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# ON THE STEREOCHEMISTRY OF THE REACTION OF 7-SUBSTITUTED NORBORNADIENES WITH IRON CARBONYLS. I. REACTION OF $Fe(CO)_5$ WITH 7-t-BUTOXYNORBORNADIENE

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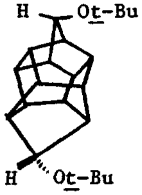
Both unsubstituted and 7-alkylated norbornenes and norbornadienes react with iron carbonyls to afford, along with other products, dimeric ketones (cyclopentanones) whose carbon skeletons possess the exo-trans-exo (XTX) configuration.[1-5] The only non-XTX dimeric ketone which has thus far been reported to result from a reaction of this type is that which is formed via the reaction of $Fe(CO)_5$ with 7,7-dimethoxy-2,3-benzonorbornadiene; this species was found to possess the exo-trans-endo (XTN) configuration.[6] We now describe new experimental evidence using 7-t-butoxynorbornadiene (1) as substrate which supports our earlier contention[6] that this remarkable switch in stereospecificity might be accounted for in terms of the direct participation of a 7-Lewis base substituent in the $Fe(CO)_5$ - promoted olefin-CO coupling reaction.

Our rationale for choosing 1 as substrate is based on the fact that 1 possesses two potentially reactive double bonds, the one syn to the 7-Ot-Bu group being the more sterically hindered. In the event that unshared electron pairs on the oxygen atom of the 7-Ot-Bu group participate directly in the reaction, it is possible that the more sterically hindered double bond may prove to be the more reactive of the two toward $Fe(CO)_5$. Thus, 1 offers a clear choice between the potentially stabilizing electronic effect of the syn-7-Ot-Bu vis-à-vis the destabilizing steric effect of this bulky substituent (which would favor reaction of $Fe(CO)_5$ with the double bond anti to the 7-Ot-Bu substituent).

The reaction of 1 with $Fe(CO)_5$ in refluxing di-n-butyl ether under nitrogen affords five products which could be separated from the crude reaction mixture via careful elution chromatography on TLC grade silica gel (1:9 ethyl acetate - hexane eluent).[7] These products (in order of increasing residence time on the chromatography column were as follows: a cage dimer, mp 131-132° (2, 14%), a dimeric ketone, mp 95-96° (3, 24%), a linear trimer diketone, mp 226-227° (4, 18%), a third ketone (5, IR: 1722 $cm^{-1}$) which has not yet been identified (12%, vide infra), and polymeric material (isolated as a viscous oil). The structures of products 2,[8] 3,[9] and 4[10] have been established via single crystal X-ray structural analysis.



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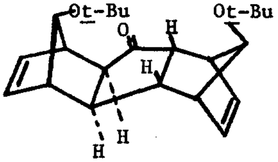
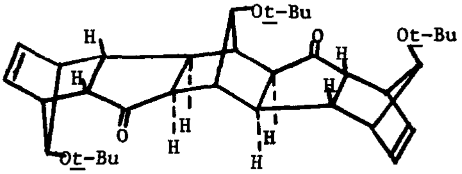


3 (SXTNS)



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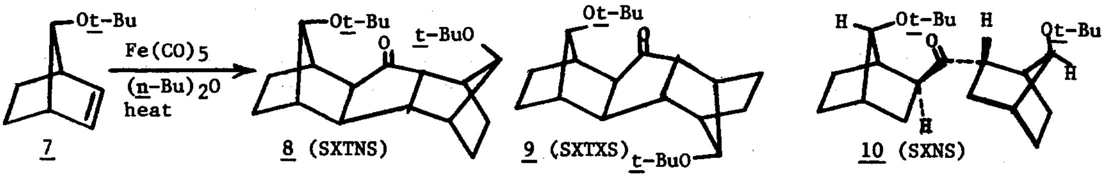
Compound 5 proved to be an unusually difficult compound to characterize. It was isolated from the reaction mixture as a viscous oil; all attempts to induce crystallization of this oil failed. The heaviest ion fragment in the mass spectrum (10 ev) of 5 occurred at m/e 492. However, when the oil was reduced with LiAlH$_4$, an alcohol was produced, the mass spectrum (70 ev) of which displayed its heaviest ion fragment at m/e 522. Further efforts aimed toward characterizing 5 are currently underway in our laboratory.

We find that dimeric ketone 3 possesses the XTN configuration; additionally, both Ot-Bu groups are syn (S) to the cyclopentanone ring in 3. Both of these observations are of potential mechanistic significance. To further delineate any role which the 7-substituent might play in determining the stereochemistry of the dimeric ketone, we examined the thermal reaction of Fe(CO)$_5$ with anti-7-t-butoxynorbornene (6)[11] and syn-7-t-butoxynorbornene (7)[12]. When compound 6 was subjected to the reaction conditions, it could be recovered unchanged, unaccompanied by any trace of ketonic material. Furthermore, no isomerization of 6 to 7 occurred under these conditions.

In contrast to this result, 7 reacted with Fe(CO)$_5$ to afford three major products, 8 (10%, mp 115-116°), 9 (24%, mp 179-180°), and 10 (12%, bp 293°/1 atm), along with at least ten other minor products (combined yield estimated by VPC to be 6%). Compound 8 was characterized by demonstrating its identity with the product formed by low pressure catalytic hydrogenation of 3. The proton NMR spectrum (100 MHz, CDCl$_3$ solvent) of 9 (IR: 1723 cm$^{-1}$, mass spectrum: parent ion at m/e 360) displayed a singlet at δ1.12 (area 18 H) corresponding to the methyl hydrogens on two magnetically equivalent Ot-Bu groups. The proton noise-decoupled $^{13}$C NMR spectrum of 9 (C$_6$D$_6$ solvent) indicated the presence of ten magnetically nonequivalent carbon atoms. The assignment of SXTXS stereochemistry for 9 is based on the results of extensive NMDR decoupling experiments[10] and on the fact the LiAlH$_4$ reduction of 9 afforded an alcohol, mp 163-164°, which was indicated by TLC on silica gel to be a single product.[13]

The proton NMR spectrum (100 MHz, CDCl$_3$ solvent) of compound 10 (IR: 1702 cm$^{-1}$, mass spectrum: parent ion at m/e 362) displayed two singlets at δ1.14 and δ1.24, corresponding to the methyl hydrogens on two magnetically nonequivalent Ot-Bu groups. The SXNS 2,2'-bisnorbornyl ketone structure



7 8 (SXTNS) 9 (SXTXS) 10 (SXNS)

suggested for 10 is consistent with this spectral information. Compound 10 most likely arises via *in situ* reduction of 8, a process which normally occurs in protic solvents.[14] However, the di-*n*-butyl ether which was used as solvent in this experiment had been previously dried over $CaH_2$ and distilled immediately prior to use. Furthermore, when the reaction was repeated in the presence of added water, compound 10 was *not* formed. Additional efforts to determine the mode of formation of 10 in this reaction are presently underway.

It is clear from this work that the *syn*-7-O*t*-Bu group plays a critical role in directing the stereochemical outcome of the iron carbonyl-promoted coupling of 1 to carbon monoxide. To the best of out knowledge, this is the first clear demonstration of the mechanistic involvement of a Lewis base substituent in reactions of this type.[15] In addition, we find that 1 couples steresospecifically with carbon monoxide to form a single dimeric ketone (3) whereas 7 couples *non*stereospecifically with CO to form three such products (8 - 10). This result suggests that the double bond in 1 which is *anti* to the 7-O*t*-Bu group may be involved mechanistically.[16] Finally, we note that there are 2,304 possible stereoisomeric linear trimeric diketones which might have been formed in the reaction of 1 with $Fe(CO)_5$. The fact that only one (structure 4) is actually formed attests to the remarkable stereospecificity and potential synthetic utility of reactions of this type.[17]

Studies aimed toward further delineation of the detailed mechanism of these and related reactions are in progress. We plan to present additional evidence in this regard and to comment extensively on this subject in the full paper.

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(15) An $Fe(CO)_3$-olefin complex of an endo,endo-5,6-disubstituted-7,7-dimethoxynorborn-2-ene has recently been isolated by Laszlo (ref. 6b) in which the iron atom is coordinated to both the norbornene double bond and to a syn-7-OMe substituent. This result is strongly suggestive of the participation of the syn-Lewis base substituent in iron carbonyl-promoted olefin-CO coupling reactions of the type studied in the present communication. However, no olefin-CO coupling product (i.e., dimeric ketone) accompanied the formation of Laszlo's complex. Hence, his experiment does not provide direct information regarding the intervention or non-intervention of complexes of this type on the energy profile of olefin-CO coupling reactions of systems (such as $Fe(CO)_5$ + 1) which can couple.

(16) It has been suggested that the sole function of the second double bond in norbornadiene is simply to add strain to the bicyclic ring system, thereby enhancing the reactivity of the remaining endocyclic double bond toward $Fe(CO)_5$ (ref. 4).

(17) We note with interest that the apparent coupling of 3 with 1 occurs with XTX stereospecificity to afford 4. A possible rationalization for this observed stereochemistry will be discussed in the full paper.