

chains of silica gel. By contrast, in the case of α -amino acids which have a hydrophilic α -alkyl substituent, the (L)-amino acid may form more stable complex than the (D)-amino acid because the hydrophilic functional group of α -alkyl substituent of the (L)-amino acid can hydrogen bond to the hydroxy group of the fixed ligand and the intercalation of the α -alkyl substituent between the octadecyl chains of silica gel becomes a less favorable process. In this event, the (L)-amino acid is retained longer than the (D)-amino acid. However, we do not rule out that the hydrophilic functional group of the α -alkyl substituent of an (L)-amino acid can coordinate to Cu(II) at the axial position of the square planar complex by replacing the hydroxy group of the fixed ligand. In that case, the chiral recognition mechanism becomes more complicated than the one shown in Figure 2. This complicated chiral recognition mechanism may be responsible for the unexplained elution order of glutamic acid and glutamine.

In conclusion, (1S, 2R)-norephedrine derivative **1** can be loaded onto a commercial reverse phase octadecyl-silica gel column and has been shown to be quite successful in the resolution of underivatized racemic α -amino acids. In order to explain elution orders, a possible structure of the ternary complex formed from the fixed ligand, amino acid and Cu(II) has been proposed. Studies to elucidate the effect of the composition and pH of the mobile phase and the concentration of Cu(II) on resolution behavior are in progress in our laboratory.

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- The *trans* conformation is known to be energetically more favorable than the *cis* conformation. See references 1(d) and 5.

Photochemical Formation of Polymer-Bound C₆₀[†]

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The recent report that the all-carbon molecules C₆₀ and C₇₀ can be made in high yield in a carbon arc has stimulated new interest in their molecular and spectroscopic properties, and their chemical properties.²⁻¹⁰ This new allotrope of carbon, C₆₀, has a graphitic closed cage structure consisting of twelve five-membered rings separated by twenty benzenoid six-membered rings. The molecule, which contains 60 atoms lying at the vertices of a truncated icosahedron, is known as buckminsterfullerene, or simply buckyball, because the geodesic domes designed by inventor Buckminster Fuller led to the initial proposal of its structure. Recently Smalley and co-workers reported one of the first chemical reactions of C₆₀.¹⁰ They found that C₆₀ undergoes Birch reduction (Li, liquid NH₃, *t*-BuOH), underscoring the aromatic character of the molecule. Olah, Malhotra and co-workers found that alkylation of the C₆₀ and C₇₀ polyanion mixture with excess methyl iodide yields a light brown solid, a mixture of polymethylated fullerenes.¹¹ An X-ray crystal structure that confirms the soccer ball-shaped carbon framework of C₆₀ was also reported.¹² In order to study the chemical reactions of C₆₀, we tried to make fullerenes and their derivatives of C₆₀.¹³⁻¹⁵ The success in the preparation of the fullerenes prompted us to study their properties, reactivities, and any possible applications.¹³⁻¹⁵

Here this paper describes the first photochemical reactions of C₆₀ (**1**) with alkenes, such as 1,3-cyclonhexadiene (**2**) and isoprene (**4**).^{13,15} The molecular forms of C₆₀ and C₇₀ were prepared by following the method of Krätschmer *et al.*² and characterized by IR, Visible/UV, and ¹³C-NMR spectra. The toluene-soluble material extracted from the graphite evaporation product is predominantly constituted of C₆₀ and C₇₀.

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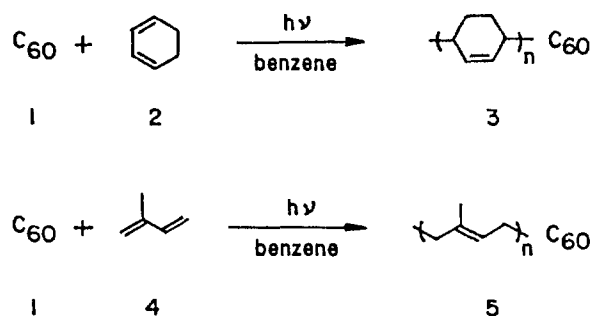


Figure 1.

The two compounds were separated by column chromatography on alumina (aluminum oxide, activated, neutral, Brockmann I, standard grade, 150 mesh). A solution of 3.0 mg (4.2×10^{-6} mole) of C_{60} (1) and 6.0 ml (6.3×10^{-2} mole) of 1,3-cyclohexadiene (2) in 30 ml of deoxygenated benzene was irradiated with 350 nm UV light to yield polymer-bound C_{60} (3). Column chromatography with *n*-hexane and ethyl acetate (gradient elution) was used to separate the desired compound of C_{60} .

Electronic absorption spectrum of the photoproduct (3) was compared with that of C_{60} .⁵ Visible/UV absorption (*n*-hexane) by C_{60} begins with an abrupt onset of 635 nm, followed by several bands of varying width (centered at 621, 598, 591, 568, 540, and 492 nm).⁵ A second onset leading to stronger absorption occurs in the form of a band at 404 nm. These are followed by bands at 328, 256, and 211 nm. The absorption bands of the photoproduct (3) were observed at 635, 607, 546, 395, and 366 nm in benzene. The product was also investigated by 300 MHz 1H -NMR spectra in benzene- d_6 . The peaks at 5.84 (b s, 1H) and 5.76 (b s, 1H), 2.11 (b s, 2H), and 1.68 ppm (b m, 4H) are attributed to the polymer-bound C_{60} (3). The IR spectrum (NaCl) exhibited bands at 3017, 2926 and 2862, 1661, 1448 and 1396, and 725 cm^{-1} , strongly suggesting the presence of ν_{C-H} ($=C-H$), ν_{C-H} (CH_2 and CH_3), $\nu_{C=C}$, δ_{C-H} (CH_2 and CH_3), and δ_{OPP} ($=C-H$, *cis*-alkene), respectively, in the new compound (3). C_{60} was also irradiated with an excess of isoprene (2-methyl-1,3-butadiene, 4) in deoxygenated benzene to yield the same type of polymer-bound C_{60} (5).¹⁶ These reactions could be rationalized by using a radical mechanism. It may be said that C_{60} acts as a free-radical initiator in these photopolymerization reactions.¹⁷ Attempts at the determination of the precise molecular structure of the polymer chain of 3 and 5 are now pursued.

Functionalization of C_{60} via the radical polymerization described here will allow chemists to go beyond buckyballs in the pursuit of new types of organic molecules. Very recently, some scientists from AT & T Bell Laboratories have created the films of buckyballs and studded them with impurities that help the molecules carry electric current.¹⁸ We are now studying the properties of these novel species and also syntheses of conjugated π system-bound buckyballs which will lead to a new class of organic conductor or conducting polymer. Syntheses of polyene or polyyne-bound buckyballs are under active investigation in our laboratory.

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16. **5**: 1H -NMR (C_6D_6); δ 4.92 (b t, 1H, $J=12.8$ Hz), 1.77 (s, 3H), and 1.74 ppm (m, 4H). IR (NaCl); ν 3081 (ν_{C-H}), 2959, 2924 and 2854 (ν_{C-H} of alkyl), 1647 ($\nu_{C=C}$), 1458 and 1387 (δ_{C-H} of CH_2 and CH_3), and 800 cm^{-1} ($\delta_{OPP}(=C-H)$, trisubstituted alkene). Visible/UV (benzene); λ_{max} 635, 607, 546, 395, and 366 nm.
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Selective Reduction by Lithium Bis- or Tris(di-alkylamino)aluminum Hydrides. IV. Transformation of Primary Carboxamides to Aldehydes by Lithium Tripiperidinoaluminum Hydride¹

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The development of simple synthetic routes to aldehyde from readily available carboxylic acids and their derivatives is an important goal in organic chemistry. During the past some 70 years, numerous efforts have been made to find simple and general synthetic routes to aldehyde^{2,3}. However, there have been lacking in methods for direct conversion of primary carboxamides into aldehydes¹.

In the course of exploring the reducing characteristics of lithium dialkylaminoaluminum hydrides, we found that lithium tripiperidinoaluminum hydride (LTPDA), readily prepared from the reaction of lithium aluminum hydride and 3 equiv. of piperidine in THF at 0°C⁴, effects such transformation in good yields.

Excess LTPDA reduces both aliphatic and aromatic primary carboxamides slowly, requiring 1 or 2 days at room temperature, with concurrent evolution of hydrogen⁵ (1 equiv. for aliphatics and 2 equiv. for aromatics).

In general, the yields from aliphatic carboxamides examined are varying with the structure, showing yields in the range of 50-80%, except for acetamide, 2-chloroacetamide, and methacrylamide.

Reductions of acetamide and methacrylamide afford poor yields of the corresponding aldehydes. However, the reagent readily converts aromatic primary carboxamides into the corresponding aldehydes in yields of 80-90%, with the exception of nitrobenzamide. The nitro group itself appears to be reduced readily by this reagent under the reaction conditions. Derivatives bearing alkyl, alkoxy, or halogeno groups are readily accommodated. Nicotinamide is also reduced to the corresponding aldehyde in a moderate yield.

The following procedure for the reduction of benzamide is illustrative. An oven-dried, 200 ml flask, fitted with a side arm and a bent adapter leading to a mercury bubbler, was flushed with dry nitrogen and charged with 6.42 g (53 mmol) of benzamide and 120 ml of THF. To this mixture was added 106 ml of 1.50 M LTPDA (159 mmol) solution in THF slowly at room temperature and the mixture was stirred for 24 h at that temperature. An amount less than 2 equiv. of hydrogen was evolved slowly. Analysis of an aliquot with (2, 4-dinitrophenyl)hydrazine yielded 92% of the corresponding

Table 1. Yields of Aldehydes in the Reduction of Representative Primary Carboxamides with Lithium Tripiperidinoaluminum Hydride in Tetrahydrofuran at Room Temperature^a

Amide	Reaction time (h)	Yield of aldehyde (%) ^b
Acetamide	48	37
2-Chloroacetamide	48	20
Trimethylacetamide	48	72
<i>n</i> -Butyramide	48	42
Isobutyramide	24	73
Methacrylamide	24	24
Caproamide	24	66(57) ^c
Octadecaneamide	48	84
Cyclohexane-carboxamide	48	60
Benzamide	24	92(81) ^d (88) ^c
<i>o</i> -Toluamide	24	89
4-Methoxybenzamide	24	94(82) ^d
2-Ethoxybenzamide	30	82
2-Chlorobenzamide	24	83
2-Nitrobenzamide	24	34
Nicotinamide	24	53

^aRatios of reagent to compound are 2 : 1 for aliphatics and 3 : 1 for aromatics. ^bAnalyzed with (2,4-dinitrophenyl)hydrazine. ^cReacted for 3 h at 50°C. ^dYields based on the analytically pure aldehydes isolated by the sodium bisulfite procedure.

aldehyde.

The rest of the reaction mixture (50 mmol) was hydrolyzed with 3 N H₂SO₄ and then saturated with sodium chloride. The separated organic layer was subjected to the sodium bisulfite isolation procedure⁶ to provide an analytically pure benzaldehyde (81%).

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