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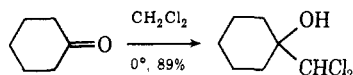
A Practical Synthesis of Polyhalomethylithium Carbonyl Adducts

Sir:

The type of reagent which results from the combination of polyhalomethane with *n*-butyllithium at low temperature, formally a polyhalomethylithium $X_2\text{-CHLi}$ or $X_3\text{CLi}$,¹ has proved to be versatile synthetic species.² The significant limitation on the broad utility of these reagents often arises from their extreme thermolability.^{1,3} Thus, the optimum reaction temperature, which is normally between -70 and -120° (internal temperature), is limited at the lower end of the range by the rate of formation and at the upper end by the tendency of carbenoids to decompose.

We now report here the successful use of lithium dicyclohexylamide⁴ as the base in a practical synthesis of polyhalomethylithium carbonyl adducts. The method involves an *in situ* carbenoid formation in the presence of carbonyl compounds, thus avoiding a troublesome procedure with the preformed carbenoid.³

A vigorously stirred solution of cyclohexanone in methylene chloride was treated with lithium dicyclohexylamide at 0° over a period of 5 min. After stirring for an additional 10 min at 0° , the reaction mixture was worked-up as usual to furnish 1-(dichloromethyl)cyclohexanol in 89% isolated yield. The scope of this



new method, illustrated by the reaction between several representative polyhalomethanes with various carbonyl compounds, is summarized in Table I.

It is noteworthy that diiodomethylithium⁵ and tribromomethylithium, both of which are extremely un-

(1) (a) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967); **11**, 473 (1972), and references therein; (b) D. F. Hoeg and D. I. Lusk, *J. Amer. Chem. Soc.*, **86**, 928 (1964); D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965); D. F. Hoeg and D. I. Lusk, *J. Organometal. Chem.*, **5**, 1 (1966).

(2) Polyhalomethylithium carbonyl adducts may be easily converted to a variety of important structural classes (*inter alia*): (a) α -chloro ketone, H. Taguchi, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, 4661 (1972); J. Villieras, C. Bacquet, and J. F. Normant, *J. Organometal. Chem.*, **40**, C1 (1972); G. Köbrich and J. Grosser, *Tetrahedron Lett.*, 4117 (1972); I. Kuwajima and Y. Fukuda, *Chem. Lett.*, 327 (1973); G. Köbrich and J. Grosser, *Chem. Ber.*, **106**, 2626 (1973); (b) α,β -unsaturated aldehyde, H. Taguchi, S. Tanaka, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, 2465 (1973); (c) α -chloroaldehyde, G. Köbrich and W. Werner, *ibid.*, 2181 (1969); (d) α -hydroxyaldehyde, J. I. Stevens, *J. Org. Chem.*, **37**, 1248 (1972), and references cited therein; (e) dichloroolefin, G. Köbrich, H. Trapp, K. Flory, and W. Drischel, *Chem. Ber.*, **99**, 689 (1966); G. Köbrich, H. Trapp, and I. Hornke, *ibid.*, **100**, 961 (1972).

(3) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

(4) R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, **95**, 582 (1973). Villieras also reported the generation of dibromomethylithium solution using lithium diisopropylamide at low temperature: J. Villieras, *J. Organometal. Chem.*, **50**, C7 (1973).

(5) As far as our knowledge, diiodomethylithium was generated for the first time by our new procedure.

Table I. Yields of Polyhalomethylithium Carbonyl Adducts^a

Polyhalomethane (equiv)	Carbonyl	Temp, °C	% yields ^b
Methylene chloride (excess)	Cyclohexanone	-78	100
Methylene chloride (excess)	Cyclohexanone	0 ^d	89
Methylene chloride (2) ^c	Cyclohexanone	-78	86
Methylene chloride (excess)	Cyclopentanone	0 ^d	66
Methylene chloride (excess)	Cyclopentanone	-20 ^d	90
Methylene chloride (excess)	Cycloheptanone	-20 ^d	88
Methylene chloride (excess)	6-Methyl-5-hepten-2-one	0 ^d	84
Methylene chloride (2) ^c	Nonanal	0 ^d	73
Methylene bromide (2) ^c	Cyclohexanone	-78	91
Methylene bromide (2) ^c	Cyclopentanone	-78	82
Methylene bromide (2) ^c	Nonanal	-78	77
Methylene iodide (2) ^c	Nonanal	-78	79 ^e
Chloroform (excess) ^c	Cyclohexanone	-78	94 ^f
Chloroform (2) ^c	Cyclohexanone	-78	92 ^f
Chloroform (excess) ^c	Cyclopentanone	-78	91
Bromoform (10) ^c	Cyclohexanone	-78	89 ^g
Bromoform (2) ^c	Cyclohexanone	-78	91 ^g

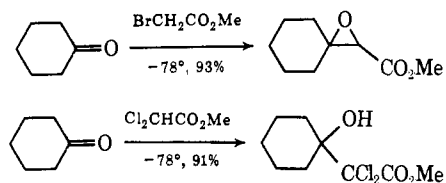
^a No attempt has been made to optimize yields. Unless specified, the reactions were carried out on a 1 mmol scale exactly as described for the larger scale preparation of 1-(tribromomethyl)cyclohexanol. All products were completely characterized by spectroscopic methods and elemental analyses. ^b Yields are based on material isolated chromatographically. ^c Tetrahydrofuran was used as co-solvent. ^d Lithium dicyclohexylamide (2 equiv) was added at 0° (or -20°) for 5 min, and the reaction mixture was stirred at 0° for 10 min. ^e Isolated by distillation, bp 140° (bath temp, 0.2 mm). ^f Mp 56° (H. Normant and T. Cuvigny, *Bull. Soc. Chim. Fr.*, 1881 (1965)). ^g Mp 74° .

stable even at -120° , can be generated effectively and the carbonyl adducts could be prepared in good to excellent yields at -78° (external cooling). Even in the presence of cyclopentanone, which is known as a readily enolizable ketone, the generation of polyhalomethylithium is favored over enolate formation; thus the corresponding adducts were produced in good yields. The success of the reaction depends crucially on the nature of lithium dialkylamide which selectively abstracts protons from substrates containing intrinsically more reactive sites toward nucleophilic attack.⁴

The following experimental procedure is illustrative of the method. A well-stirred solution of bromoform (4.35 ml, 50 mmol) and cyclohexanone (2.45 g, 25 mmol) in dry tetrahydrofuran (50 ml) was cooled to -78° (external cooling with Dry Ice-methanol bath) and was treated with lithium dicyclohexylamide (50 mmol; prepared from dicyclohexylamine (9.05 g, 50 mmol) in dry tetrahydrofuran (50 ml) with *n*-butyllithium (50 mmol, 33 ml of a hexane solution) at 0°) dropwise over a period of 15 min. The mixture was then allowed to stand for 1 hr at the same low temperature and an extractive work-up followed. The crude oil thus obtained was subjected to column chromatography (silica gel, 100 g; benzene as eluant) to yield 1-(tribromomethyl)cyclohexanol as a colorless crystalline material (7.96 g, 91% yield): mp 74° ; ir (Nujol) 3460 (OH), 1153, 977, 928, 760, 695 cm^{-1} . *Anal.* Calcd for $\text{C}_7\text{H}_{11}\text{OBr}$: C, 23.96; H, 3.16. Found: C, 23.90; H, 3.18.

The methodology described herein may be applicable to a wide variety of synthetic problems in which the relatively unstable carbenoids or carbanions are involved. Indeed, we have found that a mixture of methyl bromoacetate and cyclohexanone undergoes a facile Darzens-type reaction on treatment with lithium

dicyclohexylamide (1.2 equiv) (93% isolated yield).⁶ Similarly, methyl dichloroacetate gave a hydroxy dichloro ester in 91% yield.



(6) Attempted isolation of the corresponding hydroxy bromide was unsuccessful.

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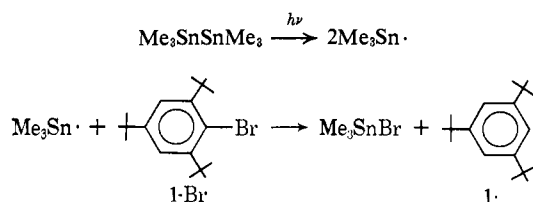
The 2,4,6-Tri-*tert*-butylphenyl Radical¹

Sir:

Phenyl is known to be a σ radical from its electronic spectrum in the gas phase² and from its epr spectrum in matrices at low temperatures.^{3,4} However, phenyl is so highly reactive that all attempts to detect it by spectroscopic methods in solution have, so far, been unsuccessful.⁵

In this laboratory, we have shown that free radicals of many different types can have their lifetimes increased substantially by attaching two (or more) *tert*-butyl groups close to the radical center.⁶ We now wish to report the successful extension of this procedure to phenyl.

Photolysis, directly in the cavity of an epr spectrometer, of a solution of 2,4,6-tri-*tert*-butylbromobenzene, 1-Br, and hexamethylditin in cyclopropane yields a spectrum (Figure 1) we attribute to 2,4,6-tri-*tert*-butylphenyl, 1 \cdot , at ambient and lower temperatures.



The stabilizing influence of the two ortho-*tert*-butyl groups is indicated by the absence of any epr spectrum when 3,5-di-*tert*-butylbromobenzene is treated in the same way as 1-Br. The spectrum of 1 \cdot can also be

(1) Issued as N.R.C.C. No. 13959.

(2) G. Porter and B. Ward, *Proc. Roy. Soc., Ser. A*, **287**, 457 (1965).

(3) J. E. Bennett, B. Mile, and A. Thomas, *Proc. Roy. Soc., Ser. A*, **293**, 246 (1966); J. E. Bennett, B. Mile, A. Thomas, and B. Ward, *Advan. Phys. Org. Chem.*, **8**, 1 (1970).

(4) P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Amer. Chem. Soc.*, **91**, 4364 (1969).

(5) However, the epr spectra of two phenyl radicals of the type $\text{RC}_6\text{H}_5\cdot$ (where $\text{R} = o\text{-C(O)N(CH}_3\text{)}_2$ and $o\text{-C(O)OCH}_3$), have been detected in solution under conditions of very rapid radical generation; see A. L. J. Beckwith, *Intra-Sci. Chem. Rep.*, **4**, 127 (1970).

(6) See, e.g., J. L. Brokenshire, G. D. Mendenhall, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 5278 (1971); G. D. Mendenhall and K. U. Ingold, *ibid.*, **95**, 2963, 3422 (1973); *Chem. Brit.*, in press; G. D. Mendenhall, D. Griller, D. Lindsay, T. T. Tidwell, and K. U. Ingold, *J. Amer. Chem. Soc.*, in press; D. Griller and K. U. Ingold, *ibid.*, **95**, 6459 (1973) and in press.

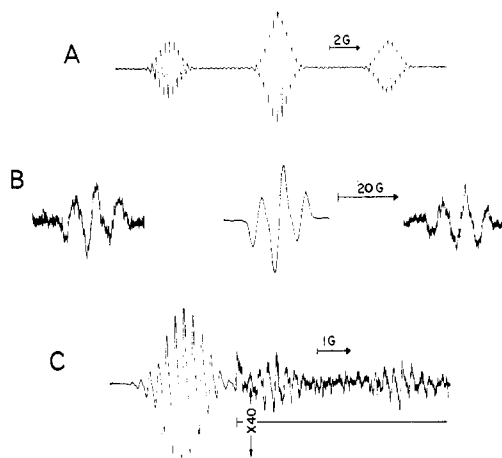
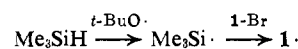


Figure 1. Epr spectrum of tri-*tert*-butylphenyl at -40° in cyclopropane: A, main triplet; B, overmodulated spectrum showing $\alpha^{13}\text{C}$ splitting; C, high field component of main triplet and ^{13}C splitting by ortho and meta carbons.

obtained by photolyzing cyclopropane solutions of 1-Br, trimethylsilane, and di-*tert*-butyl peroxide.



No epr spectrum was obtained when 1-Br alone was photolyzed under the same conditions.

The spectrum of 1 \cdot consists principally of a 1:2:1 triplet (due to the meta protons) of multiplets (due to "through-space" coupling with the protons of the ortho-*tert*-butyl groups). The spectrum is sufficiently intense to detect coupling to ^{13}C in natural abundance at the α -position and at the ortho and meta positions. The epr parameters (Table I) are in good agreement

Table I. Epr Spectral Parameters for Phenyl Radicals (hyperfine splittings in Gauss)

	1 \cdot at -40°	Phenyl		Theoretical ^c
		Exptl		
$a^{\text{H}}(\text{ortho})$		18.1 ^a	17.4 ^b	18.7
$a^{\text{H}}(\text{meta})$	7.31	6.4 ^a	5.9 ^b	6.1
$a^{\text{H}}(\text{para})$		<3.0 ^a	1.9 ^b	3.9
$a^{\text{H}}(o\text{-}t\text{-Bu})$	0.298			
$a^{13\text{C}}(\alpha)$	122.5	129 ^a		151.3
$a^{13\text{C}}(\text{ortho})$	6.16 ^d			-4.8
$a^{13\text{C}}(\text{meta})$	14.52 ^d			10.7
$a^{13\text{C}}(\text{para})$				-2.6
$a^{13\text{C}}(\text{CH}_3 \text{ of } o\text{-}t\text{-Bu})$	2.02 ^e			
g	2.00238		2.00237 ^b	

^a From ref 3 and 4. Spectrum was obtained in an H_2O matrix at 77°K , slightly different splittings being obtained in other matrices.

^b From ref 5. Spectrum was obtained in an argon matrix at 4°K .

^c From ref 7. ^d Assigned on basis of theoretical phenyl spectrum.

^e From $\text{C}_6\text{H}_5[\text{C}(\text{CD}_3)_3]$.

with those found for phenyl in matrices and also with those calculated for phenyl.⁷

For best resolution, the spectrum of 1 \cdot is measured at low power levels (≤ 0.2 mW) and low modulation (0.1 G). On raising the power a second radical becomes visible (see Figure 2) whose spectral parameters ($a^{\text{H}}(2\text{H}) = 21.70$ G, $a^{\text{H}}(6\text{H}) = 1.02$ G, $g = 2.00248$ at 0°) are identical with those of 3,5-di-*tert*-butylneophyl, 2 \cdot ,

(7) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Amer. Chem. Soc.*, **90**, 4201 (1968).