as reaction intermediates. Specifically, the oxidation of lithium dineophylcuprate is unaccompanied by the 1,2-aryl migration characteristic of free neophyl radicals, even when carried out at room temperature.[8] In addition, the oxidation of lithium di-*trans*-1-propenylcuprate yields *trans,trans*-2,4-hexadiene without loss of stereochemistry around the olefinic bonds; we have argued previously that this stereochemical result is incompatible with free propenyl radicals as reaction intermediates.[6] Similarly, the yield of butanol observed in the oxidation of **1** is much smaller than that expected from a reaction which generates free butyl radicals in a solution containing oxygen.

Second, uncomplexed butylcopper(I) can be isolated in moderate yield from incomplete oxidation of **1**. Hence, butylcopper(I) appears to be an intermediate formed rapidly in the initial stages of oxidation, which is itself oxidized in a subsequent step.[9] Examination of the oxidation of butylcopper(I) under these conditions indicates that all of the 1-butene and butanol formed in the oxidation of **1** could be accounted for by its oxidation and suggests that the *initial* oxidation of **1** yields octane and butylcopper(I) quantitatively.

Third, a wide variety of materials other than oxygen are effective oxidants in these reactants. For example, the yields of octane obtained from **1** by oxidation with nitrobenzene, Cu(II)Cl_2·TMEDA, or oxygen are equal.[10] Hence, it seems unlikely that the oxidizing agent is involved in the production of dimer in any capacity other than that of electron acceptor.

These observations, taken together, make an initially formed di-*n*-butylcopper(II), which rapidly disproportionates or further reacts to *n*-butylcopper(I) and octane, an attractive intermediate in the initial oxidation of **1**. Further evidence supporting this proposal will be presented in later papers.

[8] For a review of recent work, see R. Kh. Freidlina, *Advan. Free Radical Chem.*, 1, 211 (1965).

[9] Similar observations have been made in Glaser couplings.[2a]

[10] Even benzophenone will oxidize 1 to octane (in 25% yield); however, these other oxidizing agents produce lower yields of dimers than does oxygen in oxidation of secondary and alkynyl ate complexes.

[11] (a) National Institutes of Health Predoctoral Fellow, 1966–1967; (b) National Science Foundation Predoctoral Fellow, 1963–1967; (c) E. B. Hershberg Fellow, 1965–1966.

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1,3-Dicarbanions of Phenylacetone and Some Other Multiple Anions[1]

Sir:

A β-diketone such as acetylacetone or benzoylacetone can be converted by 2 equiv of potassium amide in liquid ammonia to its 1,3-dicarbanion I′′, as evidenced by condensations at the terminal position with electrophilic compounds[2] and by nmr.[3] Similarly, dibenzyl ketone can be converted to its 1,3-dicarbanion II′′ by this base.[4]

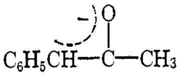
$RCO\bar{C}HCO\bar{C}H_2$ I′′

$C_6H_5\bar{C}HCO\bar{C}HC_6H_5$ II′′

No other monoketone, however, appears to have been converted satisfactorily to a 1,3-dicarbanion by an alkali amide. Phenylacetone (III) is readily converted to its monoanion III′ by 1 equiv of potassium amide in liquid ammonia but, apparently, no appreciable secondary ionization of a methyl hydrogen occurs with excess of this base.[4] Although *n*-butyllithium in ether or tetrahydrofuran (THF) is, potentially, a much stronger base than an alkali amide, the successful usage of this organolithium reagent as a base to ionize phenylacetone is precluded by our observation that this reagent attacks preferentially the carbonyl group of the ketone to form carbinol IV.

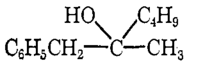
$C_6H_5CH_2COCH_3$

III



$C_6H_5\bar{C}H{-}C(=O){-}CH_3$

III′



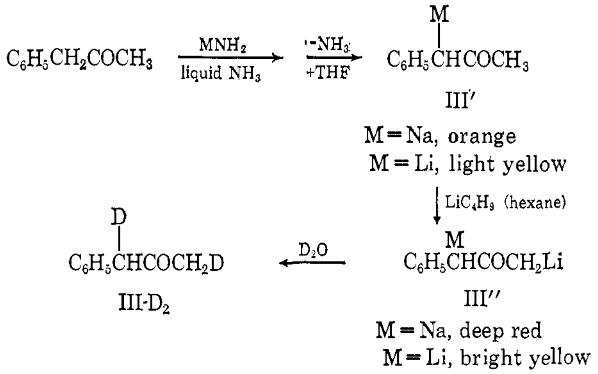
$C_6H_5CH_2{-}C(OH)(C_4H_9){-}CH_3$

IV

Since the initial reaction of phenylacetone with the alkali amide to form the monoanion III′ should nullify a subsequent attack at the carbonyl group by *n*-butyllithium, it seemed possible that the use of 1 equiv of an alkali amide followed by one of the much stronger organolithium reagent might lead to the formation of the desired 1,3-dicarbanion. This was realized in the present investigation.

The method involved addition of the ketone III in tetrahydrofuran (THF) to slightly more than 1 equiv of sodium amide or lithium amide in liquid ammonia, replacement of the ammonia with THF, and addition of slightly more than 1 equiv of *n*-butyllithium in hexane at room temperature. The formation of the 1,3-dialkali salt III′′ was indicated by production of a rather intense color (the particular color being dependent on M) and established by deuteration (Scheme I).

Scheme I



The structure of the deuterated ketone III-D_2 was supported by its nmr spectrum which showed 95–98% of one deuterium atom/molecule at the terminal methyl group and 100% of one deuterium atom/molecule at the methylene group. In a blank experiment, no deuterium was acquired by phenylacetone from deuterium oxide in the presence of sodium or lithium deuterioxide.

The 1,3-dialkali salt III′′ (M = Na or Li) underwent terminal condensations with anisaldehyde and chalcone

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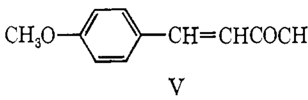
[1] Supported by National Science Foundation Grant No. GP 6486.

[2] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

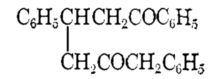
[3] M. L. Miles, C. G. Moreland, D. M. von Schriltz, and C. R. Hauser, *Chem. Ind.* (London), 1966, 2098.

[4] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **81**, 1154 (1959).

to form the α,β-unsaturated ketone V (mp 99–100°) and the conjugate addition product VI (mp 112–113°), respectively. Each of these products, which was obtained in about 50% yield, gave a satisfactory elementary analysis and a characteristic infrared spectrum.



V

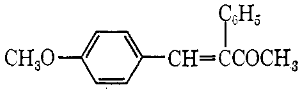


$C_6H_5CHCH_2COC_6H_5$ / $CH_2COCH_2C_6H_5$

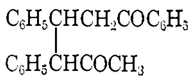
VI

The condensation of III'' with anisaldehyde was indicated to form initially the corresponding carbonyl addition product, but it was not isolated. The condensation of III'' with chalcone may have produced also some of the carbonyl addition product.

That the condensation products isolated were the terminal derivatives V and VI, not the possible methylene derivatives VII and VIII, respectively, was supported by their nmr spectra, neither of which showed peaks for an acetyl methyl group. The spectrum of V showed a methylene peak at 3.82 ppm and that of VI a corresponding methylene peak at 3.58 ppm. Also, the spectrum of V exhibited a vinyl proton at 6.80 ppm and that of VI two methylene absorptions (doublets) at 2.87 and 3.22 ppm, as well as a methinyl hydrogen at 3.91 ppm.



VII



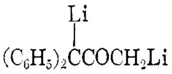
$C_6H_5CHCH_2COC_6H_5$ / $C_6H_5CHCOCH_3$

VIII

Similarly, diphenylacetone (IX), which fails to be converted by 2 equiv of potassium amide in liquid ammonia to a 1,3-dicarbanion satisfactory for terminal benzylation,[5] was converted by the present method to dilithio salt IX'', as evidenced by deuteration with deuterium oxide and by condensation with anisaldehyde to give IX-D_2 and X (mp 129–131°), respectively.

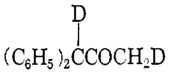
$(C_6H_5)_2CHCOCH_3$

IX



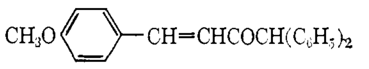
$(C_6H_5)_2C(Li)COCH_2Li$

IX''



$(C_6H_5)_2C(D)COCH_2D$

IX-D_2

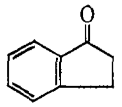


X

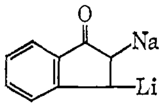
The structure of the deuterated ketone IX-D_2 was supported by its nmr spectrum, which showed 90–95% of one deuterium atom/molecule at the methyl group and about 80% of one deuterium atom/molecule at the methylene group. In a blank experiment, no deuterium was acquired from deuterium oxide in the presence of lithium deuterioxide.

The structure of the condensation product X was supported by its nmr spectrum and by agreement of its melting point with the reported value.[6]

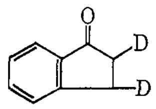
Also, 1-indanone (XI) was converted by the present method to the 1,2-dialkali salt XI'', as evidenced by deuteration with deuterium oxide to form the 1,2-dideutero product XII.



XI



XI''



XII

The structure of XII was supported by its nmr spectrum, which showed 90% of one deuterium atom/molecule at the 3 position and 100% of one deuterium atom/molecule at the 2 position.

Work is in progress not only on other condensations of dianions III'', IX'', and XI'' but also on the preparations and reactions of other 1,3, 1,2, and other types of multiple anions. Moreover, nmr determinations on such anions are contemplated.

The present method, which involves the initial usage of an alkali amide to deactivate a ketone carbonyl group so that a more strongly basic organometallic compound may be employed for secondary ionization (and even for further ionization), represents a significant advance in the study of multiple anions that have not been available through usage of either of the two bases alone. Furthermore, the method may be applicable where initial deactivation of certain other functional groups is required for satisfactory subsequent ionizations.

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[5] D. R. Bryant, Ph.D. Disseration, 1962, p 41.

[6] C. S. Marvel and M. I. Kohan, *J. Org. Chem.*, **16**, 741 (1951).

Synthesis of an 8,16-Methano-*cis*-[2.2]metacyclophane

Sir:

It is known from X-ray crystallographic data[1a] and from chemical studies[1b] that [2.2]metacyclophane,[2] first prepared by Pellegrin in 1899,[3] is represented by the three-dimensional projection I. This molecule, and apparently all [2.2]metacyclophanes reported to date,[4a–c] because of similarity in synthetic approach, possess *trans* or *anti* geometry. We wish to report the synthesis of a [2.2]metacyclophane possessing *cis* or *syn* geometry.

Condensation of 2 moles of 2,6-xylenol with *s*-trioxane in concentrated hydrochloric acid yields methylene-4,4'-bis(2,6-xylenol),[5] IIa, mp 175–177°, 72%, which is converted to methylene-4,4'-bis(2,6-dimethylanisole), IIb, mp 82–84°, 80%, by dimethyl sulfate–sodium hydroxide in a saturated sodium sulfate solution. Halomethylation of IIb by means of *s*-trioxane–hydrogen chloride followed by zinc chloride–lithium chloride in glacial acetic acid[6] produces the bis(chloro-

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[1] (a) W. Baker, J. F. W. McOmie, and J. M. Norman, *J. Chem. Soc.*, 1114 (1951); (b) C. J. Brown, *ibid.*, 3278 (1953).

[2] The numbering and nomenclature of [2.2]metacyclophanes used here is that suggested by B. H. Smith, "Bridged Aromatic Compounds," Academic Press Inc., New York, N. Y., 1964, Chapter 1.

[3] M. Pellegrin, *Rec. Trav. Chim.*,18, 458 (1899).

[4] (a) W. S. Lindsay, P. Stokes, L. G. Humber, and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961); (b) A. Hanson, *Acta Cryst.*, **15**, 956 (1962); (c) W. Baker, K. M. Buggle, J. F. W. McOmie, and D. A. M. Waters, *J. Chem. Soc.*, 3594 (1958).

[5] G. Zigeuner, R. Pitter, and K. Voglar, *Monatsh.*, 86, 517 (1955).

[6] (a) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, **75**, 6292 (1953); (b) H. W. Earhart and W. G. DePierre, U. S. Patent 2,945,894 (1960); *Chem. Abstr.*, **54**, 24547 (1960).