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TRANSFER TECHNOLOGY II. Preparation of Transfer Reagents for the Site Specific Delivery of Disubstituted Cyclobutadienes and their use in the Synthesis of Hetero Bridged Propellanes.

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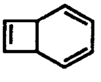
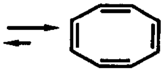
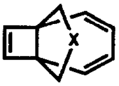
Summary: Transfer reagents (**11**) and (**18**) are used as synthetic equivalents for disubstituted cyclobutadienes in a new protocol for the synthesis of the heteropropellanes (**5**), (**6**), and (**16**).

Bicyclo[4.2.0]octa-2,4,7-trienes (BiCOTs) (**1**) are a class of unstable molecules which usually prefer to adopt the cyclooctatetraene (COT) structure (**2**),[1] since this is of lower energy and readily attained via a thermally allowed [4π+2σ] disrotatory valence isomerisation. Substituents can influence the position of equilibrium between these two forms, but few examples are known where the BiCOT form predominates. Several research groups[2] have shown that otherwise unstable ring systems can be stabilised by incorporation into a propellane system where one arm of the propellane acts as a pinching group to geometrically constrain the ring-opening process, e.g. Dewar benzene as in (**3**).[3] This has been demonstrated to apply to the BiCOT system by Paquette and his coworkers,[4] who reported the use of a polymethylene bridge in this role, e.g. (**4**, X=CH_2). In this communication we report the use of our new synthetic protocol, Transfer Technology,[5] to the preparation of hetero-bridged [4.3.2]propellanes and discuss its application to the synthesis of BiCOTs (**5**)-(**7**) .


(**1**)


(**2**)

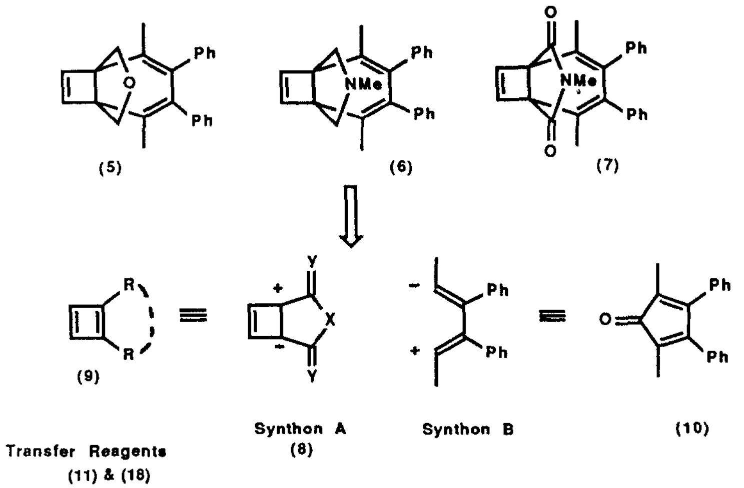

(**3**)



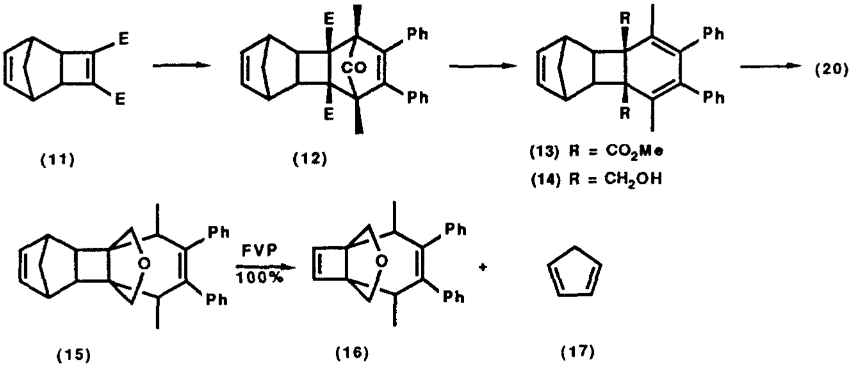
(**4**)

This synthesis of hetero-bridged propellanes, based on the retrosynthetic analysis outlined in Scheme 1, is novel as it uses Transfer Reagents to supply each of the synthons identified in the retrosynthesis. The use of cyclone (**10**) to furnish synthon-B has much precedent[6] whereas the Transfer Reagents used to supply synthons-A (**8**) are more noteworthy. By employing Transfer Reagents (**11**) and (**18**) to deliver the disubstituted cyclobutadiene moiety we can ensure that it is introduced regiospecifically into the polycyclic intermediate which , following chemical elaboration in the case of (**13**), produces the required propellane in a final deprotection step. Application to the formation of oxa-bridged dihydroBiCOT (**16**) establishes the viability of this approach, while application to the direct synthesis of BiCOTS (**5**), (**6**) and (**7**) serves to establish some of the boundary conditions for this protocol.

SCHEME 1

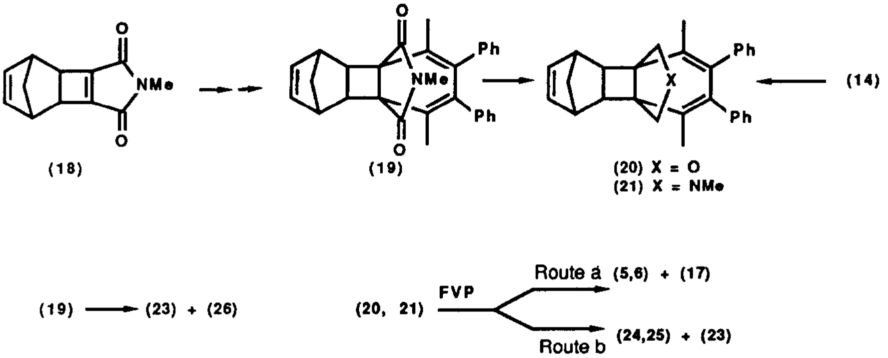


SCHEME 2

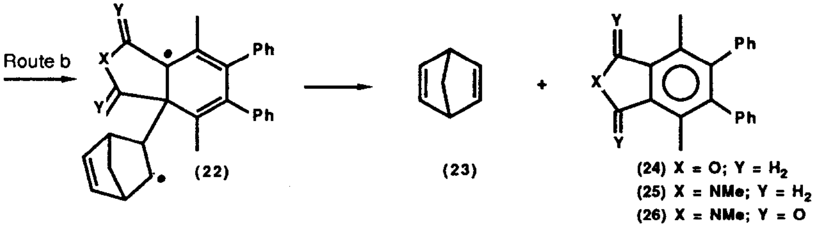


Reaction of Transfer Reagent (**11**) with cyclone (**10**) in benzene solution occurs site specifically to afford the 1:1-adduct (**12**). Photodecarbonylation of this adduct yields the corresponding diene (**13**) together with small amounts of its valence isomer .^{7} 1,4-Diol (**14**) and its dihydro counterpart^{9} are available by LAH reduction of (**13**) and, on treatment with the Mitsunobu reagent,^{8,10} are converted to their respective cyclic ethers (**20**) and (**15**) in excellent yield. F.V.P. of dihydro-cyclic ether (**15**) proceeds smoothly and produces the propellane (**16**), together with cyclopentadiene , in quantitative yield. Similar treatment of cyclic ether (**20**) again yields the expected propellane (**5**) by loss of cyclopentadiene, this time accompanied by a significant amount of the aromatic compound (**24**) and norbornadiene.

Our approach to the synthesis of the aza-bridged BiCOT (**6**) illustrates that the heteroatom-containing bridge can be introduced in cyclic form at theTransfer Reagent stage. Thus reaction of polyalicyclic maleimide (**18**) ,^{5} acting as a Transfer Reagent for *N*- methyl cyclobutadiene[1,2-c]maleimide ,^{11} with cyclone (**10**) produces exclusively a 1:1-adduct adduct which can be thermally decarbonylated to form the diene (**19**) . Selective reduction of the succinimide component of (**19**) occurs on treatment with LAH to form the pyrrolidine-containing aza-bridged propellane (**21**). F.V.P. of (**21**) is ambivalent , however, leading predominantly to a mixture of the cyclobutane cleavage products (**23**) and (**25**), while the desired aza-bridged propellane (**6**), formed *via* the Alder Rickert reaction, SCHEME 3



SCHEME 4



is a minor product (see Scheme 3). That the nature of the hetero bridge can promote cyclobutane cleavage in these systems at the expense of Alder Rickert fragmentation is further highlighted by F.V.P. of the related succimide (**19**) where exclusive formation of the phthalimide (**26**) and norbornadiene is observed to occur.

The success of this reaction protocol to produce bridged BiCOTs directly is limited by the efficiency of the cyclobutane cleavage reaction (Scheme 3, route b) relative to the Alder-Rickert process (route a) in the F.V.P. step. We consider that cyclobutane cleavage likely occurs by a non-concerted process involving a diradical intermediate of type (**22**) (Scheme 4). The efficiency of this cleavage reaction in substrates (**19**), (**20**) and (**21**) is the same as the ability of the hetero-bridging group (succinimide>>pyrrolidine≈tetrahydrofuran) to stabilise the intermediate diradical. The diene component, common to all substrates , also offers critical stabilisation to this diradical. While this contribution has not been evaluated in all cases, we do know that its removal in the oxa-bridged system has a dramatic effect in reducing the efficiency of the cyclobutane cleavage reaction, as evidenced by the reaction of the dihydro cyclic ether (**15**) which we noted above formed Alder-Rickert products exclusively. This latter reaction offers a potential solution around the limitation for producing BiCOTS by Transfer Technology as good precedent for the upgrading of cyclohexenes to cyclohexadienes in propellanes is available in the literature.[12]

This paper illustrates the value of theTransfer Technology for the synthesis of hetero bridged propellanes. In addition, it identifies a major factor affecting the efficiency of this protocol and shows that the introduction of the diene component of bridged BiCOTs is best introduced after the basic ring-system has been formed.

References and footnotes.

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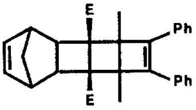
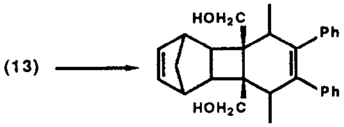
5. Preceeding communication.
6. Ogliaruso, M.A., Romanelli, M.G., and Becker, E.I., *Chem. Rev.*, 1965, **65**, 261.
7. This involves [2π+2π] disrotatory electrocyclic ring closure of the 1,4 diene to form (i).



(i)

The ^{1}H n.m.r. spectrum of this compound contains a methyl ester resonance at δ 3.14 in comparison with that of the isomeric diene (**13**) (δ 3.73). This upfield shift appears to be a general trend and we have observed similar shifts in related pairs of compounds.[8]

8. Butler, D. N., Officer, D., Pitt, I. G., Warrener , R. N., and Russell, R. A., Unpublished results.
9. Overreduction to the dihydro compound (ii) is fickle and only occurs rarely with LAH. Other methods for its formation are presently under investigation.



(ii)

10. Kurihara, T., Nakajima , Y., and Mitsunobu, O., *Tetrahedron Lett.* , 1976, 2455.
11. We contemplated using *N* - methylcyclobutadiene[1,2-c]maleimide (*N*-methylcyclobutadiene 1,2-dicarboximide) as a reagent, as we have recently shown[8] that it can be generated and trapped with furan. However, its access *via* the Transfer Reagent protocol is more versatile as the present example highlights.
12. *inter alia:* Ginsburg, D. ' Propellanes', Verlag Chemie, Weinheim 1975, p. 37.

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