(21) Calculations by Liebman and Greenberg show a similar stabilizing effect of alkyl groups on oxyallyl cations formed by ring opening of the corresponding cyclopropanones: J. F. Liebman and A. Greenberg, *J. Org. Chem.*, **39**, 123 (1974).
(22) H. M. R. Hoffmann, T. A. Nour, and R. H. Smithers, *J. Chem. Soc., Chem. Commun.*, 963 (1972).
(23) (a) J. W. Ellis, *J. Org. Chem.*, **34**, 1154 (1969); (b) H. O. House and H. W. Thompson, *ibid.*, **26**, 3729 (1961); (c) M. E. Kuehne and T. J. Giacobbe, *ibid.*, **33**, 3359 (1968); (d) G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 4426 (1955); (e) C. Fenselau in "Steroid Reactions", C. Djerassi, Ed., Holden-Day, San Francisco, Calif., 1963, p 537 ff.
(24) (a) We have recently found that **6** is converted to **7** cleanly and in high yield by the action of metallic mercury in acetic acid containing sodium acetate; the reaction is considerably slower than the electrode reaction, but affords **7** in purer form. We are exploring the scope and synthetic utility of this reaction. (b) Daniel Herr, unpublished research.
(25) A referee has suggested that those compounds affording parent ketones as product (**15–17**) might exhibit different *i–E* curves than those (e.g., **6**) affording acetoxy ketones. This is not the case: all dibromo ketones examined by us exhibit a single drawn-out *i–E* curve.[9b]
(26) L. F. Fieser, "Experiments in Organic Chemistry", 3rd ed, D. C. Heath, Boston, Mass., 1955, p 281.
(27) R. B. Wagner and J. A. Moore, *J. Am. Chem. Soc.*, **72**, 974 (1950).
(28) E. J. Corey, T. H. Topre, and W. A. Wozniak, *J. Am. Chem. Soc.*, **77**, 5415 (1955).
(29) F. G. Bordwell and K. M. Wellman, *J. Org. Chem.*, **31**, 351 (1966).
(30) T. Eicher and N. Pelz, *Tetrahedron Lett.*, 1631 (1974).
(31) Reference 13, p 325.

Stereochemistry and Mechanism of Electrophilic Additions to Tricyclo[4.2.2.0^{2,5}]deca-3,7-diene Derivatives

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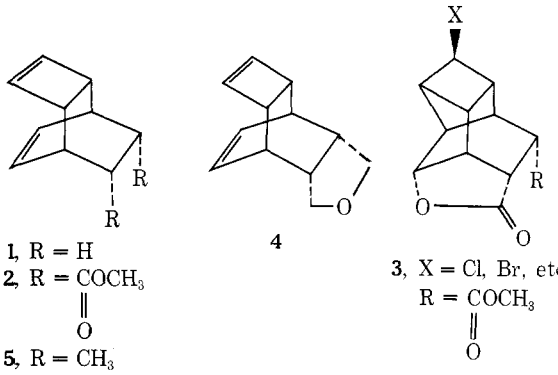
Electrophilic addition of iodine azide, mercuric acetate, nitrosyl chloride, and diborane to tricyclo[4.2.2.0^{2,5}]deca-3,7-diene derivatives **2, 4,** and **5** is described. Reaction of iodine azide with diester **2** furnishes a syn azido iodide **6**. On the other hand, IN_3 addition to **4** and **5** in acetonitrile solvent results in transannular solvent participation and tetrazoles **8** and **10** are formed via Hassner–Ritter reaction. In methylene chloride solvent dienes **4** and **5** furnish the tetracyclic azido iodides **8** and **10**. Oxymercuration of **2, 4,** and **5** with mercuric acetate yields the corresponding syn oxymercurials in high yield. The exclusive syn addition of IN_3 and $Hg(OAc)_2$ to the cyclobutene double bond of tricyclo[4.2.2.0^{2,5}]deca-3,7-dienes is interpreted in terms of the dominant role of twist strain theory. The long-range effects of substituents at C_9 and C_{10} on the reaction rates and product formation is also discussed.

Neighboring group participation by a distant double bond in carbocation reactions is now a well-established phenomenon.[2] The chemical reactivity of rigid molecules containing two isolated π bonds in favorable spatial orientation for transannular interaction provides a convenient and interesting route for generating a variety of polycyclic molecules of current interest. The addition of various electrophiles to several olefinic substrates, e.g., norbornadiene,[3] cyclic C_8,[4] C_9,[5] and C_{10}[6] 1,5-dienes, norbornadiene–cyclopentadiene adducts[7] and their chlorinated analogs (Isodrin–Aldrin series[8]), hexamethyl(Dewar benzene),[9] and 9,10-benzotricyclo[4.2.2.2^{2,5}]dodeca-3,7,9-triene,[10] has been investigated to elicit information about the nature of carbocation intermediates, proximity effects, transannular reactions, and ^{1}H NMR perturbations. Many of these reactions have found useful synthetic applications.[11,12] The tricyclo[4.2.2.0^{2,5}]deca-3,7-diene ring system **1** (R = H), readily available[13] from cyclooctatetraene via the diene synthesis, is endowed with a unique geometrical disposition of a strained cyclobutene double bond and a sterically shielded cyclohexene moiety, ideally suited for the study of transannular cyclizations and electrophilic additions. Furthermore, the variation of substituents at C_9 and C_{10} without altering the geometrical disposition of the double bonds provides an interesting variant for the study of long-range electronic effects. The addition of electrophiles to the dimethyl maleate adduct **2** of COT and its congeners has been studied by Reppe,[13] Nenitzescu,[14] and others[15,16] but no unambiguous structural assignments to the products were made. In a recent study, we[17] as well as others[18] have described the addition of halogens and pseudohalogens to **2** leading to the formation of tetracyclic lactones like **3** via a novel cross-type transannular cyclization. In continuation of these studies, we wish to describe here some interesting results of addition of iodine azide, mercuric acetate, diborane, and nitrosyl chloride to some derivatives of **1**. The additions of iodine azide and mercuric acetate have been found to be highly regio- and stereospecific syn additions and highlight the role of twist strain theory in electrophilic additions to strained olefins. The substrates selected for these studies were the diester **2**, ether **4**, and the dimethyl compound **5** in which the geometrical disposition of the double bonds and reacting site remains the same, while the availability of π electrons for participation by the C_7–C_8 double bond is altered owing to the presence of electron-withdrawing and -donating groups at C_9 and C_{10} endo position. The effect of this variation is distantly located substituents on the reaction rates and product formation is also discussed. The diolefinic substrates were prepared via a slight modification of literature procedures[14] and are described in the Experimental Section.



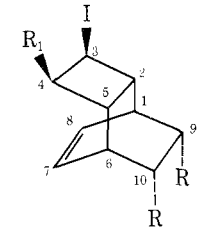
1, R = H
2, R = $COCH_3$
5, R = CH_3

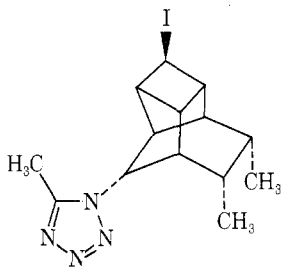
4

3, X = Cl, Br, etc.; R = $COCH_3$

Iodine Azide Additions.[19] The reaction of diester **2** with IN_3 solution prepared in situ from excess of sodium azide and iodine monochloride in acetonitrile (−5°) according to the procedure of Fowler, Hassner, and Levy[20] afforded a crystalline azido iodide **6**, mp 137°, in near-quantitative

yield. The structure of the IN_3 adduct follows from the diagnostic azide absorption at 2120 cm^{-1} and the ester bands at 1740 and 1210 cm^{-1} in the ir spectrum. The ^1H NMR spectrum showed two quartets at δ 4.32 and 3.12 due to tertiary protons attached to an iodo and azido group, respectively, along with a clean triplet at δ 6.51 due to the two olefinic protons. The syn orientation of I and N_3 substituents on the cyclobutane ring follows from the relatively sharp triplet for the two olefinic protons at C_7 and C_8 arising from the near equivalence of the vinyl hydrogens and the fortuitous near equivalence of their coupling constants. Furthermore, the 1,3-dipolar addition product **7**, mp 192–194°, of **6** with dimethyl acetylenedicarboxylate also dis-





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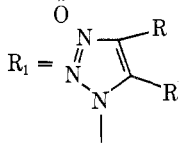
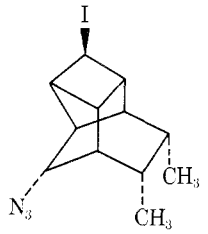
6, R = $COCH_3$
$R_1 = N_3$

7, R = $COCH_3$

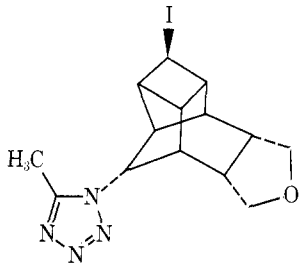




9

played, as expected, a sharp triplet at δ 6.61 for the olefinic protons. The appearance of a symmetrical triplet for the vinyl protons at C_7 and C_8 in tricyclo[4.2.2.$0^{2,5}$]dec-7-enes is diagnostic of symmetrical endo substitution at C_3 and C_4 and has been used for the unambiguous assignment[21,22] of configuration at C_3 and C_4. The structure of the syn addition product has been further confirmed by its correlation with the oxymercuration product of **2** (vide infra).

Reaction of dimethyl compound **5** with iodine azide in acetonitrile gave a crystalline solid, mp 147–148°, which analyzed for $C_{14}H_{19}N_4I$ indicating the participation of solvent in a Ritter-like reaction.[23] This product has been assigned the tetracyclic tetrazole structure **8** on the basis of spectral data. The ^1H NMR spectrum showed two singlets at δ 4.55 and 3.93 due to methine protons attached to a tetrazolyl and iodo group along with a singlet at δ 2.6 due to a tetrazolyl methyl group. The spectrum was transparent in the olefinic proton region and suggested transannular participation by the C_7–C_8 double bond.[24] The formation of **8** via cross-type cyclization[17,18] is supported by the clean singlet resonances due to C_4 and C_7 protons (expected on the basis of vicinal dihedral angles) and is in agreement with the previously assigned structure of the cyclization products[17,18] of this system. When the addition of iodine azide to the diene **5** was repeated in methylene chloride medium, an unstable azido iodide **9** was obtained in high yield as the exclusive product and is assigned structure **9** on the basis of its ir spectrum (2110 cm^{-1}, azide) and ^1H NMR spectrum (δ 4.16 and 3.75, singlets due to HCN_3 and HCI) which is analogous to **8**. The azido iodide **9** was also found to be formed, although in small quantity, along with the tetrazole **8** in acetonitrile solvent. Similarly, the addition of iodine azide to the ether **4** in acetonitrile furnished the tetrazole **10** as the major product in methylene chloride the unstable tetracyclic azido iodide **11** was obtained.



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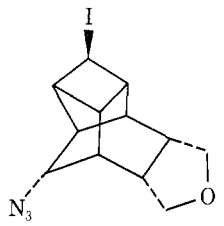
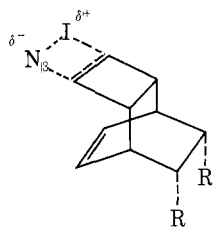
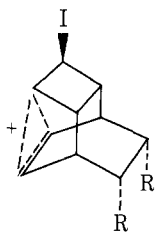


11

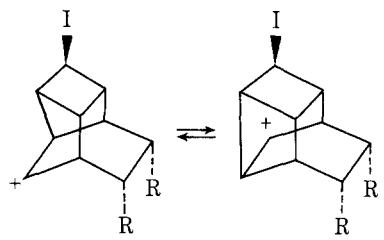
The addition of iodine azide to olefins has been shown by Hassner[25] to be a highly regio- and stereospecific process. The reaction proceeds via the electrophilic attack of IN_3 on the olefin with the formation of a three membered ring iodonium ion intermediate and preferential back-side opening resulting in the anti addition of the reagent. Numerous examples of such anti additions are recorded in the literature.[25] The formation of **6** from **2** appears to be the first example of a syn addition of IN_3 to an olefin. Several mechanistic alternatives can be considered to account for this stereospecific syn addition. These may include a concerted four-centered collapse via transition state **12**, shielding of the endo face through intervention of either a bridged ion **13** or a pair of rapidly equilibrating classical ions **14**, and dominance of twist strain factors as proposed by Traylor.[26]



12, R = $COCH_3$

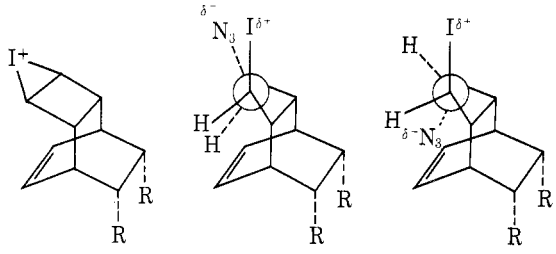


13, R = $COCH_3$



14, R = $COCH_3$

The four-centered syn addition of IN_3 has been considered[25] by Hassner and rejected on the grounds that it is symmetry forbidden and the large radius of iodine precludes a syn collapse. Also, complete variation in product formation in going from **2** to **5** without any apparent change in the geometry of the olefinic moieties is not compatable with this mechanism. Therefore, we do not see any compelling reason to invoke this four-centered polarized molecular addition in the present case. The intervention of **13** or **14** is discounted on the grounds that the presence of electron-withdrawing carbomethoxy substituents at C_9 and C_{10} markedly decreases the availability of electrons from the participating C_7–C_8 double bond and should force more of the reaction of **2** through the iodonium ion **15**. This con-

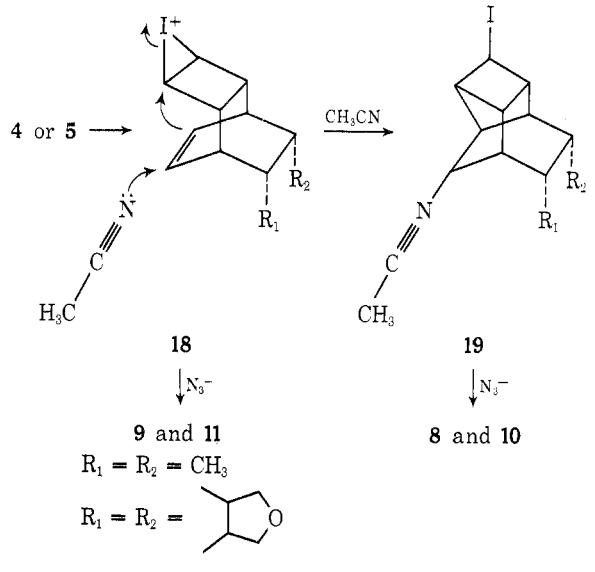


15, R = $COCH_3$ 16, R = $COCH_3$ 17, R = $COCH_3$

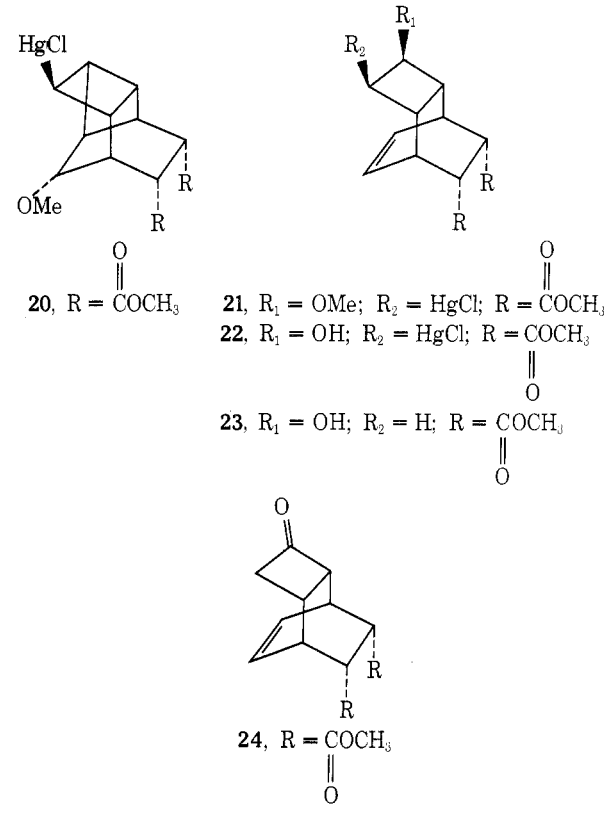
tention is supported by the fact that in the IN_3 addition to dimethyl compound **5** and ether **4**, where facile π participation and formation of ions related to **13** and **14** is possible, only cyclized tetracyclic products are formed and no syn addition product has been encountered. We, therefore, believe that the formation of syn addition product **6** is best rationalized on the basis of twist strain theory[26] and the syn transition state **16** is favored over the anti-coplanar transition state **17**. Lastly, the formation of syn product in this case, as well as in oxymercuration reaction (vide infra), cannot be attributed to steric factors (shielding of the endo face of cyclobutene by the cyclohexene moiety) as predominant formation of anti products in radical[27] and polar additions[16] to **2** is well documented.

The formation of the tetrazoles **8** and **10** from **5** and **4**, respectively, is rationalized on the basis of the solvent-assisted opening of the initially formed iodonium ion **18** to give the Ritter reaction intermediate **19**, which undergoes cycloaddition with azide ion to form the substituted tetrazoles. When the reaction is carried out in CH_2Cl_2 only the azido iodide results via the participation and nucleophilic capture by the azide ion (Scheme I).

Scheme I



Mercuric Acetate Additions. Methoxymercuration of diester **2** has been investigated by Cookson et al.,[15] resulting in the formation of a solid, mp 190–192°, to which they assigned the tetracyclic structure **20**. Repetition[28] of this methoxymercuration in our hands led to the formation of a crystalline organomercurial, mp 193–195°, whose ^1H NMR spectrum exhibited a 2 H olefinic proton triplet at δ 6.7, a 3 H methoxyl singlet at δ 3.23, and a multiplet due to a proton attached to the methoxy group at δ 3.55 along with other resonances compatible with structure **21**. Similarly, hydroxymercuration of **2** furnished the addition product



20, R = $COCH_3$

21, R_1 = OMe; R_2 = HgCl; R = $COCH_3$

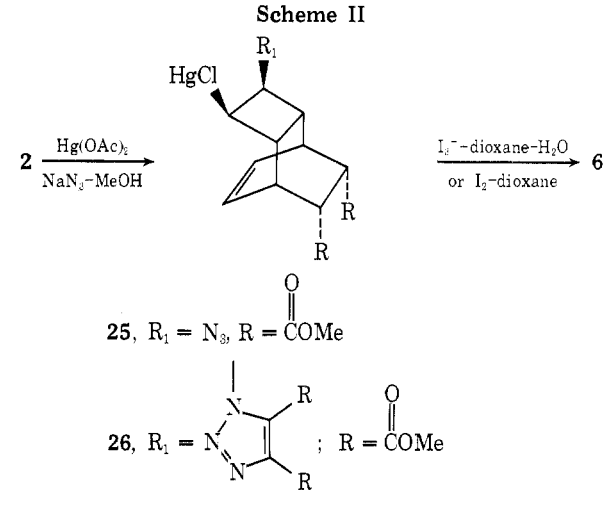
22, R_1 = OH; R_2 = HgCl; R = $COCH_3$

23, R_1 = OH; R_2 = H; R = $COCH_3$

24, R = $COCH_3$

22, mp 164–165°, which displayed in its ^1H NMR spectrum a 2 H olefinic proton signal at δ 6.71 indicating addition to one of the double bonds of **2**. Regiospecific addition to the cyclobutene ring was established via hydroxymercuration–demercuration of **2** to **23** and oxidation with CrO_3–pyridine reagent to the known[29] cyclobutanone **24**. The syn stereochemistry of the oxymercuration products **21** and **22** was demonstrated on the basis of ^1H NMR data[21,22] and chemical correlation with the IN_3 adduct **8** as shown in Scheme II. Reaction of **2** with $Hg(OAc)_2$ in methanol in the pres-

Scheme II



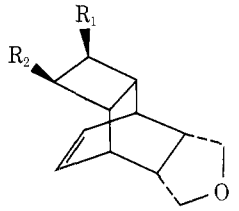
25, R_1 = N_3, R = COMe

26, R_1 = ; R = COMe

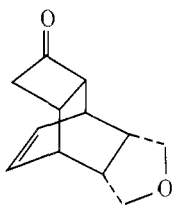
ence of azide ion furnished the azido mercurial **25**, mp 155–157°. The azido mercurial **25** as well as its dipolar addition product **26** with dimethyl acetylenedicarboxylate showed clean triplet signals for the C_7–C_8 olefinic protons. Iodination of **25** with I_2 or triiodide ion in dioxane gave a crystalline product identical in all respects with **8**. The iodination of organomercurials with triiodide ion in polar medium has been shown[30] to proceed with retention of configuration.

Methoxymercuration of ether **4** and dimethyl compound

5 proceeded rapidly and smoothly to furnish the syn methoxymercurials 27 and 28 which showed olefinic trip-



27, R_1 = OMe; R_2 = HgCl
29, R_2 = HgCl; R_1 = OH
31, R_2 = H; R_1 = OH



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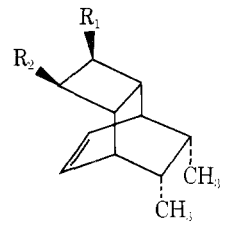
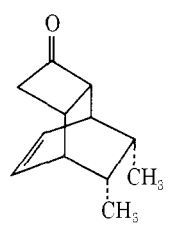


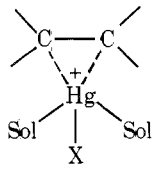
28, R_2 = HgCl; R_1 = OMe
30, R_2 = HgCl; R_1 = OH
32, R_2 = H; R_1 = OH



34

lets at δ 6.56 and 6.53, respectively. The selective addition to the cyclobutene double bond in each case was established via a reaction sequence involving hydroxymercuration to **29** and **30**, demercuration with $NaBH_4$ to **31** and **32**, and chromium trioxide–pyridine oxidation to cyclobutanones **33** and **34**, respectively. The rate of methoxy- and hydroxymercuration of the dienes greatly increased (see Experimental Section) in going from **2** to **4** and **5**, indicating a strong transannular depression in the reactivity of the cyclobutene ring as a result of variation in substituents (electron-withdrawing ester to electron-donating methyl group) at C_9 and C_{10}. Similar observation was also made in the case of IN_3 addition (see Experimental Section).

The oxymercuration of simple olefins is known to be a stereospecific anti addition.[31] On the other hand, addition of mercuric salts to strained olefins like norbornene[26,32] and bicyclo[2.1.1]hexene[33] has been shown to be a stereospecific syn addition. Several mechanistic schemes based on molecular addition, twist strain theory, torsional effects, formation of equilibrating classical ions, and nonclassical participation have been proffered to explain the formation of syn exo products, particularly in case of norbornene.[26] Among these, the last three explanations have been eliminated on the grounds that the factors controlling the stereochemistry of addition in strained olefins are not related to those governing the exo:endo rate ratios in norbornyl solvolysis.[33] Recently, Bach and Richter[34] have studied in detail the oxymercuration of bicyclo[2.2.2]oct-2-ene and explain the formation of both syn and anti addition products via a common solvated mercurinium ion intermediate **35**. It has been suggested by them that syn oxymercurials may arise via the attack of displaced ligand (X^-) on **33** before the solvent separation and the anti oxymercurials result via usual back-side displacement. In the present case, oxymercuration of dienes **2**, **4**, and **5** with $Hg(OAc)_2$ in methanolic and aqueous medium proceeds without the formation of any detectable amounts of acetoxymercuration product and thus rules out a molecular mechanism involving the collapse of the acetate ligand on mercury in the intermediate **36** to furnish the syn products. The exclusive formation of syn products in oxymercuration of **2**, **4**, and **5**, and the consistent absence of products arising out of either carbonium ion rearrangement or transannular participation is best rationalized in terms of the twist strain theory.[26] The syn transition state **37** is favored over the strained anticoplanar transition state **38**. It is conceivable that the bond



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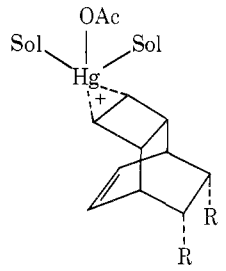

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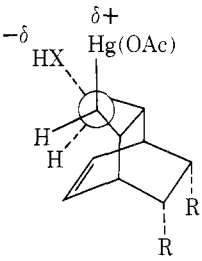

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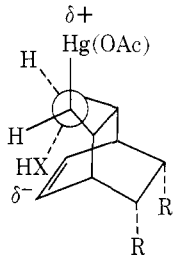

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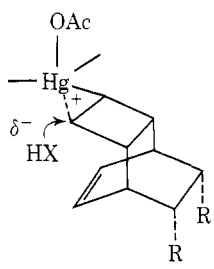
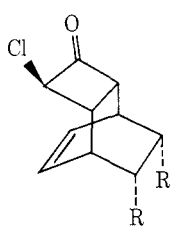
opposition inherent in the transition state for syn addition can be minimized via the conversion of **37** to an unsymmetrical ion **39**. This can be expected in view of the relatively long carbon–mercury bond distance in the π complex of ~2.3 Å.[35]

The oxymercuration of dienes **2**, **4**, and **5** represents the first example of syn addition to a cyclobutene. The cyclobutene itself has been shown to furnish exclusively anti products[36] on oxymercuration. It is quite surprising that no transannular participation is observed during oxymercuration of our system in marked contrast to the behavior of 1,5-cyclooctadiene,[4] Dewar benzene,[37] norbornadiene,[3] and 9,10-benzotricyclo[4.2.2.$2^{2,5}$]dodeca-3,7,9-triene.[10] Further, the contrasting behavior of dienes **2**, **4**, and **5** toward iodine azide, halogens,[17] iodine nitrate,[17] etc. (rearrangement) on one hand and of mercuric acetate, nitrosyl chloride, benzenesulfinyl chloride,[17] etc. (no rearrangement) on the other is in agreement with Traylor's suggestion[26] that rearrangements during such additions to strained systems are governed by the nature of the electrophilic addend and its ability to stabilize the neighboring positive charge.

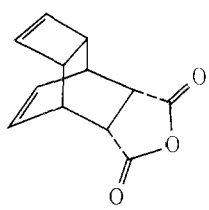
Miscellaneous Additions. The addition of nitrosyl chloride generated in situ with diester **2** led to the formation of unrearranged chloro ketone **40** formed through the acid hydrolysis of the oxime and no 1:1 adduct was encountered. Hydroboration of **2** in acetic acid[38] proceeded smoothly to give the alcohol **23** identical with the oxymercuration–demercuration product of **2**. Finally, the addition of chlorosulfonyl isocyanate (CSI) to **2** was investigated but to our surprise[39] only the anhydride **41** was formed in this reaction in high yield.



39



40, R = $COOCH_3$



41

Experimental Section[40,41]

9,10-Dicarbomethoxytricyclo[4.2.2.0^{2,5}]deca-3,7-diene (2). This compound was prepared[13] by the reaction of COT–maleic anhydride adduct with methanol in the presence of catalytic amounts of concentrated H_2SO_4 as described in the literature. Distillation (130°, 12 mm) and crystallization from petroleum ether gave colorless crystals: mp 48°; ir (KBr) 1745 cm^{-1} (ester); ^{1}H NMR (CCl_4) δ 5.75–5.95 (olefinic, 4 H, m), 3.51 (CH_3OC=O, 6 H, s) and 2.65–2.95 (CH ring, 6 H, m).

Tricyclic Ether[14] 4. The above diester (5 g) in dry tetrahydrofuran (THF, 50 ml) was reduced with $LiAlH_4$ (2.3 g) for 8 hr at reflux temperature. Decomposition with moist ether and dilute H_2SO_4 and usual work-up furnished a diol **40** as glistening, stout needles: mp 115° (lit.[14] 117°); ir (KBr) 3300, 1040 cm^{-1} (hydroxyl); ^{1}H NMR ($CDCl_3$) δ 5.76 (olefinic, 4 H, m), 4.2 (HO–, 2 H, s), 3.56 (–CH_2OH, 4 H, m), and 2–2.8 (CH ring, 6 H, envelope). In a 250-ml round-bottom flask fitted with a Dean-Stark apparatus, diol (4.0 g) in dry benzene (50 ml) containing *p*-toluenesulfonic acid (100 mg) was placed and the mixture was refluxed for nearly 6 hr. The reaction mixture was poured into aqueous sodium bicarbonate and the benzene layer was separated. The organic phase was washed, dried, stripped of solvent, and distilled to give 3 g of **4** as a colorless, mobile liquid: bp 88–90° (3 mm); mp 38°; ir (neat) 1110 cm^{-1} (ether); ^{1}H NMR (CCl_4) δ 5.83 (olefinic, 4 H, m), 3.5 (–CH_2OCH_2–, 4 H, pair of q), and 2.17–2.73 (CH ring, 6 H, envelope).

9,10-Dimethyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene (5). The diol **40** (4.0 g) in dry pyridine (25 ml) was allowed to react with an excess of methanesulfonyl chloride (7 ml) and the reaction mixture was kept in a refrigerator for 12 hr. The reaction mixture was poured into ice water and extracted with CH_2Cl_2 (2 × 50 ml). The CH_2Cl_2 extract was washed successively with dilute HCl (3 × 50 ml), sodium bicarbonate (2 × 50 ml), and brine. Drying and removal of solvent gave 5.3 g of the dimesylate: mp 136–137°; ir (KBr) 1155, 1330 cm^{-1} (sulfonate). Anal. Calcd for $C_{14}H_{20}O_6S_2$: C, 48.25; H, 5.79. Found: C, 48.85; H, 5.68.

To a stirred slurry of $LiAlH_4$ (2.5 g) in dry THF (50 ml), a solution of the dimesylate (5 g in 25 ml of THF) was added dropwise and the mixture was refluxed for 8 hr. The reaction mixture was quenched by the careful addition of moist ether followed by 25 ml of 10% dilute H_2SO_4. The organic material was extracted with petroleum ether (3 × 25 ml), washed, and dried. Removal of solvent and distillation gave 2.1 g of a colorless oil: bp 100–102° (bath, 11 mm); ir (neat) 710, 745, 770, 788 (characteristic strong bands), 1640, 3140 cm^{-1} (olefinic); ^{1}H NMR (CCl_4) δ 5.5–6.23 (olefinic, 4 H, m), 1.5–3 (CH ring, 6 H, envelope), and 0.93 (CH_3CH, 6 H, d, J = 7 Hz).

Addition of Iodine Azide to Diester 2. The procedure described by Hassner[20] was followed for the iodine azide addition reactions. To a stirred slurry of sodium azide (0.3 g, 4.8 mmol) in 10 ml of dry acetonitrile in a 50-ml round-bottom flask cooled to −5° was added freshly prepared iodine monochloride (0.8 g, 6 mmol) over a period of 5 min. The mixture was allowed to stir for a few minutes and the diester **2** (1 g, 4 mmol) in acetonitrile (5 ml) was added dropwise. After the reaction mixture was allowed to attain room temperature, the mixture was stirred for 2 hr. The brownish slurry was poured into water (50 ml) and extracted with ether (2 × 25 ml). The ethereal extract was washed with 5% sodium thiosulfate followed by brine, dried, and stripped of solvent to yield a white solid residue (1.45 g, 90%). Recrystallization from petroleum ether gave 4-azido-3-iodo-9,10-dicarbomethoxytricyclo-[4.2.2.0^{2,5}]dec-7-ene (**6**) as colorless microcrystals: mp 137°; ir (KBr) 2120 (azide), 1740 and 1210 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 6.5 (olefinic, 2 H, t), 4.33 (HCN_3, 1 H, q), 3.61 (CH_3OC=O, 6 H, s), 3.12 (HCI, 1 H, q), 2.65–3.55 (CH ring, 7 H, envelope). Anal. Calcd for $C_{14}H_{16}O_4IN_3$: C, 40.28; H, 3.83; N, 10.07. Found: C, 40.34; H, 3.91; N, 10.14. A mixture of **6** (0.1 g, 0.24 mmol) and dimethyl acetylenedicarboxylate (0.5 g, 3.35 mmol) in benzene (15 ml) was refluxed for 4 hr. Removal of solvent and crystallization from benzene gave the crystalline adduct **7**: mp 192–194°; ir (KBr) 1740 and 1210 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 6.67 (olefinic, 2 H, t), 4.73 (triazolyl methine and HCI, 2 H, m), 4.01 (CH_3OC=O of triazole, 6 H, d), 3.63 (CH_3OC=O, 6 H, s), and 2.83–3.27 (CH ring, 6 H, envelope). Anal. Calcd for $C_{20}H_{22}O_8N_3I$: C, 42.94; H, 3.97; N, 7.51. Found: C, 43.20; H, 4.15; N, 7.46.

Addition of Iodine Azide to 9,10-Dimethyltricyclo[4.2.-2.0^{2,5}]deca-3,7-diene (5). A. In Acetonitrile Solvent. Iodine azide prepared in situ by the action of iodine monochloride (0.1 g, 0.8 mmol) on sodium azide (50 mg, 0.8 mmol) in acetonitrile (5 ml) was treated with 0.1 g (0.6 mmol) of **5** at −5° for 1 hr. Usual work-up gave 0.18 g of a viscous residue. Crystallization from benzene–petroleum ether (1:4) gave 110 mg (46%) of pale needle shaped crystals of tetrazole derivative **8**: mp 147–148°; ir (KBr) 1500, 1450, 1440 cm^{-1} (characteristic –N=N– and –C=N– absorption); ^{1}H NMR ($CDCl_3$) δ 4.55 (tetrazolyl methine, 1 H, broad s), 3.93 (HCI, 1 H, s), 2.6 (tetrazolyl methyl, 3 H, s), 1.05 (CH_3CH, 6 H, m). Anal. Calcd for $C_{14}H_{19}N_4I$: C, 45.41; H, 5.18; N, 15.13. Found: C, 45.29; H, 5.3; N, 15.03. The mother liquor from the crystallization of tetrazole **8** was concentrated and its ir spectrum and TLC showed the presence of azido iodide **9**.

B. In Methylene Chloride Solvent. Iodine azide prepared in situ by the action of iodine monochloride (0.1 g, 0.8 mmol) on sodium azide (50 mg, 0.8 mmol) in methylene chloride (5 ml) at −5° was treated with dimethyl compound **5** (0.1 g, 0.6 mmol) for 2 hr. Usual work-up gave 180 mg (88%) of azido iodide **9** as a colorless oil: ir (neat) 2120 cm^{-1} (azide); ^{1}H NMR (CCl_4) δ 4.16 (HCN_3, 1 H, broad s with fine structure), 3.75 (HCI, 1 H, s), 1.16 (CH_3CH, 6 H, m), 1.9–3.6 (CH ring, 8 H, envelope).

Addition of Iodine Azide to Ether 4. A. In Acetonitrile Solvent. Iodine azide prepared in situ by the action of iodine monochloride (0.2 g, 1.6 mmol) on sodium azide (0.1 g, 1.6 mmol) in acetonitrile (5 ml) was treated with ether **4** (0.2 g, 1.1 mmol) at −20° for 1 hr. Usual work-up as described earlier furnished 0.35 g of a pale yellow liquid product. This was adsorbed on a silica gel (20 g) column and chromatographed. Elution with benzene gave 70 mg (18%) of azido iodide **11**: ir (neat) 2120 cm^{-1} (azide); ^{1}H NMR (CCl_4) δ 4.9 (HCN_3, 1 H, d, J = 2 Hz), 3.4–4.1 (HCI and –CH_2OCH_2–, 5 H, m), 1.9–3.5 (CH ring, 8 H, envelope).

Further elution of the column with benzene–ethyl acetate (1:1) furnished 250 mg (56%) of tetrazole **10**. Recrystallization from carbon tetrachloride furnished pale crystalline flakes: mp 152–153°; ir (neat) 1515, 1475, and 1400 cm^{-1} (characteristic –N=N– and –C=N– absorption); ^{1}H NMR (CCl_4) δ 4.78 (tetrazolyl methine, 1 H, broad s), 4.0 (HCI, 1 H, s), 2.5 (tetrazolyl methyl, 3 H, s), 3.4–4 (–CH_2OCH_2–, 4 H, m). Anal. Calcd for $C_{14}H_{17}N_4OI$: C, 43.76; H, 4.47; N, 14.6. Found: C, 44.09; H, 4.39; N, 14.38.

B. In Methylene Chloride Solvent. Iodine azide prepared in situ by the action of iodine monochloride (0.2 g, 1.6 mmol) on sodium azide (0.1 g, 1.6 mmol) in CH_2Cl_2 was treated at −5° with **4** (0.2 g, 1.1 mmol). Usual work-up as described earlier gave **11** as a pale oily residue (350 mg, 94%), almost single component by TLC. This was identical in all respects with the minor azido iodide formed in acetonitrile medium.

Methoxymercuration of Diester 2. To a solution of diester (0.5 g, 2 mmol) in absolute methanol (15 ml), mercuric acetate (0.7 g, 2.2 mmol) was added and the reaction mixture was stirred for 20 hr at room temperature (20°). After the reaction was complete (TLC), methanol was distilled off on a rotary evaporator and the residue was treated with a saturated sodium chloride solution (20 ml). The reaction mixture was further diluted with water (30 ml) and extracted with methylene chloride (2 × 25 ml), washed, and dried. Removal of solvent gave 1.0 g (96%) of solid methoxymercurial **21**. Recrystallization from benzene–CH_2Cl_2 furnished white crystalline flakes: mp 193–195°; ir (KBr) 1740, 1210 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 6.7 (olefinic, 2 H, t), 3.6 (CH_3OC=O, 6 H, s), 3.23 (CH_3OC, 3 H, s), 2.6–3.2 (CH ring, 8 H, envelope). Anal. Calcd for $C_{15}H_{19}O_5HgCl$: C, 34.95; H, 3.72. Found: C, 35.03; H, 3.86.

Hydroxymercuration of Diester 2. In a small flask, fitted with a magnetic stirrer, was placed 0.7 g (2.2 mmol) of mercuric acetate. A 1:1 mixture of water–THF (15 ml) was added followed by the diester **2** (0.5 g, 2 mmol) in THF (5 ml). The reaction mixture was stirred at room temperature (20°) for 7 hr until the yellow color was completely discharged. Treatment with saturated brine solution and work-up as described above gave 1.1 g of hydroxymercurial **22** in quantitative yield: mp 164–165°; ir (KBr) 3400 (hydroxyl), 1740 and 1210 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 6.71 (olefinic, 2 H, t), 4.02 (HCOH, 1 H, m), 3.61 (CH_3OC=O, 6 H, s), 2.6–3.45 (CH ring, 8 H, envelope). Anal. Calcd for $C_{14}H_{17}O_5HgCl$: C, 33.55; H, 3.41. Found: C, 33.52; H, 3.30.

Hydroxymercuration–Demercuration[42] of Diester 2. Diester (0.5 g, 2 mmol) in 1:1 water–THF (15 ml) was treated with mercuric acetate (0.7 g, 2.2 mmol) as described above. After 7 hr at 20°, a solution of 3 N sodium hydroxide (5 ml) followed by a mixture of sodium borohydride (50 mg) in 5 ml of 3 N NaOH was added. The reduction of the oxymercurial was complete in a few minutes and the mercury droplet settled on the base of the reaction flask. Sodium chloride was added to saturate the aqueous layer and extraction was carried out with ether (2 × 30 ml). Drying and removal of solvent gave 0.5 g (98%) of **23** as a colorless oil: bp 180–90° (bath, 0.5 mm); ir (neat) 3400 (hydroxyl), 1740 and 1200 cm^{-1} (ester); ^{1}H

NMR (CCl_4) δ 6.3 (olefinic, 2 H, t), 3.68 (HCOH, 1 H, m), 3.51 (CH_3OC=O, 6 H, s), 1.7–3.2 (CH ring, 9 H, envelope). Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.14; H, 6.81. Found: C, 62.99; H, 6.89.

Chromium Trioxide–Pyridine Oxidation[43] of 9,10-Dicarbomethoxytricyclo[4.2.2.0^{2,5}]dec-7-en-3-ol (23). A solution of alcohol **23** (0.5 g, 1.9 mmol) in pyridine (5 ml) was added dropwise to an efficiently stirred slurry of CrO_3–pyridine complex [prepared from CrO_3 (1 g) in pyridine (5 ml)] cooled in an ice bath. After stirring for 3 hr the reaction mixture was poured into water and extracted with ether (2 × 20 ml). Washing, drying, and removal of solvent gave 0.4 g (80%) of dicarbomethoxytricyclo[4.2.2.0^{2,5}]dec-7-en-3-one (**24**). Recrystallization from petroleum ether–benzene (4:1) gave white microneedles: mp 94° (lit.[29] 93–95°); ir (KBr) 1775 (cyclobutanone), 1745 and 1200 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 6.63 (olefinic, 2 H, t), 3.63 (CH_3OC=O, 6 H, s), 2.6–3.43 (CH ring, 7 H, envelope).

Mercuration of Diester 2 in the Presence of Azide Ion. A mixture of diester **2** (0.5 g, 2 mmol), mercuric acetate (0.7 g, 2.2 mmol), and sodium azide (0.15 g, 2.4 mmol) in methanol (15 ml) was stirred at room temperature (20°) for 15 hr. The solvent was removed under reduced pressure and the residue was treated with saturated brine solution. Extraction with CH_2Cl_2 (2 × 25 ml), removal of solvent, and crystallization from benzene–petroleum ether (4:1) gave 1 g (95%) of azido mercurial **25:** mp 155–157°; ir (KBr) 2120 (azide), 1740, 1210 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 6.48 (olefinic, 2 H, t), 3.82 (HCN_3, 1 H, m), 3.58 (CH_3OC=O, 6 H, s), 2.7–3.2 (CH ring, 7 H, envelope). Anal. Calcd for $C_{14}H_{16}O_4N_3HgCl$: C, 31.94; H, 3.07; N, 7.99. Found: C, 32.08; H, 3.23; N, 8.01.

A mixture of azido mercurial **25** (0.1 g, 0.2 mmol) and dimethyl acetylenedicarboxylate (0.5 g, 3.5 mmol) in dry benzene (10 ml) was refluxed for 6 hr. Removal of solvent and crystallization from benzene gave 0.11 g of the crystalline adduct **26:** mp 210–212°; ir (KBr) 1740 and 1200 cm^{-1} (ester). Anal. Calcd for $C_{20}H_{22}O_8N_3HgCl$: C, 35.93; H, 3.32; N, 6.29. Found: C, 36.18; H, 3.04; N, 6.50.

Iodination of Azido Mercurial 26 with I_2 and Triiodide Ion. To a solution of azido mercurial **26** (0.45 g, 0.9 mmol) in dioxane (10 ml) was added 300 mg of iodine crystals and the mixture was left aside at room temperature (20°) for 4 hr. The reaction mixture was poured into water, extracted with CH_2Cl_2 (2 × 25 ml), and washed successively with 10% sodium thiosulfate and brine. Removal of solvent and crystallization from petroleum ether gave 0.35 g (98%) of azido iodide **6,** mp 137°. This compound was identical (mixture melting point, ir) with the azido iodide obtained from IN_3 addition to **2**. Repetition of the above experiment in aqueous dioxane and in the presence of potassium iodide lead to exactly identical results.

Methoxymercuration of Ether 4. A mixture of ether **4** (0.1 g, 0.6 mmol) and mercuric acetate (225 mg, 0.7 mmol) in absolute methanol (5 ml) was stirred at room temperature for 1 hr. Usual work-up as described for **2** and crystallization from benzene gave 0.21 g (82%) of the methoxymercurial **27:** mp 179–180°; ir (KBr) 920, 1100 cm^{-1} (ether); ^{1}H NMR ($CDCl_3$) δ 6.56 (olefinic, 2 H, broad t), 3.53 (HCOMe, 1 H, m), 3.23 (CH_3OC, 3 H, s), 3.47 and 3.86 ($-CH_2OCH_2$, 4 H, a pair of t, J = 8 Hz), 2.1–3.0 (CH ring, 8 H, envelope). Anal. Calcd for $C_{13}H_{17}O_2HgCl$: C, 35.38; H, 3.89. Found: C, 35.81; H, 3.56.

Hydroxymercuration of Ether 4. A mixture of ether **4** (0.45 g, 1.5 mmol) and mercuric acetate (0.2 g, 1.1 mmol) in 1:1 water–THF (10 ml) was stirred at room temperature for 3 hr. Work-up as described earlier gave 0.4 g (81%) of hydroxymercurial **29:** mp 182–183°; ir (KBr) 3650 (hydroxyl), 1050 and 915 cm^{-1} (ether); ^{1}H NMR ($CDCl_3$) δ 6.58 (olefinic, 2 H, diffused t), 4.52 (HCOH, 1 H, q), 2.1 (–OH, 1 H, s), 3.2–4 ($-CH_2OCH_2-$ and HCHgCl, 5 H, m), 2.3–1 (CH ring, 6 H, envelope). Anal. Calcd for $C_{12}H_{15}O_2HgCl$: C, 33.73; H, 3.55. Found: C, 34.06; H, 3.73.

Hydroxymercuration–Demercuration[42] of Ether 4. A mixture of ether **4** (0.4 g, 2.2 mmol) and mercuric acetate (0.9 g, 2.8 mmol) in 1:1 water–THF (15 ml) was stirred at room temperature for 3 hr. Sodium hydroxide (5 ml, 3 N) and sodium borohydride (125 mg) in aqueous NaOH (5 ml, 3 N) were added to the reaction mixture and stirring continued for 1 hr. Usual work-up as described above gave 0.37 g (84%) of the alcohol **31:** bp 150–160° (bath, 2 mm); mp 89–90°; ir (KBr) 3550 (hydroxyl), 910 cm^{-1} (ether). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.95; H, 8.40. Found: C, 74.69; H, 8.77.

Chromium Trioxide–Pyridine Oxidation[43] of 31. The alcohol **31** (0.25 g, 1.3 mmol) in pyridine (5 ml) was added to a stirred slurry of CrO_3–pyridine complex (prepared from 0.5 g of CrO_3 in 5 ml of pyridine) in an ice bath. The reaction was terminated after 1 hr by pouring into water and organic material was extracted with CH_2Cl_2 (2 × 25 ml). Washing, drying, and removal of solvent gave 0.2 g (80%) of ketone **33:** bp 130–135° (bath, 2 mm); mp 62°; ir (KBr) 1780 (cyclobutanone), 1020 cm^{-1} (ether). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.75; H, 7.43; Found: C, 75.90; H. 7.61.

Methoxymercuration of 9,10-Dimethyltricyclo[4.2.2.0^{2,5}]-deca-3,7-diene (5). A mixture of dimethyl compound **5** (0.1 g, 0.6 mmol) and mercuric acetate (225 mg, 0.7 mmol) in absolute methanol (5 ml) was stirred at room temperature for 1 hr. Usual work-up as already described and crystallization from benzene gave 0.22 g (82%) of the methoxymercurial **28:** mp 126–127°; ir (KBr) 1060, 1100 cm^{-1} (ether); ^{1}H NMR ($CDCl_3$) δ 6.53 (olefinic, 2 H, t), 3.5 (HCOMe, 1 H, m), 3.2 (CH_3OC, 3 H, s), 0.83 (CH_3CH, 6 H, m), 1.7–2.9 (CH ring, 7 H, envelope). Anal. Calcd for $C_{13}H_{19}OHgCl$: C, 36.52; H, 4.49. Found: C, 36.77; H, 4.38.

Hydroxymercuration of 5. A mixture of **5** (0.16 g, 1 mol) and mercuric acetate (0.35 g, 1.1 mmol) in 1:1 water–THF (10 ml) was stirred at room temperature for 3 hr. Usual work-up furnished 0.35 g (85%) of hydroxymercurial **30:** mp 137–138°; ir (KBr) 3450 and 1020 cm^{-1} (hydroxyl); ^{1}H NMR ($CDCl_3$) δ 6.55 (olefinic, 2 H, m), 4.5 (HCOH, 1 H, m), 3.9 (HCHgCl, 1 H, m), 2.03 (–OH, 1 H, s), 0.78 (CH_3CH, 6 H, J = 6.5 Hz), 1.6–3 (CH ring, 6 H, envelope). Anal. Calcd for $C_{12}H_{17}OHgCl$: C, 34.87; H, 4.15. Found: C, 35.12; H, 4.23.

Hydroxymercuration–Demercuration[42] of 5. The hydrocarbon **5** (0.35 g, 2.2 mmol) and mercuric acetate (0.8 g, 2.5 mmol) in 1:1 water–THF were stirred for 3 hr at room temperature. A 3 N solution of sodium hydroxide (5 ml) followed by sodium borohydride (75 mg) in 3 N aqueous NaOH (5 ml) was added and stirring continued for a further period of 1 hr. Usual work-up gave 0.32 g (82%) yield of 9,10-dimethyltricyclo[4.2.2.0^{2,5}]dec-7-en-3-ol (**32**): bp 120–125° (bath, 2 mm); ir (neat) 3540 cm^{-1} (hydroxyl). Anal. Calcd for $C_{12}H_{18}O$: C, 80.83; H, 10.19. Found: C, 80.51; H, 9.96.

Chromium Trioxide–Pyridine Oxidation[43] of 9,10-Dimethyltricyclo[4.2.2.0^{2,5}]dec-7-en-3-ol (32). The alcohol **32** (0.2 g) in pyridine (5 ml) was oxidized with CrO_3–pyridine reagent as described earlier. Usual work-up gave 0.16 g (80%) of 9,10-dimethyltricyclo[4.2.2.0^{2,5}]dec-7-en-2-one (**34**): bp 100–110° (bath, 2 mm); ir (neat) 1780 cm^{-1} (cyclobutanone).

Nitrosyl Chloride Addition to Diester 2. The diester **2** (1 g, 4 mmol) was dissolved in methanol (15 ml) and cooled to −5°. Isoamyl nitrite (7 ml, 16.5 mmol) was added followed by careful addition of concentrated HCl (4 ml) with vigorous stirring. The stirring was continued for 4 hr and the reaction mixture poured into ice water. Extraction with ether (2 × 25 ml), washing, and drying furnished 1.2 g (90%) of chlorocyclobutanone **40:** mp 164–165°; ir (KBr) 1780 (cyclobutanone), 1745, 1210 cm^{-1} (ester); ^{1}H NMR ($CDCl_3$) δ 6.44 (olefinic, 2 H, t), 4.26 (HCCl, 1 H, t, J = 4 Hz), 3.7 (CH_3OC=O, 6 H, s), 2.64–3.6 (CH ring, 6 H, envelope). Anal. Calcd for $C_{14}H_{15}O_5Cl$: C, 56.28; H, 5.07. Found: C, 56.56; H, 5.40.

Hydroboration[38] of Diester 2. The diester (0.5 g, 2 mmol) in dry THF (15 ml) was cooled in an ice bath and sodium borohydride (0.2 g, 5 mmol) and acetic acid (300 mg) were added with rapid stirring. After 4 hr 20% NaOH (5 ml) and 4 ml of 30% H_2O_2 were carefully added and stirring was continued for another 1 hr. Extraction with CH_2Cl_2 (2 × 25 ml), washing, and drying gave 0.51 g (96%) of alcohol **23** identical with the oxymercuration–demercuration product of diester **2**.

Addition of Chlorosulfonyl Isocyanate to Diester 2. To a CH_2Cl_2 (5 ml) solution of diester **2** (0.3 g, 1.2 mmol) cooled in an ice bath, chlorosulfonyl isocyanate (0.3 g) in 2 ml of CH_2Cl_2 was added. The reaction mixture was stirred overnight at room temperature and CH_2Cl_2 evaporated under reduced pressure. Crystallization from acetone–benzene mixture gave 0.22 g (82%) of anhydride **41:** mp 166–167° (lit.[13] 168°); ir (KBr) 1830 and 1765 cm^{-1} (anhydride).

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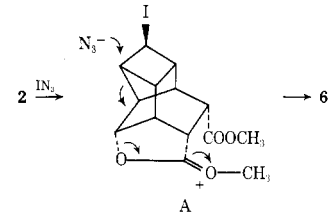
Registry No.—**2,** 35211-83-7; **4,** 5773-44-4; **5,** 5773-43-3; **6,** 55999-16-1; **7,** 56116-39-3; **8,** 56689-19-1; **9,** 56689-20-4; **10,** 56689-21-5; **11,** 56689-22-6; **21,** 52730-89-9; **22,** 52730-90-2; **23,** 52748-22-

8; **24,** 56689-23-7; **25,** 56689-24-8; **26,** 56689-25-9; **27,** 56689-26-0; **28,** 56689-27-1; **29,** 56689-28-2; **30,** 56689-29-3; **31,** 10203-63-1; **32,** 10203-66-4; **33,** 56689-30-6; **34,** 56689-31-7; **40,** 56689-32-8; 9,10-bis(hydroxymethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7-diene, 56711-59-2; 9,10-bis(hydroxymethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7-diene dimesylate, 55054-05-2; iodine azide, 14696-82-3; dimethyl acetylenedicarboxylate, 762-42-5; mercuric acetate, 1600-27-7; nitrosyl chloride, 2696-92-6.

References and Notes

(1) Junior Research Fellow of CSIR, 1973–present.
(2) S. Winstein, M. Shatavsky, C. J. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77,** 4183 (1955); W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78,** 5653 (1956); J. A. Berson in "Molecular Rearrangements", Part I, P. de Mayo, Ed., Interscience, New York, N.Y., 1963, p 111.
(3) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956); K. C. Pandey and S. Winstein, *Tetrahedron Lett.*, 3393 (1964); E. Vedejs and M. F. Solomon, *J. Org. Chem.*, **37,** 2075 (1972).
(4) H. Franz, W. Hoebold, R. Hoehn, G. Mueller-Hagen, R. Mueller, W. Pritzkow, and H. Schmidt, *J. Prakt. Chem.*, **312,** 622 (1970); T. S. Cantrell and B. L. Strasser, *J. Org. Chem.*, **36,** 670 (1971); J. N. Labows and D. Swern, *ibid.*, **37,** 3004 (1972); C. Ganter, K. Wicker, W. Zwahalen, and K. Sehaffner-Sabba, *Helv. Chim. Acta*, **53,** 1618 (1970).
(5) G. Nagendrappa and D. Devaprabhakara, *Tetrahedron Lett.*, 4687 (1970).
(6) J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32,** 3285 (1967); J. G. Traynham and H. H. Hsieh, *ibid.*, **38,** 868 (1973).
(7) L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, **82,** 5363 (1960); P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 590 (1960); P. Bruck, D. Thompson, and S. Winstein, *ibid.*, 405 (1960).
(8) S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Am. Chem. Soc.*, **82,** 5377 (1960); C. W. Bird, R. C. Cookson, and E. Crundwell, *J. Chem. Soc.*, 4809 (1961).
(9) H. Hogeveen, P. W. Kwant, E. P. Schudde, and P. A. Wade, *J. Am. Chem. Soc.*, **96,** 7578 (1974), and references cited therein.
(10) N. C. Yang and J. Libman, *J. Am. Chem. Soc.*, **94,** 9228 (1972).
(11) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Am. Chem. Soc.*, **86,** 3162 (1964).
(12) E. Vedejs, R. A. Gable, and P. D. Weeks, *J. Am. Chem. Soc.*, **84,** 5842 (1972); G. R. Underwood and B. Ramamoorty, *Tetrahedron Lett.*, 4125 (1970).
(13) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560,** 1 (1948).
(14) M. Avram, C. D. Nenitzescu, and E. Marcia, *Chem. Ber.*, **90,** 1857 (1957); M. Avram, G. Mateescu, and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **636,** 174 (1960).
(15) R. C. Cookson, J. Hudec, and J. Marsden, *Chem. Ind. (London)*, 21 (1961).
(16) D. G. Farnum and J. P. Snyder, *Tetrahedron Lett.*, 3861 (1965).
(17) P. K. Dutta, M.S. Thesis, Indian Institute of Technology, Kanpur, 1974; G. Mehta and P. N. Pandey, manuscript under preparation.
(18) T. Sasaki, K. Kanematsu, and A. Kondo, *J. Org. Chem.*, **39,** 2246 (1974).
(19) The addition of iodine azide to **2** has been reported in a preliminary communication: G. Mehta, P. K. Dutta, and P. N. Pandey, *Tetrahedron Lett.*, 407 (1975).
(20) F. W. Fowler, A. Hassner, and L. A. Levy, *J. Am. Chem. Soc.*, **89,** 2077 (1967).
(21) J. P. Snyder and D. G. Farnum, *J. Org. Chem.*, **31,** 1699 (1966).
(22) We have consistently and fruitfully used this method for configurational assignment of substituents on the cyclobutane ring of this system. In many cases, we have also prepared both the syn and anti substituted cyclobutanes derived from **1** and these results fully compliment the findings of Snyder and Franum.[21]
(23) Solvent participation and tetrazole formation during IN_3 addition to olefins has been observed recently and the reaction quite aptly termed a Hassner–Ritter reaction: D. Ranganathan, S. Ranganathan, and A. K. Mehrotra, *Tetrahedron Lett.*, 2265 (1973); see also D. Ranganathan, S. Ranganathan, and A. K. Mehrotra, *Synthesis*, 356 (1973).
(24) Recently, transannular Hassner–Ritter reaction during the addition of IN_3 to medium ring C_9 and C_{10} dienes has been observed: S. N. Moorty, D. Devaabhakara, and K. G. Das, *Tetrahedron Lett.*, 257 (1975).
(25) A. Hassner, *Acc. Chem. Res.*, **4,** 9 (1971).
(26) T. G. Traylor, *Acc. Chem. Res.*, **2,** 152 (1969). A referee has made the interesting suggestion that the syn addition of IN_3 to **2** may arise via an intermediate A formed through the carbomethoxy participation. Azide ion assisted opening of A (see arrows) might lead to **6**. However, we



A

find that the iodolactone (**3**, X = I) related to the intermediate A is recovered unchanged when subjected to either the reaction conditions of IN_3 addition (ICl and sodium azide in acetonitrile at −5°) or more stringent conditions (sodium azide in aqueous acetonitrile reflux) for prolonged period of time. Furthermore, attempts to fragment the lactones **3** under a variety of other conditions also proved unsuccessful.[17]
(27) G. I. Fray, G. R. Geen, D. I. Davies, L. T. Parfitt, and M. J. Parrott, *J. Chem. Soc., Perkin Trans. 1*, 729 (1974).
(28) After the completion of the present study oxymercuration of **2** has been reported: T. Sasaki, K. Kanematsu, A. Kanodo, and Y. Nishitani, *J. Org. Chem.*, **39,** 3569 (1974).
(29) A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *J. Am. Chem. Soc.*, **76,** 1096 (1954).
(30) S. Winstein and T. G. Traylor, *J. Am. Chem. Soc.*, **78,** 2597 (1956).
(31) W. Kitching, *Organomet. Rev.*, **3,** 611 (1968); P.B.D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems", American Elsevier, New York, N.Y., 1966.
(32) T. G. Traylor and A. W. Baker, *Tetrahedron Lett.*, 14 (1959).
(33) F. T. Bond, *J. Am. Chem. Soc.*, **90,** 5321 (1968).
(34) R. D. Bach and R. F. Richter, *J. Am. Chem. Soc.*, **94,** 4747 (1972).
(35) R. D. Bach and H. F. Henneike, *J. Am. Chem. Soc.*, **92,** 5589 (1970).
(36) Unpublished results quoted in ref 26; R. D. Bach and R. F. Richter, *J. Org. Chem.*, **38,** 3442 (1973).
(37) G. R. Krow and J. Reilly, *Tetrahedron Lett.*, 3133 (1972); L. A. Paquette, S. A. Lang, Jr., M. R. Short, B. Parkinson, and J. Clardy, *ibid.*, 3141 (1972).
(38) V. Hach, *Synthesis*, 340 (1974).
(39) Cyclobutenes are known to react with CSI with great facility: D. H. Aue, H. Twuhashi, and D. F. Shellham, *Tetrahedron Lett.*, 3719 (1973); L. A. Paquette and G. R. Crow, *ibid.*, 2139 (1968).
(40) Melting points and boiling points are uncorrected. Melting points were taken in capillaries on a Fisher-Jones melting point apparatus. Boiling points refer to bath temperature in those cases where short-path bulb-to-bulb distillations were carried out. The petroleum ether corresponds to the fraction of bp 60–80°. All solvent extracts were washed with brine and dried over anhydrous sodium sulfate. Infrared spectra were recorded on a Perkin-Elmer Model 137B spectrophotometer as neat liquids or solids as KBr disks. ^1H NMR spectra were obtained on approximately 10–15% solutions in CCl_4 or $CDCl_3$ on a Varian A-60 spectrometer. The chemical shifts are reported in parts per million downfield from internal tetramethylsilane at 0.00 as internal standard. The abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively. Microanalysis were performed by Mr. A. H. Siddiqui in the microanalytical laboratory of our department.
(41) The azido iodides **9** and **11** were extremely labile and satisfactory analytical values for them could not be obtained.
(42) H. C. Brown and P. Geoghegan Jr., *J. Am. Chem. Soc.*, **89,** 1522 (1967).
(43) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75,** 422 (1953).