Table I. Reaction of Organocopper Reagents with Conjugated Acetylenic Acids[a]

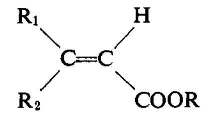
Run	Organometallic reagent	$RC\equiv CCOOR$ (mmoles)	$Cu:C\equiv C-$	Yield, % Starting material	II	III	VIII	Over-all
73	CH_3Cu^b	Ia (20)	2.3:1	0	82	18	0	90
	CH_3Li^c			0	7	90	3	
77	$(CH_3)_2CuLi^b$	Ia (20)	2.3:1	0	7	93	<1	
	CuI^c			0	15	85	<1	84
88	$C_6H_5Cu^b$	VIa (20)	2.3:1	12	11	77	0	
	$C_6H_5Li^c$			4	12	84	0	75
91	$(C_6H_5)_2CuLi^b$	VIa (20)	2.3:1	4	10	86	0	
	CuI^c			4	16	80	0	88
80	CH_3Cu^b	Ib (30)	1.5:1	11	36	53	0	
	CH_3Li^c			0	0	0	53[d]	72
50	$(CH_3)_2CuLi$	Ib (30)	1.5:1	4	19	35	7[d]	73[c]

[a] A solution of the acetylenic compound in 20 ml of ether was added with a syringe during 30 min under nitrogen to the copper compound in 70 ml of ether cooled at −60°. The reaction mixture was stirred at −60° for 1 hr and left for 20 hr at room temperature. [b] Half of the solution or supernatant was withdrawn and poured on ice and HCl. [c] The remainder of the reaction mixture was cooled to −60° and this reagent was added in an equivalent amount to the organocopper compound. The mixture was left for 24 hr at room temperature, then poured on ice and HCl. [d] A mixture of unidentified additional products containing also a small amount of dimethylcarbinol was obtained.

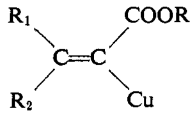
β-methylcinnamic acid (IIa). Addition of methyllithium (equivalent amount to the copper reagent) to this enolate caused an isomerization of the enolate, and the *trans*-β-methylcinnamic acid (IIIa) was obtained on protonation (Table I). A similar product was obtained on addition of the dimethylcopper–lithium reagent to Ia. The larger amount of IIa in the methylcopper addition is not due to the stabilization of the *cis*-enolate (IVc) by the larger relative amount of Cu in the solution, since addition of CuI to the product of reaction of dimethylcopper–lithium with Ia did not change essentially the ratio of the products. Moreover, addition of phenylcopper to tetrolic acid (VIa) and subsequent hydrolysis gave predominantly the product of over-all *cis* addition IIIa. The same product was obtained in the diphenylcopper–lithium addition to VIa.

$C_6H_5C\equiv CCOOR$

Ia, R = H
b, R = CH_3
c, R = Cu



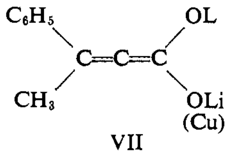
II, $R_1 = CH_3$; $R_2 = C_6H_5$
III, $R_1 = C_6H_5$; $R_2 = CH_3$



IV, $R_1 = C_6H_5$; $R_2 = CH_3$
V, $R_1 = CH_3$; $R_2 = C_6H_5$

$CH_3C\equiv CCOOR$

VI



VII

$C_6H_5(CH_3){=}CHCOCH_3$

VIII

The addition of methylcopper to Ia or VIa is not 100% stereospecific despite the fact that the enolate IVc did not change its configuration for several days at room temperature. This is probably due to a temperature effect during the step of addition itself. Our reactions were carried out at −60° whereas the reported additions to the esters[1,2] were carried out at −78 and −100°. The isomerization may be due to the transformation of the copper enolates to lithium enolates or to a rapid equilibrium between these species. The lithium enolates of the salts undergo probably a rapid inversion of configuration. There is also the possibility that the lithium in these enolates is near the oxygen (VII) and the stereochemistry of the product is determined by the protonation step. A lithium enolate is also probably obtained during the dimethylcopper–lithium additions.[6]

It is not clear whether the steric course of the methylcopper addition to the ester Ib is due to a lower specificity during the addition to esters at the temperature of our study or to an equilibration of the copper enolates of the esters[7] that could be faster than in the case of the acids. No data are known on the equilibration of these enolates.

It is of interest that addition of methylcopper to Ib gives an anion whose ester function is attacked by added excess methyllithium to give the ketone VIII.

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(5) The composition of the product was analyzed by nmr[3] and in several cases by glpc[3] (after transformation of the acids into their methyl esters).

(6) A distinct possibility is the formation of a copper enolate with a methyl group on the copper. This enolate is expected to dissociate more easily than the enolate formed in the methylcopper addition, where the copper is probably coordinated with less basic groups, such as ether or halide anions.

(7) We are investigating this point.

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A Planar Azetidinium Compound

Sir:

Questions about the planarity or nonplanarity of saturated organic four-membered ring systems are the

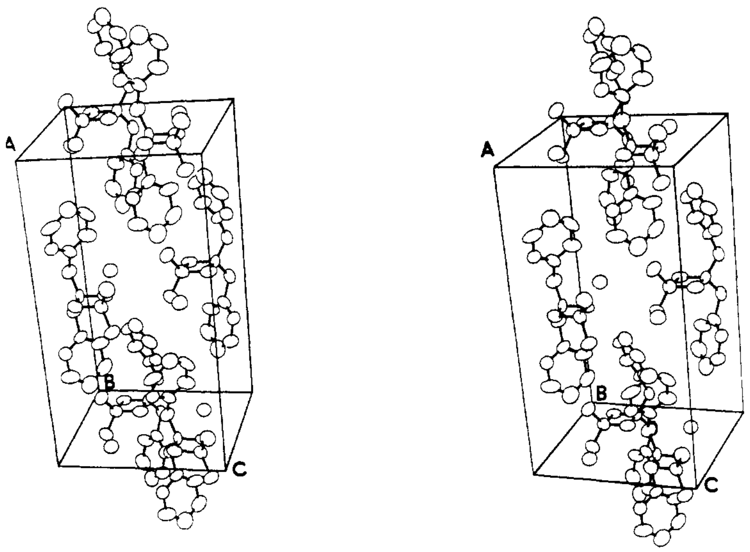

Figure 1. Packing diagram for 1,1-dibenzyl-3,3-dimethylazetidinium bromide. The two views constitute a stereoscopic pair and can be viewed with a small hand stereoscope.

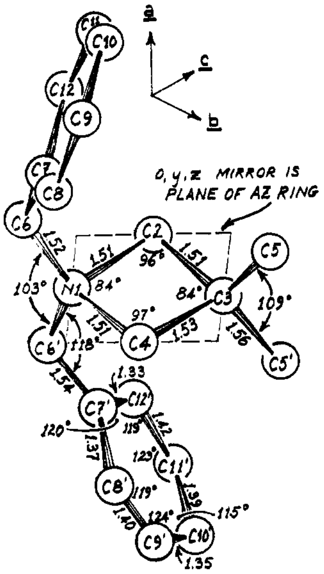

Figure 2. Schematic drawing of the cation indicating angles and distances. Standard deviations of bond angles are ±1° and of bond distances ±0.01 Å.

subject of considerable current interest. Numerous structural investigations[1,2] on cyclobutane derivatives have found both planar and buckled rings. A recent study[3] has found a planar diazetidinium ring but each of the three reported structures[2,4,5] containing an azetidinium ring have found some degree of ring buckling. The dihedral angles found are 166 ± 1° in N-methyl-N-*t*-butyl-3-hydroxyazetidinium methanesulfonate,[2] 169 ± 1° in L-azetidine-2-carboxylic acid,[4] and 175.5 ± 2° in 1-benzyl-1,2,2-trimethylazetidinium bromide.[5] However, the disorder in the latter structure and the somewhat large standard deviation do not exclude the possibility of a planar ring.

We have determined the molecular structure of 1,1-dibenzyl-3,3-dimethylazetidinium bromide by a single-crystal X-ray diffraction study. This is the first reported structure determination in which a definitive planar azetidinium ring has been found. The material was prepared by reaction of 1-benzyl-3,3-dimethylazetidine[6] with benzyl bromide in acetonitrile.[7] The compound crystallizes in space group $Cmc2_1$ with four formula weights in a unit cell of dimensions a = 18.092, b = 9.040, and c = 9.713 Å. Diffractometer data were collected using both Cu Kα and Mo Kα radiation, and the structure was solved by means of superposition techniques.

At the present state of refinement the residual R = 0.075 and the weighted residual R_w = 0.059. The azetidinium ring is required by space group symmetry to lie in the mirror plane at 0, y, z. This, together with the fact that the thermal ellipsoids, shown in the packing diagram (Figure 1), give no indication of disorder across the mirror, establishes unequivocally that this is a planar azetidinium compound. The mirror symmetry of the molecule also requires that the intermolecular packing forces above and below the mirror be identical, thus excluding the possibility of any asymmetric steric effects upon the ring.

Another important property of this structure is revealed from a consideration of the bond distances and angles, as shown in Figure 2. The bond distances in the ring are similar to those recently reported for puckered azetidinium rings.[2,4,5] However, the bond angles in the ring of the planar compound are significantly different from 90°, with ∠NCC = 96–97° and ∠CCC = 83–84°. This additional strain in the ring is undoubtedly the result of (exocyclic) 1,3 or 1,2 steric

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(1) E. Adman and T. N. Margulis, *J. Amer. Chem. Soc.*, **90**, 4517 (1968).

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interactions between ring substituents. Such an interpretation is consistent with the small values of the C5–C3–C5′ and C6–N–C6′ angles shown in Figure 2. A more detailed discussion of the structure of this and related compounds will be presented in a subsequent paper.

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A Reinvestigation of Nitrogen-15 Chemical Shifts of *para*-Substituted Nitrobenzenes[1]

Sir:

Recently several research groups[2–4] have determined ^{14}N chemical shifts for *para*-substituted nitrobenzenes, which deviate both in magnitude and sign from ^{15}N shifts for corresponding compounds reported 3 years ago.[5] These striking discrepancies prompted us to reinvestigate the substituent effects on the ^{15}N chemical shifts of nitrobenzenes because there seemed no obvious reason as to why the ^{14}N and ^{15}N shifts should differ widely.

Table I. Nitrogen Chemical Shifts of the Nitro Group in *para*-Substituted Nitrobenzenes[a]

Substituent	$^{15}N^{b}$	$^{14}N^{c}$	$^{14}N^{d}$	$^{14}N^{e}$	$^{15}N^{f}$
NH_2	4.4			−0.9	−0.3
$NHCOCH_3$	3.1				
H	0.0	0	0	0.0	0.0
OCH_3	4.4		−1	0.1	0.2
F	3.6				1.1
Cl	2.1				2.3
Br	1.3				2.7
CN	−2.6	6		3.8	3.3
CHO			4.5		
NO_2	−3.9		5	4.6	4.6
COOH		5			
Error	±0.2	±4	±1.4	±0.5	±0.2

[a] A positive value of the chemical shift indicates a shift upfield from nitrobenzene. The values in the last column were obtained for acetone solutions. Apart from this, the nmr measurements and the synthesis of the labeled compounds followed the previous description.[5] [b] Reference 5. [c] Reference 2. [d] Reference 3. [e] Reference 4. [f] This work.

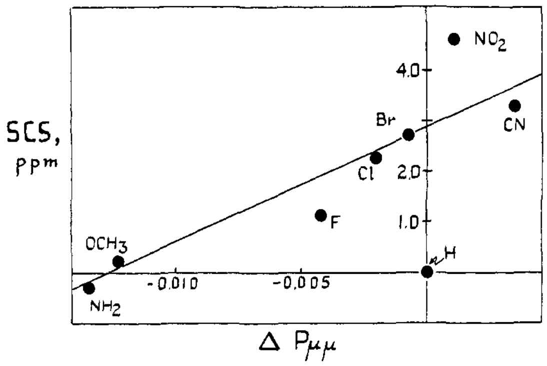

Figure 1. ^{15}N-substituent chemical shifts (SCS) as a function of changes in π-electron density, $\Delta_{\mu\mu}$, from simple HMO theory.

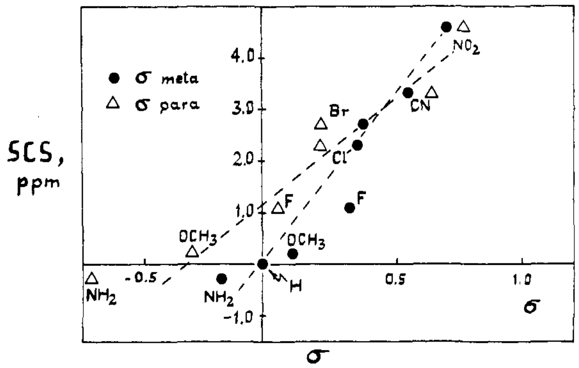

Figure 2. ^{15}N-substituent chemical shifts (SCS) and Hammett constants σ_m and σ_p.[7]

A summary of the results is presented in Table I. The substituent chemical shifts in the first column clearly differ both in sign and magnitude from the values found in four other investigations, which are largely consistent with one another. The only explanation we can offer for some of the erroneous shifts previously reported is that the field sweep was taken in the wrong direction.

The results indicate that the influence of the substituents on the ^{15}N chemical shifts of nitro groups is slightly different from their influence on ^{19}F chemical shifts.[6] Attempted correlations with the π-electron density, $P_{\mu\mu}$, on the nitrogen atom (Figure 1) or the π-bond order, $P_{\mu\nu}$, of the C–N or the N–O bonds show strong deviations from linearity. Especially striking is the reversal of *p*-dinitrobenzene and *p*-nitrobenzonitrile, as well as the fact that the best line does not go through the origin of the plot. Probably changes in π-electron density exert only a minor influence on the ^{15}N resonances of nitrobenzenes. This is also indicated by the correlation of ^{15}N shifts with the Hammett constants[7] σ_p and σ_m as shown in Figure 2. All substituents now fall in the right sequence, except for methoxy with σ_p. The fit with the σ_m seems better than for σ_p,

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