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CROWN ETHER CATALYZED GENERATION OF ADAMANTYLIDENE CARBENE FROM ω-BROMOMETHYLENEADAMANTANE AND POTASSIUM t-BUTOXIDE[1]

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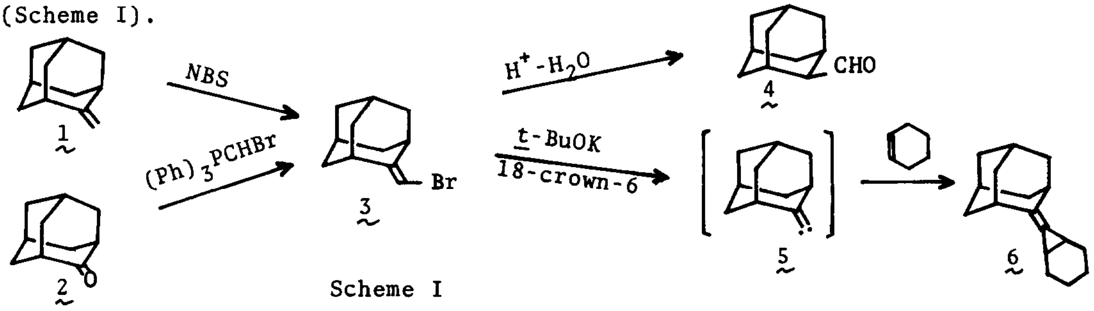
As an extension of our studies on the synthesis of adamantane derivatives by utilizing carbenic species,[2] we wish to report synthesis of some adamantylidenecyclopropane derivatives _via_ generation of adamantylidenecarbene from ω-bromomethyleneadamantane (3) and _t_-BuOK.[3]

Bromination of methyleneadamantane (1) with 1.5~2.0-fold excess NBS under reflux in benzene or carbon tetrachloride catalyzed with benzoyl peroxide afforded ω-bromomethyleneadamantane (3), mp 26.0-28.0° in 40-43% yields after chromatography. The assigned structure was supported by appearance of a characteristic singlet signal at δ 5.48 in the nmr spectrum.[4,5] The Wittig reaction of adamantanone (2) with bromomethylenetriphenylphosphorane[6] gave also 3 in 53% yield. The bromide 3 was not stable to acid and was converted to 2-adamantanecarboxaldehyde (4)[7] on treatment with 10% hydrochloric acid (Scheme I).



Scheme I

Dehydrobromination[8] of **3** with *t*-BuOK (2-fold excess) in refluxing cyclohexene containing a catalytic amount of 18-crown-6 (5-10 mol% to *t*-BuOK) afforded 7-adamantylidenebicyclo[4.1.0]heptane (**6**), an adamantylidenecarbene adduct to cyclohexene in 58% yield: bp 72-74°C (1 mm); n_D^{28} 1.5475; nmr (CCl_4) δ 2.66 (broad s, 2H) and 2.2-1.07 (m, 22H). It is well known that certain crown ethers are powerful complexing agents for alkali metal cations and provide highly reactive bared anions.[9,10] In order to confirm such catalytic effect of 18-crown-6 for the present α-dehydrobromination of **3** with *t*-BuOK, the yields of **6** were compared between the catalyzed and uncatalyzed reactions as shown in Table I. The data in Table I indicate clearly the catalytic effect of 18-crown-6 for the dehydrobromination of **3**.

Above results suggest the utility of vinyl bromide **3** as a stable precursor to adamantylidenecarbene (**5**). In fact, the additions of **5** to several other olefins were successful under the 18-crown-6 catalyzed conditions as depicted in Scheme II. The dehydrobromination of **3** in norbornene under the similar conditions but using toluene as a solvent yielded 3-adamantylidenetricyclo[3.2.1.$0^{2,4}$]octane (**7**) as an oil (67%): n_D^{15} 1.5597; nmr ($CDCl_3$) δ 2.56 (broad s, 2H), 2.39-1.05 (m, 20H) and 0.85 (ABq, *J*=9.6 Hz, $J/\Delta\delta$=0.400, 2H). The assigned exo configuration of **7** was supported by appearance of the characteristic AB quartet signal assignable to C_8 bridge methylene protons in the nmr spectrum. Similarly, the reaction of **3** with *t*-BuOK in norbornadiene afforded an adduct **9** in 38% yield: mp 86-88°; nmr (CCl_4) δ 2.75 (broad s, 2H) and 2.20-1.16 (m, 20H). **9** was characterized as 3-adamantylidenetetracyclo[3.3.0.0.$^{4,6}0^{2,8}$]octane because of the absence of vinyl proton signals. The formation of **9** can be rationalized in terms of the thermal valence isomerization of an initial carbene adduct **8** since 3-alkylidenetricyclo[3.2.1.$0^{2,4}$]oct-6-enes, alkylidenecarbene adducts to norbornadiene are well known to rearrange thermally to the corresponding 3-alkylidenetetracyclo[3.3.0.0.$^{4,6}0^{2,8}$]octanes.[11]

The reaction of **3** with *t*-BuOK in 2,5-dimethyl-2,4-hexadiene under the similar conditions using toluene as a solvent afforded an adduct **11** (41% yield): mp 70-74°; nmr ($CDCl_3$) δ 4.79 (broad d, *J*=9.0 Hz, 1H) and 2.3-1.05 (m, 27H).

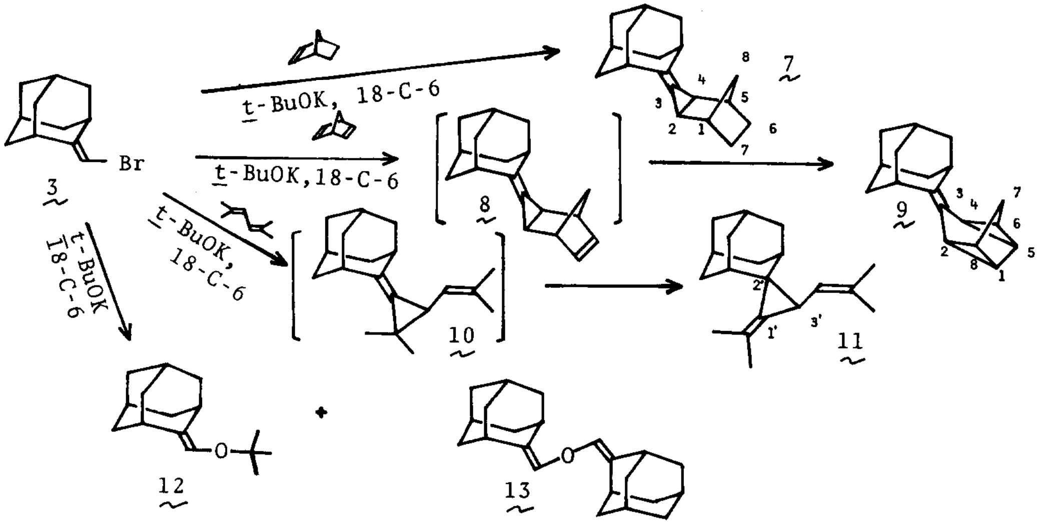
The structure of 11 was tentatively assigned as adamantane-2-spiro-2'-(3'-isobutenyl-1'-isopropylidene)cyclopropane because of absence of the characteristic allylic bridgehead proton signals and appearance of only allylic methyl protons signals in the nmr spectrum. The formation of 11 could be rationalized by thermal isomerization of an initially produced carbene adduct 10[12](Scheme II).

The dehydrobrominations of ω-bromocamphene[13] and ω-bromolongifolene[4b] with t-BuOK are known to afford the corresponding bicyclo[3.2.1]oct-2-yne derivatives, however, the dehydrobromination of 3 in the absence of olefins afforded only ω-t-butoxymethyleneadamantane (12) (90%) and bisadamantylidenedimethyl ether (13) (2%). Compound 12 had n_D^{17} 1.5119; ir (neat) 1665 cm^{-1}; nmr (CDCl$_3$) δ 5.93 (s, 1H), 3.00 (broad s, 1H), 2.27 (broad s, 1H), 2.11-1.50 (m, 12H) and 1.23 (s, 9H), and 13 had mp 245-249°; ir (KBr) 1660 cm^{-1}; nmr (CDCl$_3$) δ 5.95 (s, 1H), 3.03 (broad s, 1H), 2.22 (broad s, 1H) and 2.1-1.5 (m, 12H). The assigned structures of 12 and 13 were further supported by

TABLE I. Comparison of yields of 6 between catalyzed and uncatalyzed reactions[a]

React.time,hr	Yield(cat.),%	React.time,hr	Yield(uncat.),%
12	42.6	20	3.1
21	75.8	25	3.0
31	97.1	36	7.2

[a] A mixture of 3, t-BuOK (2-fold excess) and 18-crown-6 (5 or 0 mol% to t-BuOK) in cyclohexene was refluxed under argon atmosphere and crude reaction mixture was analyzed on glc at appropriate reaction times.



Scheme II

their conversions to **4** characterized as 2,4-dinitrophenylhydrazone with acid.[14] These results indicate that the ring expansion of **5** or potassium salt of **3** to homoadamant-4-yne is prohibited by the geometrical constrain and **5** reacted with *t*-BuOH produced under the reaction conditions affording **12**.[15] The reaction of **12** with **5** may produce the divinyl ether derivative **13**.[15]

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