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THE SYNTHESIS OF TRICYCLO[4.3.0.0^{3,8}]NONANE (TWIST-BRENDANE) AND HOMOADAMANTANE. A NEW ROUTE TO HOMOADAMANTANES

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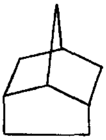
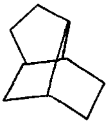
In a recent communication (1), Schleyer and Wiskott pointed out that of the conceivable tricyclononanes only four (I-IV) do not possess three or four-membered rings or highly strained skeletons. Brendane (I), brexane (II) and noradamantane (III) are known (2). We now wish to report the synthesis of the fourth member of this series, tricyclo[4.3.0.0^{3,8}]nonane (IV), colloquially termed "twist-brendane" (1), and to describe the unambiguous preparation of homoadamantane (V) via a common intermediate.



I



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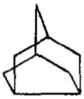

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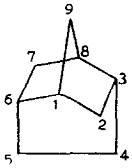

IV

Formally, twist-brendane can be derived from homoadamantane (V) by the extrusion of two oppositely situated methylene bridges. Unfortunately, common entries into the latter system (3) do not provide derivatives appropriately substituted for this operation. A new route to homoadamantanes was therefore required. To this end we were successful in inserting an ethylene bridge between the C3 and C7 carbon atoms of dimethyl bicyclo[3.3.1]nonane-2,6-dione-3,7-dicarboxylate (VI) (4) to give the dimethyl homoadamantane-10,11-dione-3,6-dicarboxylate (VII). The dionediacid VIII, obtained from VII by acid hydrolysis, was converted to the <u>bis</u>-α-bromoketone IX, which was then subjected to a double Favorskii-type ring contraction (5), affording twist-brendane-3,6-dicarboxylic acid (X). Reductive dehalogenation of the halohydrocarbon mixture XI, prepared from X by a Hunsdiecker reaction, furnished twist-brendane.

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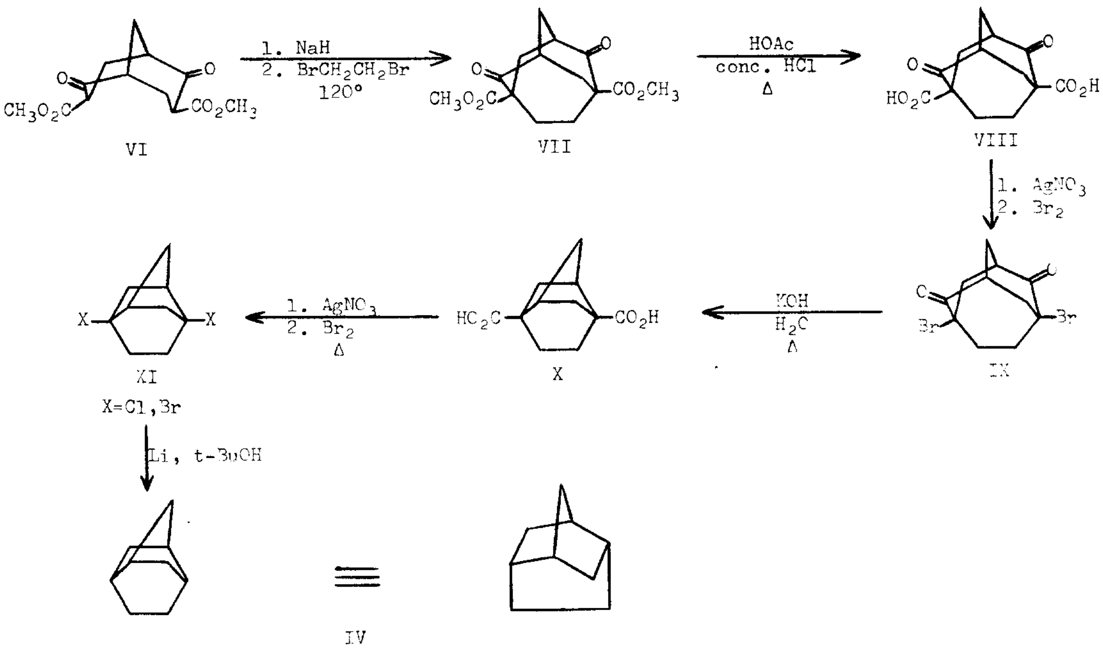
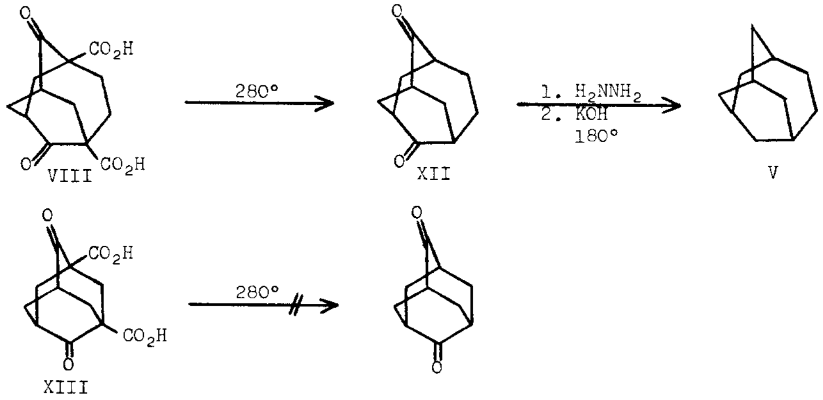


Thus, the disodium salt of bicyclononane dionediester VI, prepared with sodium hydride in glyme (6), was heated with ethylene bromide at 120° for 20 hours to give dimethyl homoadamantane 10,11-dione-3,6-dicarboxylate (VII) [yield, 44%; mp 197-198°; C=O stretch, 5.75 μ; 5.87 μ] (7). The product VII contains the requisite functional groups, properly situated, for the ultimate preparation of IV. Hydrolysis, using a mixture of acetic and hydrochloric acids, afforded the dionediacid VIII [yield, 92%; mp 288-290° (with gas evolution); C=O stretch 5.75 μ and 5.85 μ (5% THF sol'n.)]. The di-silver salt of VIII, obtained by neutralizing the acid to phenolphthalein endpoint and treating with silver nitrate, was converted by a Hunsdiecker reaction to 3,6-dibromohomoadamantane-10,11-dione (IX) [yield, 31%; mp 277-278°; C=O stretch 5.81 μ], using bromine in refluxing carbon tetrachloride. Hot aqueous ethanolic potassium hydroxide smoothly effected a double Favorskii-type ring contraction, transforming IX into twist-brendane-3,6-dicarboxylic acid (X) [yield, 98%; mp 378-382°]. Diacid X was assigned its structure on the basis of its spectral properties (OH stretch 3.79 μ, C=O stretch 5.92 μ; no vinylic pmr absorptions) and the behavior of similar α-bromoketones (5). The Hunsdiecker reaction was again employed, this time to convert the di-silver salt of X to a mixture of chloro and bromo-twist-brendanes XI in 70% yield. Reductive dehalogenation of this mixture with lithium and t-butyl alcohol in tetrahydrofuran furnished twist-brendane (IV) in 46% yield. In addition to the method of preparation, the melting point of IV (165-166°, totally submerged sealed capillary) readily distinguishes it from the other three tricyclononane isomers; brexane (II) is a liquid while brendane (I) and noradamantane (III) have melting points of 98-99° and 203-204° respectively (2). The pmr spectrum of IV exhibited two broad singlets at δ 2.33 and δ 1.86 (2H each, methine) and a poorly resolved multiplet between δ 1.7-0.9 (10H, methylene). The hydrocarbon gave a molecular ion peak at m/e 122 (relative abundance, 26) with more intense peaks at m/e 93 (ra, 41), 80 (ra, 90), 79 (ra, 59), 67 (ra, 41), 41 (ra, 32) and 39 (ra, 32) and a major peak at m/e 81; isotopic analysis was in accord with the empirical formula.

Homoadamantane (V) has been previously prepared only by solvolytic rearrangement pathways (3). While the results leave little room for doubt, the routes involved do not permit an unambiguous assignment of structure. We were able to prepare V in an unequivocal manner. Thus homoadamantane-10,11-dione-3,6-dicarboxylic acid (VIII), a key intermediate in the preparation of twist-brendane, was readily decarboxylated by neat pyrolysis at 280° to give homoadamantan-10,11-dione (XII) [yield, 80%; mp 303-304°; C=O stretch 5.87 μ]. By contrast, adamantane-2,6-dione-1,5-dicarboxylic acid (XIII) was inert at this temperature. These results are readily explained by consideration of the transition state recently suggested for the decarboxylation of highly strained bicyclic β-keto acids (8). Ferris and Miller thus proposed that increasing overlap between the sp^3 orbital of the developing carbanion (from the C-CO_2H bond) and the p orbital of the adjacent ketone group should lead to more facile decarboxylations. Where the orbitals are orthogonal, decarboxylations should be difficult, if not impossible. In VIII the interacting orbital angle is <u>ca</u>. 70° (9), allowing for some stabilization of the incipient carbanion by the ketone function; while in XIII the orbitals are orthogonal, preventing any form of assistance thru overlap.



To prepare the parent hydrocarbon, dione XII was subjected to a Wolff-Kishner reduction, using hydrazine hydrate in triethylene glycol followed by heating at 180° with potassium hydroxide to give homoadamantane V [yield, 85%; mp 259-260°, reported (10) mp 258-259°]. The pmr spectrum (CCl_4 as solvent) of V shows a complex multiplet between δ 2.4-1.0.

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