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Preliminary communication

Carbonation of some perhaloaryllithium compounds

D.S. SETHI, M.R. SMITH, JR. and H. GILMAN
Chemical Laboratory, Iowa State University, Ames, Iowa 50010 (U.S.A.)

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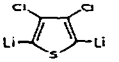
In connection with a study concerned with the use of *sym*-perhaloaryl ketones, one of the methods which suggested itself for the synthesis was the carbonation of perhaloaryllithium compounds. It was earlier shown[1] that the admission of gaseous carbon dioxide at moderate temperatures to an ether solution of phenyllithium gave, subsequent to hydrolysis, 70% of benzophenone and 4% of benzoic acid. Under corresponding conditions, *p*-tolyllithium gave 77–81% of di-*p*-tolyl ketone and 1% of *p*-toluic acid. It was also reported that a mixed ketone such as n-butyrophenone could be prepared from lithium butyrate and phenyllithium. A survey of this general reaction by Schöllkopf[2] has just appeared in Houben–Weyl, together with some experimental procedures.

We are now reporting that when perhaloaryllithium compounds are used instead of phenyllithium, under corresponding conditions, essentially no ketone is obtained and the yield of acid is quite high. The perhaloaryllithium compounds used were: pentafluorophenyl-, pentachlorophenyl-, tetrachloro-4-pyridyl-, trichloro-2-thienyl- and 3,4-dichloro-2,5-dilithiothiophene. The general results are included in Table 1, and the identity of each compound was established by comparisons with authentic samples.

TABLE 1

CARBONATION OF SOME PERHALOARYLLITHIUM COMPOUNDS

RLi compound	Yield (%)	
	Ketone	Acid
C_6H_5Li	86–88	~4–6
C_6F_5Li	–	90
C_6Cl_5Li	–	71
$(4\text{-}C_5Cl_4N)Li$	–	69[a]
$(2\text{-}C_4Cl_3S)Li$	–	95
	–	87

[a] A mixture of tetrachloro-4-carboxypyridine (85–90%), and tetrachloro-2-carboxypyridine (10–15%).

In order to correlate our findings with those obtained some time ago, experiments were repeated with the gaseous carbonation of phenyllithium. We have found even higher yields of benzophenone (86–88% *vs.* 70%); and the yields of benzoic acid were 4–6% *vs.* 4%.

The trichloro-2-thienyllithium is quite stable in refluxing ether, at which temperature the gaseous carbon dioxide was admitted at a moderate to slow rate (as was done in the initial experiments[1] with phenyllithium). We have found that even the relatively lesser stable pentafluorophenyllithium undergoes no significant decomposition when kept for a short time at about 0°, during which the gaseous carbon dioxide was admitted. Under such conditions the yield of pure pentafluorobenzoic acid was 90%.

In the experiments with 3,4-dichloro-2,5-dilithiothiophene there was no evidence of a polymeric polyketone, and the yield of 3,4-dichloro-2,5-dicarboxythiophene was 87%.

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