(less than half of the actual amount present) was recovered by simple fractional distillation, although a greater proportion could be recovered by gas chromatography. Thus in most experiments, the yield of isocyanate was estimated by adding an excess of *t*-butylamine to the reaction mixture and recovering the *t*-butylalkyl- or arylurea 4. Typical yields were: N,N-di-*t*-butylurea, m.p. 240 ± 2° (lit.[10] m.p. 242–243°), 96% from pivalamide; N-*t*-butyl-N-(α-phenylbutyl)-urea,[8] m.p. 192–193°, 97% from α-methyl-α-phenyl-butyramide; N-*t*-butyl-N-cyclohexylmethylurea,[8] m.p. 150–151°, 74% from cyclohexaneacetamide; N-*t*-butyl-N-cyclohexylurea, m.p. 226 ± 2° (lit.[11] m.p. 227°), 88% from cyclohexanecarboxamide.

The isocyanate could also be hydrolyzed directly to the amine hydrochloride 5 by adding the dimethylformamide solution to hydrochloric acid and heating the mixture under reflux. For example, from cyclocarboxamide a 49% yield of cyclohexylamine hydrochloride was obtained.

Typical procedures follow: to a mixture of 0.03 mole of amide, 0.03 mole of powdered lead tetraacetate, and 70 ml. of dry *t*-butyl alcohol warmed to 50–60° 10 ml. of triethylamine was added dropwise (*ca.* one drop every 3–4 sec.) with no additional heating. The initial reddish color of the mixture faded to white (or pale pink) within a few minutes. At this point conversion to the isocyanate was essentially complete and the remainder of the triethylamine could be added more quickly. The reaction mixture was allowed to stand for several days at room temperature during which time the disappearance of infrared band at *ca.* 2260 cm.$^{-1}$ could be used as a qualitative test for completeness of conversion to the urethan. The mixture was evaporated to *ca.* 30 ml. and poured onto crushed ice and 15 ml. of acetic acid. The urethan was collected, dried, and recrystallized from a hydrocarbon solvent.

To a stirred solution of 0.02 mole of amide in 100 ml. of dry, distilled dimethylformamide was added 0.02 mole of powdered lead tetraacetate. The addition caused the solution to become light red. As the reaction proceeded to completion the temperature rose to *ca.* 60°, and the color faded. (For aromatic amides, 5 ml. of triethylamine was added after the addition of lead tetraacetate.) When the solution was colorless again, 7 ml. of *t*-butylamine was added, and the disubstituted urea was precipitated by pouring the reaction mixture over 100 g. of crushed ice and water. The ureas could be recrystallized from ethanol.

The mechanism, scope, limitations, and extensions of this oxidative rearrangement are under study.

(10) B. Brauner, *Chem. Ber.*, 12, 1875 (1879).
(11) R. N. Lacey, *J. Chem. Soc.*, 1633 (1960).

Henry E. Baumgarten, Andris Staklis

Avery Laboratory, University of Nebraska
Lincoln, Nebraska 68508

Rearrangement of Bromomethylenecycloalkanes with Potassium *t*-Butoxide

Sir:

Rearrangement of 2-bromo-1,1-disubstituted ethylenes to acetylenes has long been known in examples where the substituents are aromatic[1] and has recently been shown to occur where the substituents are aliphatic.[2] 1,2-Dibromo-2-methylpropane[2] or 1-bromo-2-methyl-1-propene,[3] on heating with potassium *t*-butoxide in nonpolar solvents, were converted into 2-butyne and 1-*t*-butoxy-2-methyl-1-propene,[3] and it was suggested that the vinyl ethers II and III obtained by heating ω-bromocamphene with potassium *t*-butoxide form by way of endocamphyne (I).[2] We now wish to report that the action of potassium *t*-butoxide on
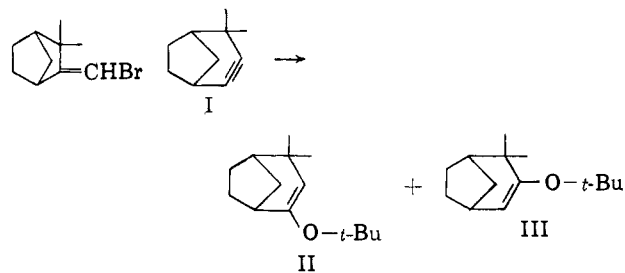
bromomethylenecycloalkanes provides a useful, new method for generating highly strained cycloalkynes.[4]

When ω-bromocamphene (0.046 mole) was heated for 4 hr. with sublimed potassium *t*-butoxide (0.090 mole) and 1,3-diphenylisobenzofuran (0.046 mole) in toluene, there was obtained a 94% yield of a mixture of *exo* and *endo* adducts IV and V, m.p. 185–186° and 178–179°.[5]
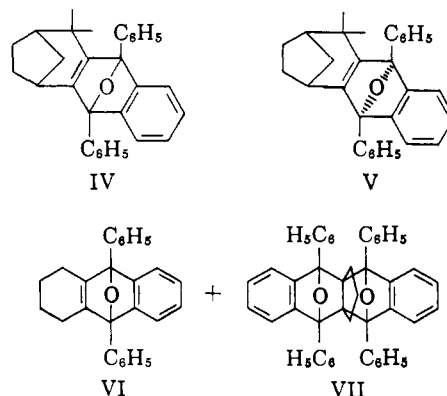
Other strained cycloalkynes were generated by similar treatment of the appropriate bromomethylenecycloalkane[6] and were captured as 1,3-diphenylisobenzofuran adducts. Cyclohexyne, generated from bromomethylenecyclopentane, was trapped in 35% yield as the adduct VI, m.p. 170–171.5°, and cyclopentyne, produced from bromomethylenecyclobutane, was captured in 12.3% yield as a 1:2 adduct VII of unknown stereochemistry, m.p. 247–249°. This adduct was identical with a sample of VII kindly supplied by Professor G. Wittig.[7]

(1) *Cf.* W. M. Jones and R. Damico, *J. Am. Chem. Soc.*, 85, 2273 (1963); W. Tadros, A. B. Sakla, M. S. Ishak, and E. R. Armanious, *J. Chem. Soc.*, 4218 (1963), and references cited therein.
(2) J. Wolinsky, *J. Org. Chem.*, 26, 704 (1961).
(3) J. Privett, M. S. Thesis, Purdue University, 1962.
(4) Evidence for the transient existence of strained cycloalkynes has been provided by L. K. Montgomery and J. D. Roberts, *J. Am. Chem. Soc.*, 82, 4750 (1960), and G. Wittig and A. Krebs, *Chem. Ber.*, 94, 3260 (1961).
(5) Satisfactory elemental analyses and spectral data were obtained for all new compounds.
(6) The bromomethylenecycloalkenes used in this study were prepared by the decarboxylative debromination of α-bromo-1-bromocycloalkylacetic acids. The details of these preparations will be described in a forthcoming publication.

Stable cycloalkynes can also be prepared by these rearrangements. However, the yield is sharply reduced by a competing, novel side reaction and by the base-catalyzed isomerization of the initially formed cycloalkyne to cycloalkadienes.[8] The reaction of bromomethylenecyclooctane with sublimed potassium *t*-butoxide at 200–240° afforded a trace of *t*-butoxymethylenecyclooctane and a 65% yield of a hydrocarbon mixture comprised of cyclononyne (9%), 1,2-cyclononadiene (27%), 1,3-cyclononadiene (25%), methylenecyclooctane (1%), and bicyclo[6.1.0]non-1-(2)-ene (VIII, 40%). The bicyclic olefin VIII displayed a weak C=C absorption peak at 5.70 μ.[9] and n.m.r. signals characteristic of a single olefinic proton at 5.88 p.p.m.[10] relative to tetramethylsilane, and was converted to bicyclo[6.1.0]nonane by catalytic hydrogenation. The spectral properties of VIII agree well with those of bicyclo[7.1.0]dec-1(2)-ene (IX) which was prepared from 1,2-cyclononadiene[11] by the Simmons–Smith procedure.[12]
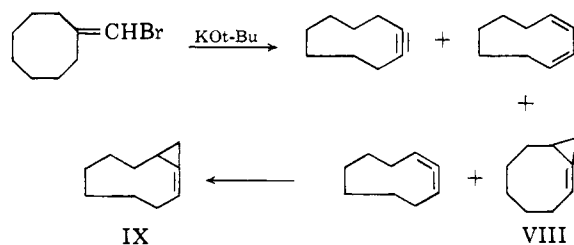
Bromomethylenecyclodecane and bromomethylenecyclododecane gave an array of products similar to those obtained from bromomethylenecyclooctane. The major product from bromomethylenecycloheptane was *t*-butoxymethylenecycloheptane, but a small amount (*ca.* 5%) of a mixture of methylenecycloheptane, 1,3-cyclooctadiene, bicyclo[5.1.0]oct-1(2)-ene, and bicyclo[5.1.0]oct-2-ene was also obtained.

When 1-bromo-2-ethyl-1-hexene (0.068 mole) was heated with sublimed potassium *t*-butoxide (0.107 mole), not only were 3-octyne (41.5% yield) and its isomerization products 2-octyne and two unidentified allenes produced, but also appreciable quantities (*ca.* 30% yield) of 1-ethyl-3-methyl-1-cyclopentene (X) were formed.

The formation of alkylidenecyclopropanes of type VIII and the cyclopentene X suggests the intermediacy of alkylidenecarbenes XI and XII in these transformations. Cyclopropenes would be produced in the former case and require a subsequent base-catalyzed isomerization of the olefinic double bond to give VIII.[13,14]

(7) The cyclopentyne–diphenylisobenzofuran adduct described in the literature[4] is the 1:2 adduct VII and not a 1:1 adduct as originally suggested: G. Wittig, private communication.

(8) *Cf.* D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *J. Am. Chem. Soc.*, **85**, 1553 (1963), and W. R. Moore and H. R. Ward, *ibid.*, **85**, 86 (1963).

(9) J. P. Chesick, *ibid.*, **85**, 2720 (1963).

(10) The alternate formulation of the bicyclic olefin as bicyclo[6.1.0]-non-1(9)-ene was excluded on the basis that cyclopropenes generally exhibit C=C absorption at 5.25–5.68 μ and olefinic proton n.m.r. signals at fields lower than 6.65 p.p.m. *Cf.* G. L. Closs, L. E. Closs, and W. A. Boll, *ibid.*, **85**, 3796 (1963).

(11) L. Skattebøl, *Tetrahedron Letters*, 167 (1961).

(12) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(13) *Cf.* M. G. Ettlinger and F. Kennedy, *Chem. Ind.* (London), 891 (1957).
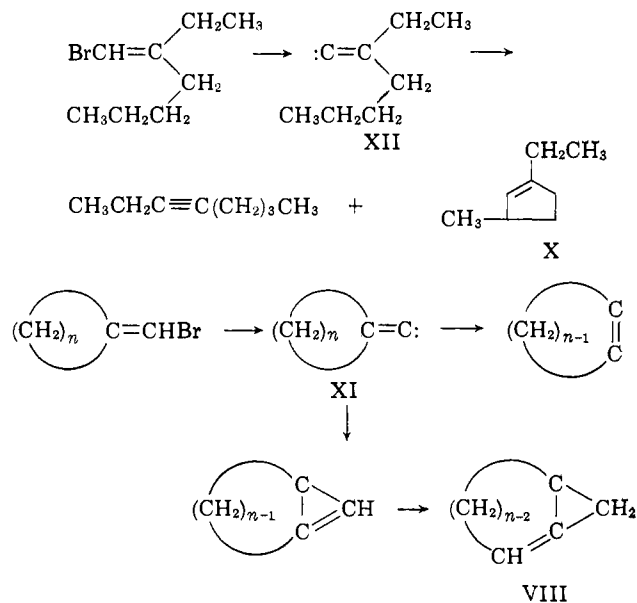
An alkylidenecarbene has been suggested as an intermediate in the formation of alkylidenecyclopropanes from 1,1-dibromo-2-methyl-1-propene and methyllithium in the presence of olefins.[15] The formation of alkylidenecyclopropanes in low yield by the reaction of vinyl or allyl chlorides, potassium *t*-butoxide, and olefins in tetrahydrofuran has been reported.[16] This reaction is also assumed to involve intermediate alkylidenecarbenes.[17]

Additional evidence for the intervention of alkylidenecarbenes in the rearrangement of vinyl bromides was provided by conducting the reaction in the presence of a large excess of cyclohexene. When bromomethylenecyclopentane (0.065 mole), potassium *t*-butoxide (0.065 mole), and cyclohexene (0.49 mole) were heated in *p*-cymene, 7-cyclopentylidenebicyclo[4.1.0]-heptane (XIII) was isolated (11%). Alkylidenecyclopropanes XIV (3%)[16] and XV (2%) were similarly produced from 1-bromo-2-methyl-1-propene and ω-bromocamphene, respectively.
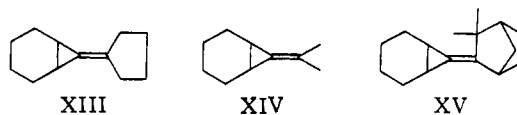
(14) The absence of detectable amounts of allylic *t*-butyl ethers among the products of the reaction of potassium *t*-butoxide with vinyl bromides in nonpolar solvents appears to eliminate the intermediacy of an alkenylcarbene ii derived from anion i.
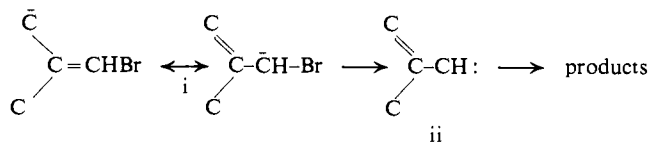
(15) H. D. Hartzler, *J. Am. Chem. Soc.*, **86**, 526 (1964).

(16) M. Tanabe and R. A. Walsh, *ibid.*, **85**, 3522 (1963).

(17) Evidence is not presently available to exclude rigorously the involvement of an alkenylcarbene in these transformations.

(18) Gulf Oil Company Fellow, 1963–1964.

Karen L. Erickson,[18] Joseph Wolinsky
Department of Chemistry, Purdue University
Lafayette, Indiana