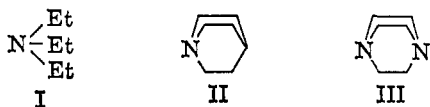alogy to the 1:2 base:lithium ratio found earlier, complexes formed with the dibasic species III were anticipated to have an empirical formula with 4 alkyllithium units/TED unit, *i.e.*, $R_2Li_2-TED-R_2Li_2$.

Thus we have found that when it is added to solutions of organolithium reagents, TED forms crystalline precipitates with every reagent tested, which include those with organic groups of methyl, ethyl, *n*-butyl, *t*-butyl, phenyl, 2-thienyl, benzyl, and 9-fluorenyl, making possible the isolation and characterization of the complex.[5] In most cases *addition of just 0.25 mole of TED/g.-atom of lithium causes quantitative precipitation of the organometallic reagent*, and analysis of the crystalline product agrees with the anticipated empirical formula.[6] Formation of 1:4 complexes with the aryllithium reagents, phenyl and 2-thienyl, seems particularly interesting.

Only in the two cases of benzyl- and 9-fluorenyllithium did the complexes which precipitated contain 1 mole of the TED/organolithium unit. Formation of a 1:1 complex in just these two cases most likely was because only in these cases could the organic group exist as a carbanion stabilized by benzyl-type charge delocalization. The benzyl- and 9-fluorenyllithium reagents are similarly distinguished by their formation of insoluble complexes with triethylamine; the complexes of other lithium reagents with triethylamine are quite soluble.[1c,2]

For lithium reagents, most of which are liquids when pure, the amine complexes constitute the first general, nondestructive technique for obtaining crystalline derivatives; these derivatives can be conveniently used in conventional reactions of the lithium reagents, in some cases with exceptional results (*vide infra*). Some preliminary observations have been made in applications of TED to the complexation of other organometallics. No mercury, boron, or aluminum alkyl solutions we have examined form precipitates when the amine is added. However, Grignard reagents do form crystalline complexes with TED and, similarly, dialkylmagnesium reagents are precipitated, even from dioxane solution. Diethylzinc also is readily precipitated by TED. The stoichiometry of formation of these new complexes will be reported subsequently.

Base catalysis of reactions of lithium alkyls is striking, particularly for metalation.[7] For example, although thiophene in hexane solution does not react with butyllithium alone, 2-thienyllithium is rapidly

(4) Use of a diamine was suggested by our previous observation[1c] that dioxane, an oxygen analog of III, formed an insoluble complex with butyllithium, but the complex was so reactive as to be difficult to characterize with assurance.

(5) A benzene solution of TED was normally added to a solution of lithium reagent in hydrocarbon solvent, but in the case of methyl- and phenyllithium, ether was present.

(6) The stoichiometry of the 1:4 TED-alkyllithium complexes has been determined both by analysis of the amount of organometallic left in standard solutions after precipitation with known quantities of TED and by potentiometric titration of the hydrolysate of the isolated complexes themselves. Further, hydrolyses of the complexes have been shown to yield TED and the expected hydrocarbons, and carbonation to yield the expected carboxylic acids.

(7) W. A. Butte (*J. Org. Chem.*, **29**, 2928 (1964)) has also observed this striking catalysis of metalation, particularly using amines capable of chelation.

and essentially quantitatively formed if 0.5 mole equiv. of triethylamine is present. Hydrocarbon aromatics, particularly benzene and its homologs, are more difficult to metalate and have been generally resistant to this reaction with lithium alkyls in ethereal solvents.[8] Such metalations can now be conveniently effected by catalysis with one of the sterically less demanding *t*-amines. Thus conversion of toluene to benzyllithium by a lithium alkyl is easily promoted by II, III, or trimethylamine; *e.g.*, with a 0.1 *M* solution of the latter in toluene containing *sec*-butyllithium, standing overnight at room temperature followed by carbonation gives a 75% yield of pure phenylacetic acid. In many respects amine catalysis makes the lithium alkyls react like the generally more active sodium and potassium alkyls. In this manner phenyllithium can be used to prepare benzyllithium from toluene, which is akin to the standard preparation of benzylsodium from phenylsodium.[9] The alkyllithium–amine reaction metalates *t*-butylbenzene on the ring, which is also a metalation previously accomplished only with sodium and potassium alkyls.[10] Refluxing benzene itself with butyllithium–triethylenediamine followed by carbonation produces benzoic acid in essentially quantitative yield.

It appears that those attributes which make an amine a particularly effective complexing agent also make that amine a particularly effective reaction catalyst, but it is not clear whether these two things are coincidental or are consequential. We are convinced though that low steric requirements of a neutral base is a prime attribute for both effects.

(8) As a leading reference to earlier attempts to use lithium alkyls to metalate such hydrocarbons as benzene and toluene, see H. Gilman and J. W. Morton, *Org. Reactions*, **8**, 265, 290 (1954), and H. Gilman and B. J. Graj, *J. Org. Chem.*, **28**, 1725 (1963).

(9) J. F. Nobis and L. F. Moormier, *Ind. Eng. Chem.*, **46**, 539 (1954).

(10) *Cf.* R. A. Benkeser, D. J. Foster, and D. M. Sauve, *Chem. Rev.*, **57**, 867 (1957); R. A. Benkeser, Abstracts of Papers, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 1962, p. 4Q.

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## Reductive Coupling of Alcohols to Hydrocarbons

Sir:

By means of experiments presupposing the valence change II → IV for an appropriate metal, we have been able to effect, in a single laboratory operation, the heretofore unknown reductive coupling of an alcohol (ROH) to a hydrocarbon (R–R). Experiments were designed in accordance with eq. 1,[1] which represents a reduction principle (2) of potentially broader utility in

$$R-OH \longrightarrow [(RO)_2Ti] \longrightarrow R-R + TiO_2 \qquad (1)$$
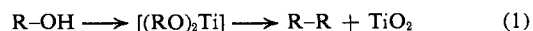
the field of synthetic organic chemistry.

(1) Although there is formal analogy between the titanium (II) alkoxide structure and that of acyclic dialkoxycarbenes (RO–C–OR), the latter apparently do not lose carbon dioxide, but instead give rise to diverse other products: R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 197 (1964); D. M. Lemal, E. P. Gosselink, and A. Ault, *ibid.*, 579 (1964).

$$(org)_x(metal)^{m+} \longrightarrow (org')_x + (metal)^{n+} \quad (n > m) \qquad (2)$$
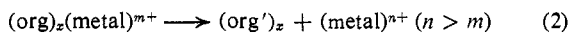
In a representative experiment, titanium tetrachloride (0.5 mole equiv.) was added with cooling to an anhydrous benzene suspension of sodium benzyloxide (generated *in situ* using oil-free sodium hydride). Potassium metal (1.0 mole equiv.) was added to the resulting pale olive-green suspension of the titanium-(IV) dichloride dialkoxide[2]; the mixture was refluxed briefly to disperse the metal, and then the whole was stirred for approximately 20 hr. in order to complete the reduction. The solvent was removed by distillation under a stream of nitrogen, and the black residue, presumed to be the titanium(II) dialkoxide,[3] was heated from 100 to 140° until the color changed to light gray, indicating formation of titanium dioxide. Addition of ether, alcohol, and water, followed by filtration and evaporation, gave *bibenzyl* in 51% (v.p.c.) yield (based on recovered benzyl alcohol).

In other cases, results were varied and depended upon the structure of the alcohol, the nature of the solvent, and the character of the reducing agent employed. Under conditions similar to those described above, *allyl alcohol* was converted in 38% (v.p.c.) yield to *biallyl*. *Squalene* was produced in similar yield on carrying out the reduction sequence (glyme solvent) with *farnesol*. Attempts to produce coupled hydrocarbon from *n*-amyl alcohol and cyclohexylmethanol were unsatisfactory under the described conditions, in that at best only traces of the desired materials were detected. By the same method, phenol was converted (after final pyrolysis at 210–235° for 16 hr.) to a mixture of products, including biphenyl (2.5%) and other substances believed to be *o*-phenylphenol and *o,m,p*-terphenyls. The product nature and distribution in the phenol case are suggestive of a radical type decomposition in the final, thermal stage.

Our interpretation of the course of the over-all reaction rests in part on the following observations (experiments with benzyl alcohol, and benzene as solvent. (1) Refluxing of the titanium(IV) dichloride dialkoxide mixture without prior reduction afforded diphenylmethane in almost quantitative yield, a known reaction of this type of titanium derivative.[4] (2) When sodium was utilized as the reducing agent, consumption of the metal was incomplete, and mixtures of bibenzyl, diphenylmethane, and benzyl alcohol ultimately resulted. This behavior is ascribable to titanium(III) species: extrusion of titanium dioxide leaves benzyl radical, which couples, and benzylcarbonium ion, which attacks solvent to give diphenylmethane. (3) Samples removed either before or after potassium reduction, but before heating, yielded on alcoholysis only benzyl alcohol, ruling out benzyl chloride as a participant. (4) If decomposition of the black organotitanium residue was interrupted and alcohol–water added, a blue or purple precipitate formed [Ti(II) → Ti(III)] which immediately turned white on contact with air [Ti(III) → Ti(IV)]. Large amounts of benzyl alcohol were recovered.

(2) Titanium compounds of this type are known and have been prepared in a similar manner: A. N. Nesmeyanov, E. M. Braĭnina, and R. Kh. Freĭdlina, *Dokl. Akad. Nauk SSSR*, **94**, 249 (1954); *Chem. Abstr.*, **49**, 3000 (1955).
(3) Whether the alkoxide is mono- or polymeric is unknown.
(4) L. M. Bobinova and G. A. Razuvaev, *J. Gen. Chem. USSR*, **33**, 2329 (1963).

In further exploratory experiments, substitution of silicon species for titanium intermediates was attempted. By using silicon tetrachloride as reagent and glyme as solvent, but otherwise adhering to the original specified conditions, an *ca.* 2:1 mixture of toluene and bibenzyl was identified as product, along with starting material, benzyl alcohol. The nature of the reduced intermediates is obscure.

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Structure of a Transient Dimer of Acetylene

Sir:

The following conclusions regarding the structure of a transient dimer of acetylene are based on measured rates of exchange between isotopically labeled species (H–D and C^{12}–C^{13}), as investigated under strictly homogeneous conditions in the gas phase, in high argon dilution. The kinetics indicate that the dimer is generated by the association of vibrationally excited monomers. Such an encounter may be schematically represented by α, β, γ, or δ leading to I–V. Our data
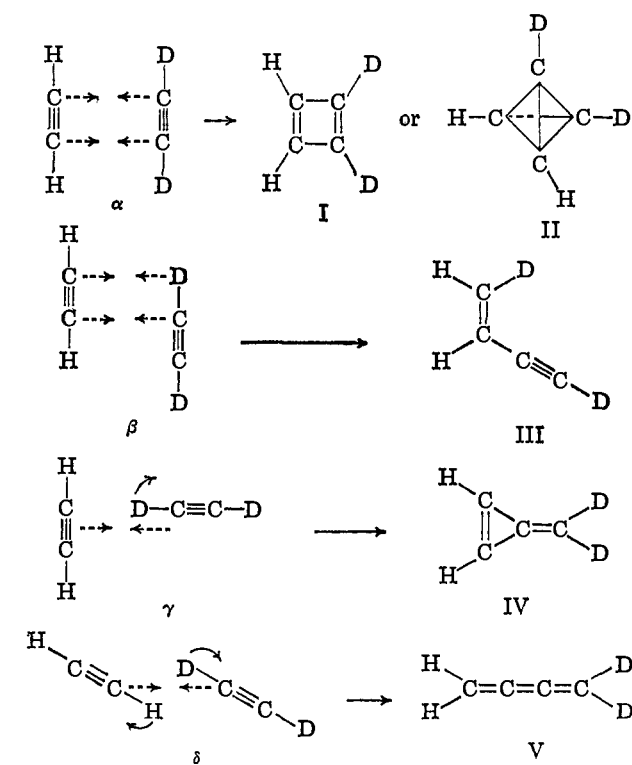
excluded all but one of these possibilities.

To place these experiments in proper context it is necessary to recall that the homogeneous gas phase reaction between acetylene and deuterium has been studied in a shock tube and its mechanism established.[1] Over the temperature range 1300–1665°K. the em-

(1) K. Kuratani and S. H. Bauer, *J. Am. Chem. Soc.*, **87**, 150 (1965).
(2) Note erroneous units given for $(k_1 k_3/k_2)$ at the conclusion of ref. 1. Also, the last two sentences of the paper are incorrect.