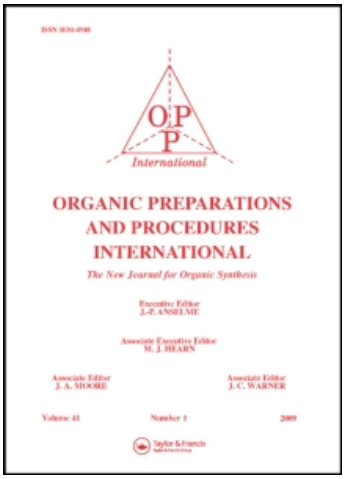

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A CONVENIENT PREPARATION OF α,α-DIPHENYLACETOPHENONE

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(s, 3, $COCH_3$).

6. The cis axial-equatorial relationship for the hydrogens at the 1 and 6 positions of purified 1 was confirmed by the magnitude of their coupling constant (J = 4.03 Hz) as ascertained by double resonance experiments. Composed of 13 sharp lines, the ^{13}C NMR of 1 is also in harmony with the presence of a single stereoisomer. We are assuming that the bulky 3-buten-2-one side chain of 1 occupies an equatorial ring position, thereby precluding the possibility of a trans equatorial-equatorial relationship for the 1 and 6 ring position protons of 1.
7. This yield of pure 1 represents a 57% recovery of the available 1 in the mixture. We have found that a less conservative collection of 1 by HPLC seriously compromises its purity.

A CONVENIENT PREPARATION OF α,α-DIPHENYLACETOPHENONE

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(1/13/79)

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Although several mechanistic studies and synthetic applications of alkali aromatic ketyls[1-4] have been recently published, there have been no further study of the reaction of phenyllithium with carbon monoxide since the work of White-

sides, et al.[5] In that paper the benzophenone ketyl was shown to be an intermediate but several mechanistic questions remained unresolved.

As part of a detailed investigation of the mechanism of the reaction, we have established conditions which account for the total fate of phenyllithium and, secondly, minimize the formation of by-products. Only four products were formed: α,α-diphenylacetophenone (I) is the major product, benzophenone (II), benzoin (III) and α,α-diphenyl-α-hydroxyacetophenone (IV).

$$PhLi \xrightarrow[2.\ H_2O]{1.\ CO} \underset{I}{PhCCHPh_2} + \underset{II}{PhCPh} + \underset{III}{PhCCHPh} + \underset{IV}{PhCCPh_2}$$

Solvent and temperature effects, among other variables, were studied. The solvents tested were: diethyl ether, n-hexane, tetrahydrofurane and dimethoxyethane, but the best yields were obtained using phenyllithium as a fine powder, with no solvent. Some representative results are gathered in the Table.

TABLE.- Product Yield (%) from Solid PhLi and CO[a]

Temp. (°C)	PhLi (mmole)	I	II	III	IV
0	4.4	42	33	15	9
0	5.0	44	33	13	9
25	6.1	56	25	11	7
25	3.7	63	20	10	6.5
60	4.2	70	19	7	3
60	4.9	78	14	5	2
110[b]	5.0	94	1.5	-	-

a) The yields represent % conversion. b) 4.5% of phenyllithium was converted to triphenylcarbinol.

As it can be observed the conversion to I increases with the temperature of reaction while the yield of II decreases, as it has been observed in diethyl ether solution.[5] The reactions leading to products III and IV were also minimized at high temperatures. All the reported yields were obtained by glpc; for the reactions carried out at 60° and 110°, I was also isolated by standard techniques.

It is worth mentioning that the previous preparations of I from benzoin[6] (yield: 51%, 41% over-all starting from benzaldehyde[7a]) or from triphenylethylene[8] (yield: 59%, 35% over-all from benzyl chloride[9]), are more laborious than that described here. Furthermore, the synthetic capabilities of the alkali aromatic ketyls are very well known;[10] the reaction is now being examined in an attempt to introduce organic groups before the hydrolytic quenching. Preliminary runs with butyl are promising but methyl iodide treatment gave a mixture of products as previously observed with similar anions.[2]

EXPERIMENTAL

Melting points are uncorrected. All compounds reported here were fully characterized by mass spectrometry (using a Varian Mat CH7 spectrometer), infrared (determined on a Perkin Elmer 137 spectrophotometer), ultraviolet (recorded on a Beckman DK2A spectrophotometer) and nuclear magnetic resonance (determined on a Varian A-60 spectrometer) spectroscopy and showed spectral characteristics consistent with the spectra of authentic samples. The glpc analyses were carried out on a 5830 Hewlett-Packard Gas Chromatograph. Reactions involving phenyllithium were carried out using standard techniques for manipulation of oxygen and water-sensitive compounds.[11]

Phenyllithium was prepared by a method adapted from that of Schlosser and Ladenberger;[12] no difference was observed by using freshly prepared butyllithium or the commercial solution in n-hexane. Carbon monoxide was generated by standard procedures[7b] and purified by passing through a column of potassium hydroxide and then bubbling through a solution of benzophenone ketyl in toluene.

Reaction of Phenyllithium with Carbon Monoxide.- The phenyllithium contained in a tube capped with a No-air stopper was exposed to carbon monoxide (1 atm pressure). The white solid turned immediately to pink, then to red and when the gas absorption had ceased was a brownish purple powder. n-Undecane was added as internal glpc standard, then n-hexane to form a homogeneous suspension (10 ml). A 1.0 ml aliquot of the reaction mixture was quenched with water, extracted with ether and the dried ($MgSO_4$) ether layer was analyzed by glpc.

Isolation and Characterization of the Products.- The remaining solution was worked up in a similar way and the ether layer was distilled at reduced pressure. The white residue was treated with methanol and the crystals collected. A yield of 60% of I, mp. 137° was obtained from the reaction mixture carried out at 60°. The methanolic solution was passed through a column of silica gel with benzene-methanol mixture as eluent. Fractions containing II and III were collected and characterized by their mp., spectra and tlc behaviour. Comp. IV is produced only in small amount and was identified by glpc-ms.

Product Balance by glpc.- The reaction mixture was analyzed by glpc on a 3% SE 30 on Chromosorb W column at 50-250°. On this column benzoin and benzil have the same retention time but only benzoin was isolated by column chromatography and fully characterized.

Standard Preparation of I.- n-Butyllithium (10 ml of a 1.2 N hexane solution) was transferred by a syringe to a 20 ml centrifuge tube (nitrogen atm) containing several glass pearls, and capped with a No-air stopper. Iodobenzene (1.6 ml) was

added dropwise and PhLi precipitated as white crystals, which were thrice washed with n-hexane added by a syringe and dried at 60° and 10 mm Hg pressure. The tube was heated at 110° and carbon monoxide (1 atm pressure) was passed through a length of tygon tubing and hypodermic needle. Fast gas absorption ocurred in the first 10 min, then it slowed and ceased completely (8 mmole of CO) in 4 hr. The resulting reaction mixture was allowed to cool to room temperature, next it was suspended in n-hexane (10 ml), hydrolyzed with water (5 ml), extracted with diethyl ether and dried over magnesium sulfate. Distillation of the ether at 30° and reduced pressure rendered 1.03 g (94% yield) of I, crystallization from methanol gave mp. 137°.

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AN IMPROVED PREPARATION OF CORONENE

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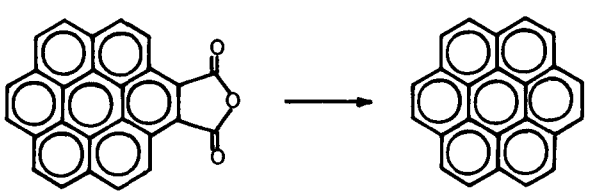
Synthesis of coronene is generally on a mg scale. Our attempts to increase the scale were frustated until we developed a heater and improved glassware[1] which enabled successfully carrying out the reaction at the required temperature. Previously reported yields of coronene were 66% (mp. 425-428°)[2] and 73% crude with 18% purified.[3] We consistently obtained pure coronene in 80% yield, mp. 434-438° (uncorr.) on a gram scale.



I II

EXPERIMENTAL

Melting points were determined on Mel-temp capillary melting point apparatus with a 90-510° thermometer from H-B instru-