RCH$_2$ ... O ... Ph ... LDA →
N
OMe

4

R ... O ... Ph
H ... N
R'—X···Li ←——OMe

5a

↕

H ... O ... Ph
R ... N
R'—X···Li ←——OMe

5b

→

Ph
O
R ... N ... OMe
H
R'

6

H$^+$ ↓

(S)-3(R' > R)

higher priority, always gives the S enantiomer, whereas reversal of this order gives the R enantiomer.

Further studies to evaluate the nature of this process revealed that the asymmetric synthesis was independent of the temperature at which the proton was removed from **4**. Thus, lithio salts **5** (a and b) were generated at -22, -45, and $-78°$ but were all alkylated at $-78°$ to ultimately give (S)- or (R)-**3** in comparable enantiomeric purity. On the other hand, alkylation of **5** (a and b) at various temperatures gave significantly different optical yields of **3** (Table II). That lower temperatures increase stereoselectivity is no surprise since the $\Delta\Delta G^{\ddagger}$ for the competing transition state would be enlarged.[4]

The above results now allow a preliminary suggestion regarding the mechanism of this asymmetric synthesis. The proton removal from **4** gives rise to two isomeric lithiooxazolines **5** (a and b) which are probably interconvertible. Attack by the electrophile must be assumed to occur from the bottomside since it would be difficult to rationalize topside approach in view of the profound effect of methyl sulfate $vs.$ methyl iodide. The rate of alkylation on **5a** must be faster than that in **5b** due to diminished steric interaction between the incoming R group and the R group already present. For methyl sulfate (or tosylate) a bulkier complex (**5a**) between the lithium cation and the oxygen atoms over that formed with methyl iodide results in widening the relative rates of attack on **5a** and **5b** causing greater stereoselectivity. If, as assumed, alkylation consistently occurs from the bottomside, this would lead to **6** which upon acidic cleavage provides the carboxylic acids **3**. All facts in hand to date are consistent with this mechanism and although further refinements are still necessary, it provides a useful working hypothesis to allow rational planning of future syntheses.[5]

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β-Oxido Carbenoids as Synthetic Intermediates. A Facile Ring Enlargement Reaction

Sir:

A number of important ring enlargement reactions have been devised within the last 10 years for the synthesis of macrocyclic derivatives.[1] These reactions assume an even greater importance with the increasing availability of certain medium- and large-ring compounds.[2]

The best current methods for a one-carbon ring enlargement involve (a) diazomethane reaction[3] or (b) the Tiffeneau–Demjanov rearrangement.[4] Both methods are of limited value in preparative work because of either the variety of products formed (for a) or the number of steps involved (for b).[5] We report herein a highly effective method for circumventing such difficulties based on the use of β-oxido carbenoids.[6]

Treatment of the dibromide **1** in tetrahydrofuran with 2 equiv of n-butyllithium in hexane at $-78°$ for 30 min and $0°$ for 5 min led to 89% isolated yield of pure cyclotridecanone (**5**). Evidently the β-oxido carbenoid **2** was first formed and decomposed smoothly to the enolate **4**, probably via β-oxido carbene **3**[7] (Scheme I). Similarly, cyclohexanone, cycloheptanone, cyclooctanone, and cyclononanone were prepared from the corresponding dibromides in 92,[8,9] 70,[8,10] 80,[11] and 87%[11] yields, respectively.

Clearly, the principal side reaction in this case would be due to replacement of hydrogen by lithium[12] followed by decomposition to β-oxido monobromocarbene which would produce bromocyclotridecanone after hydrolysis.[6] It soon became apparent, however, that the major reaction pathway in the present case was

(1) For reviews see (a) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968; (b) P. R. Story and P. Busch, *Advan. Org. Chem.*, **8**, 67 (1972).

(2) G. Wilke, *Pure Appl. Chem.*, **17**, 179 (1968).

(3) (a) C. D. Gutsche, *Org. React.*, **8**, 364 (1954); (b) ref 1a, Chapter 4.

(4) P. A. S. Smith and D. R. Baer, *Org. React.*, **11**, 154 (1967); see, also, D. A. Evans, G. L. Carroll, and L. K. Truesdale, *J. Org. Chem.*, **39**, 914 (1974).

(5) For example, U. Schöllkopf and P. Böhme, *Angew. Chem., Int. Ed. Engl.*, **10**, 491 (1969).

(6) (a) H. Taguchi, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, 4661 (1972); (b) J. Villieras, C. Bacquet, and J. F. Normant, *J. Organometal. Chem.*, **40**, C1 (1972); (c) G. Köbrich and J. Grosser, *Tetrahedron Lett.*, 4117 (1972); (d) I. Kuwajima and Y. Fukuda, *Chem. Lett.*, 372 (1973); (e) G. Köbrich and J. Grosser, *Chem. Ber.*, **106**, 2626 (1973).

(7) Carbene induced ring enlargement: M. Fărcasiu, D. Fărcasiu, T. Conlin, M. Jones, Jr., and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **95**, 8207 (1973); A. D. Wolf and M. Jones, Jr., *ibid.*, **95**, 8209 (1973).

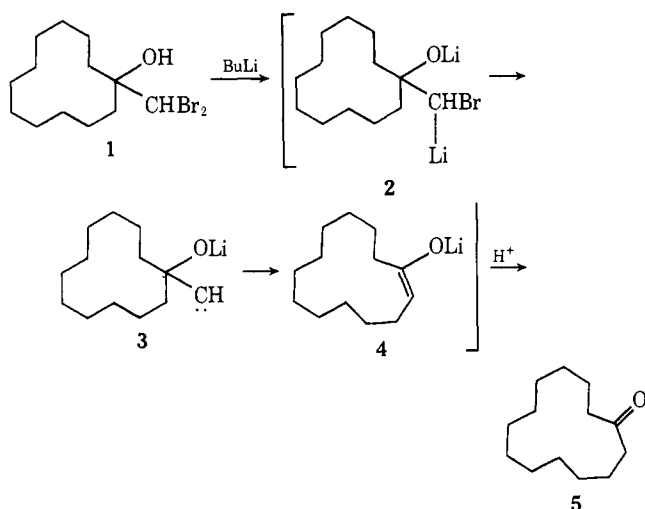(8) Yields calculated from 2,4-DNP derivatives.

(9) 2,4-DNP: mp 157–158°, lit. mp 160° (Z. Rappoport, "Handbook of Tables for Organic Compound Identification," The Chemical Rubber Co., Cleveland, Ohio, 1964).

(10) 2,4-DNP: mp 143–144°, lit. mp 147° (ref 9).

(11) Identical in all respects with an authentic sample.

(12) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **6**, 41 (1967); **11**, 473 (1972).

(4) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971, p 40.

(5) All mono- and disubstituted oxazolines are new compounds and have been satisfactorily characterized by spectroscopic and elemental analytical methods.

Scheme I

found to be a halogen–lithium exchange rather than a hydrogen–lithium exchange process,[12] since no more than 5% impurities could be detected in the unpurified ketonic products.

This approach depends crucially on the recently developed method for the *in situ* generation of dibromomethyllithium from methylene bromide in the presence of carbonyl compounds using lithium dicyclohexylamide as the base.[13,14] Thus, the over-all transformation is a two-step sequence, both of which are easy to operate and also highly efficient.

The following procedure is illustrative of the new reaction. The dibromide **1** (356 mg, 1.00 mmol) was dissolved in dry tetrahydrofuran (3 ml) under nitrogen and cooled to $-78°$. To the stirred solution was added n-butyllithium (1.35 ml of a 1.55 M hexane solution, 2.10 mmol) dropwise over a period of 30 min.[15] The resulting pale yellow solution was stirred for 30 min at $-78°$ and 5 min at $0°$, quenched by pouring into ice cold 1 N hydrochloric acid, and extracted with ether repeatedly. The ethereal layers were washed with brine, dried (Na$_2$SO$_4$), and concentrated *in vacuo* to afford cyclotridecanone in 89% yield after preparative layer chromatography on silica gel (benzene, R_f = 0.44).[11]

(13) H. Taguchi, H. Yamamoto, and H. Nozaki, *J. Amer. Chem. Soc.*, **96**, 3010 (1974).

(14) Depending on the structure of the cyclic ketone, the dibromomethyllithium carbonyl adduct may rapidly form epoxide, even at low temperature. The reaction should be performed at $-100°$, with vigorous stirring, to minimize that pathway.

(15) The addition of n-butyllithium was carried out rather slowly to minimize the epoxide formation, see ref 14.

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Stereospecific Photochemical Reactions of Group VIb Metal Tetracarbonyl Norbornadiene Complexes with [13]CO

Sir:

Chromium tetracarbonyl norbornadiene has been implicated as an intermediate in the photoassisted
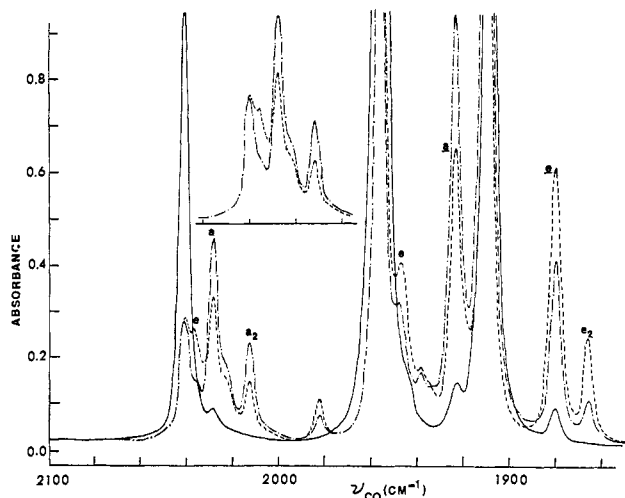

Figure 1. Infrared spectra in ν (CO) region of W(CO)$_4$(NBD): (a) ——, [13]CO natural abundance; (b) —·—, after photolysis with 92% [13]CO for 2 min; (c) ————, after standing in the dark at 37° for 45 min. The a and e designations correspond to bands of axially and equatorially mono-[13]CO substituted species, respectively, whereas, a$_2$ and e$_2$ correspond to exclusively di-[13]CO substituted axially and equatorially, respectively.

hydrogenation of norbornadiene with chromium hexacarbonyl.[1,2] In addition, the intermediacy of Cr(CO)$_4$-(NBD) has been demonstrated in the photochemical dimerization of norbornadiene with Cr(CO)$_6$.[3] We have, therefore, undertaken a study to establish the nature of the species produced from the photochemical reactions of group VIb (NBD)M(CO)$_4$ complexes. We wish to report in this communication initial results on the photochemical production of [13]CO labeled complexes of (NBD)M(CO)$_4$. This study has as well allowed for an unambiguous assignment of the CO stretching vibrations in these molecules.

Irradiation of the M(CO)$_4$(NBD) complexes was carried out in a water-jacketed 25-ml Pyrex cell employing a 450-W Hanovia Mercury lamp ($\lambda > 2800$ Å) for M = Cr and W, and a 100-W lamp for the less stable species where M = Mo. A 20.9% or a 92.0% [13]CO enriched carbon monoxide atmosphere was continuously recirculated within the closed system by a variable speed Masterflex tubing pump. The course of the enrichment reaction was followed by withdrawing samples with a hypodermic syringe at approximately 1-min time intervals. Infrared spectral measurements were used to follow the extent of enrichment. All three samples were rapidly enriched with [13]CO producing various mono- and disubstituted species with [13]CO as well as small quantities of M(CO)$_6$. Figure 1 illustrates the [13]CO enriched spectra observed for W(CO)$_4$(NBD) in hexane solution employing 92% [13]CO. It was possible to assign all the bands in the spectra by computing their positions using a restricted CO force field.[4] Table I contains the calculated and observed ν(CO) bands for the [13]CO enriched species of W(CO)$_4$(NBD).

(1) L. Wilputte-Steinert, International Conference on Organometallic Chemistry, Moscow, 1971.

(2) G. Platbrood and L. Wilputte-Steinert, *J. Organometal. Chem.*, **70**, 393 (1974).

(3) W. Jennings and B. Hill, *J. Amer. Chem. Soc.*, **92**, 3199 (1970).

(4) Frequencies were calculated with an iterative computer program using an energy-factored block matrix for the carbonyl stretching vibrations as described elsewhere; see, *e.g.*, C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, **12**, 1075 (1973). Agreements between calculated and observed frequencies were generally with ± 0.5 cm^{-1}.