniques using slightly modified nmr tubes.[5] Solvents were stored over sodium benzophenone ketyl and were distilled on the vacuum line directly into the sample tubes. The sample of cyclopentadienyllithium was of commercial origin (Alfa Inorganics). The remaining anions were prepared by treating the respective hydrocarbon with lithium metal in the appropriate solvent.

[5] R. H. Cox, E. G. Janzen, and J. L. Gerlock, *J. Amer. Chem. Soc.*, **90**, 5906 (1968).

[6] J. B. Gruntzner, J. M. Lawlor, and L. M. Jackman, private communication.

[7] V. R. Sandel, S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 495 (1968).

[8] (a) H. H. Freedman, V. R. Sandel, and B. P. Thill, *ibid.*, **89**, 1762 (1967); (b) G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **86**, 1345 (1967).

[9] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

[10] L. L. Chan and J. Smid, *ibid.*, **90**, 4654 (1968).