Tetrahedron Letters No. 32, pp 2741 - 2744, 1976. Pergamon Press. Printed in Great Britain.

CONVENIENT SYNTHETIC ROUTES TO TRICYCLO[4.1.0.$0^{2,7}$]HEPT-3-ENE AND ITS DERIVATIVES[1]

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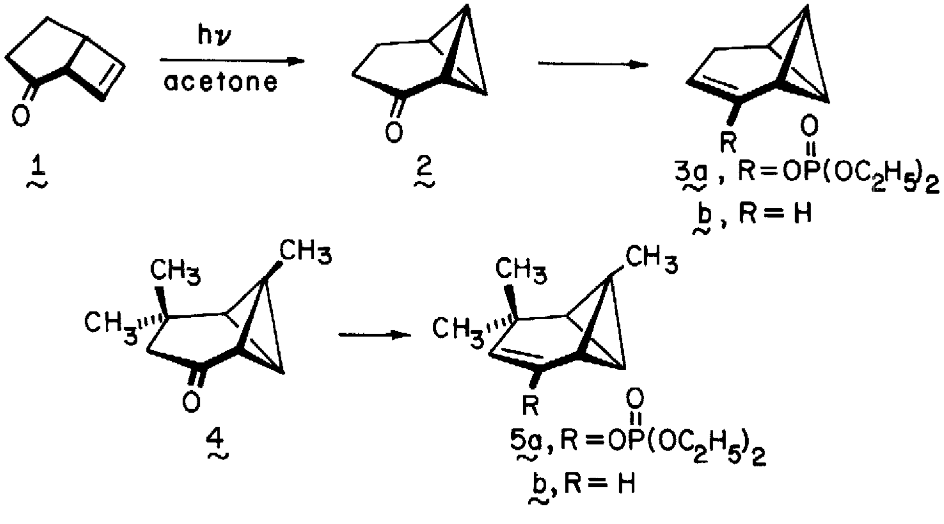
(Received in USA 27 April 1976; received in UK for publication 24 June 1976)

Tricyclo[4.1.0.$0^{2,7}$]hept-3-ene (3b) with its conjugated bicyclobutane ring and double bond has not heretofore commanded widespread attention as a precursor of yet more highly strained molecules because of its inaccessibility. Klummp and Vrielink first prepared 3b by reaction of 7,7-dibromo-3-norcarene with methyllithium at 0°, but the realized yields never exceeded 1-5%.[3] In the only other relevant report, Christl and Brüntrup succeeded in elaborating 3b more efficiently,[4] but their procedure involves a three-step ring expansion of elusive benzvalene. For reasons outlined in the accompanying paper,[5] we have developed two straightforward routes to 3b and several of its derivatives, such that tricycloheptenes as a class are now conveniently available.

The first approach is typified by the sequence 1 → 3. Acetone-sensitized irradiation of bicyclic enone 1[6] according to Ipaktschi[7] afforded the tricycloheptan-2-one 2 which upon conversion to enol phosphate 3a and subsequent lithium-ammonia reduction[8] was transformed uniquely to the desired hydrocarbon 3b. Analogous treatment of 4[7] gave 5b [$\delta_{TMS}^{CDCl_3}$ 5.64 (dd,



1

2

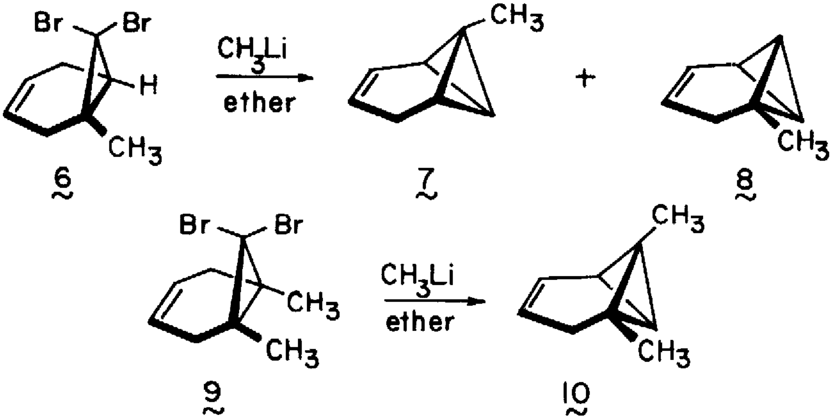
3a, R = $OP(O)(OC_2H_5)_2$
b, R = H

4

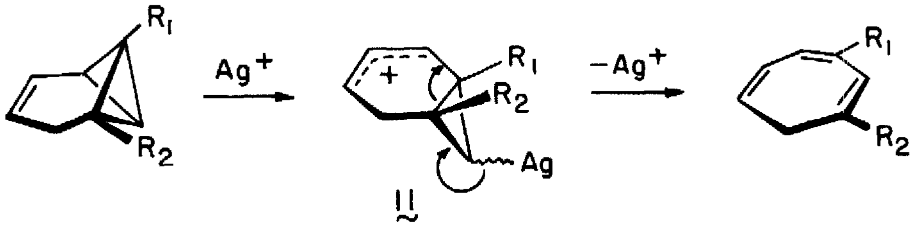
5a, R = $OP(O)(OC_2H_5)_2$
b, R = H

J = 10 and 4 Hz, 1), 4.93 (dt, *J* = 10 and 2 Hz, 1), 2.00 (m, 2), 1.60 (s, 3), 1.50 (m, 1), 0.93 (s, 3), and 0.87 (s, 3)], vpc analysis again providing indication of 40-50% overall conversion from ketone. Isolation of 3b and 5b by preparative scale vpc was rather inefficient (ca 40% return) due to their high volatility. In neither reduction was central bond cleavage in evidence as is seen under somewhat more vigorous conditions.[9]

Alternatively, alkyl tricyclo[4.1.0.0^{2,7}]hept-3-enes can be directly prepared by carbenoid cyclization of 7,7-dibromo-3-norcarene derivatives. For example, exposure of 6 to ethereal methyllithium at 0° led efficiently to a 3:1 mixture of 7 [$\delta_{TMS}^{CDCl_3}$ 6.00-5.70 (m, 1), 5.40-5.00 (m, 1), 2.40-2.17 (m, 1), 2.17-1.85 (m, 3), 1.57 (s, 3), and 1.33 (t, *J* = 3 Hz, 1)] and 8 [$\delta_{TMS}^{CDCl_3}$ 6.10-5.70 (m, 1), 5.55-5.20 (m, 1), 2.35-2.10 (m, 1), 2.05-1.90 (m, 2), 1.66 (d, *J* = 3 Hz, 2), and 1.11 (s, 3)] in 50% vpc isolated yield. Comparable elaboration of 10 also proceeded very smoothly (40% after vpc isolation). We, like Klummp,[3] have not achieved equivalent success with the parent dibromide, but the otherwise efficient closure of these 7-norcarenylidenes[10] seemingly rules out his suggestion that ''foiled carbenes'' (arising from p_π interaction) may be involved.



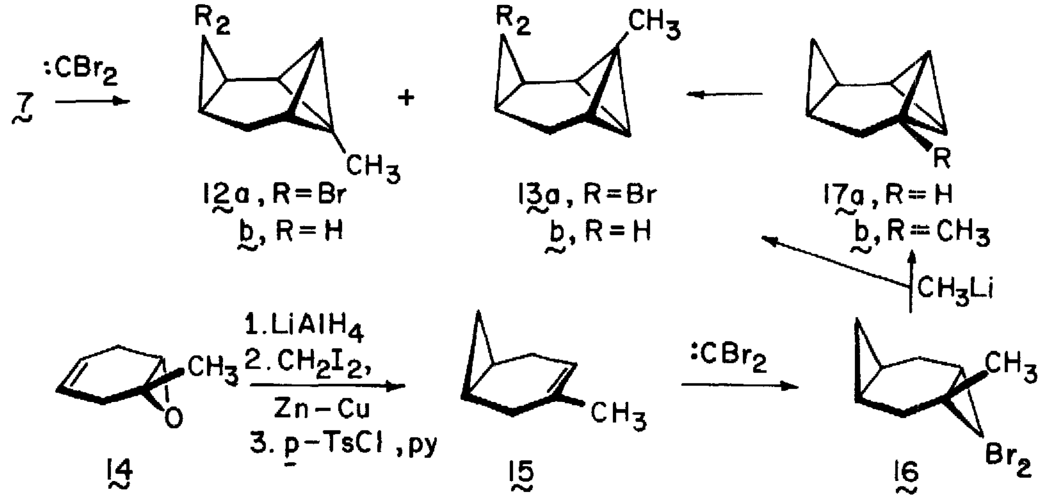
Reaction of 7 and 8 with catalytic quantities of silver perchlorate in benzene at 25° resulted in instantaneous Type α rearrangement[11] with formation of 3- and 1-methylcycloheptatriene,[12] respectively. Thus, attack of Ag$^+$ at that less sterically congested edge bond which can generate a transient allylic cation is highly favored, deargentation with accompanying fission of the diametrically opposed C-C bond (see 11) subsequently delivering product. The quantitative isomerization of doubly labeled 10 exclusively to 1,3-dimethylcyclohepta-



11

triene [$\delta^{CDCl_3}_{TMS}$ 6.23 (d with fine splitting, *J* = 5 Hz, H_4), 6.00 (dd, *J* = 9 and 5 Hz, H_5), 5.82 (s, H_2), 5.28 (m, H_6), 2.30 (d, *J* = 7 Hz, methylene group), 2.00 (s, 1-Me), and 1.97 (d, *J* = 1.5 Hz, 3-Me)] is additionally revealing from this mechanistic standpoint.

When treated with bromoform and potassium tert-butoxide, 7 was converted in 70% yield to a mixture of 12a and 13a. To establish the stereoselectivity of dibromocarbene attack, this mixture was reduced with lithium and tert-butyl alcohol in tetrahydrofuran to the tetracyclo[5.1.0.$0^{2,4}$.$0^{3,5}$]octanes 12b and 13b (60:40). In accord with these assignments, methylation of the parent hydrocarbon (17a)[1,13] (n-BuLi, TMEDA; CH_3I) was also found to give 12b and 13b, and in a rather similar ratio (3.5:1). Suitable distinction between these isomers was achieved by the independent synthesis of 13b starting from 14[14] as outlined.



7

12a, R=Br
b, R=H

13a, R=Br
b, R=H

17a, R=H
b, R=CH3

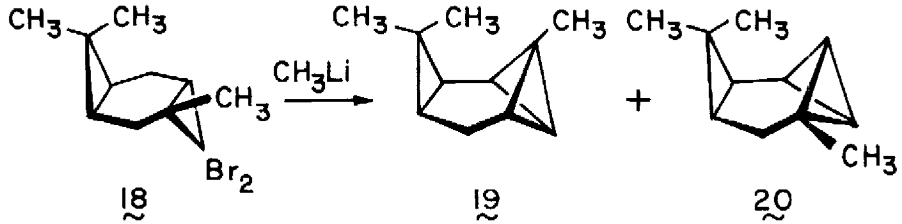
14

15

16

The data indicate that attack on 7 by dibromocarbene expectedly exhibits some partiality for that tricycloheptene surface lacking the bridgehead methyl substituent. Analogously, the methylation of 17a proceeds preferentially at the bridgehead carbon distal from the cyclopropane ring.

On this basis, the capability of the angular methyl group in 16 to direct carbenoid capture predominantly to the proximal α-methylene group (13b/17b = 5:1) is noteworthy. Owing to the strongly exothermic nature of this reaction, it is not warranted to attribute this product distribution to steric influences.[15] That other causative factors are at play is further attested to by the behavior of 18 (from 3-carene) which cyclizes predominantly to 19



instead of 20 (ratio 3:1). This apparent frustration of thermodynamics arises because of the early timing of the transition state and the dependence of reactivity on geometric proximity and C-H bond electronegativities[15] (closely balanced in the present examples).[16]

References and Footnotes

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(16) The partial financial support of the National Science Foundation is gratefully acknowledged.