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HETERODIENOPHILES—V[1]

A STEREOCHEMICAL STUDY OF ALDIMINE–DIENE CYCLOADDITIONS

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Abstract—A study has been made of *exo*/*endo* ratios in the formation of azabicyclics *via* cycloadditions of cyclopenta- or cyclohexa-1,3-diene with N-carbethoxy and N-*p*-toluenesulfonyl trichloromethyl imines, N-*p*-toluenesulfonyl trifluoromethyl imine, and N-phenyl-5-methoxyhydantoin. For N-carbethoxy imines both thermal and acid catalyzed cycloadditions were investigated with acid catalysis being notably evident. Cyclic *Z*-imines afford *endo* adducts while acyclic imines afford *exo*/*endo* mixtures.

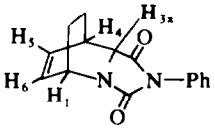
Although cycloadditions of aldimines **1** with conjugated dienes provide convenient routes to a number of nitrogen heterocyclic systems,[1,2] the stereochemical results of such reactions have been little studied.[1,2b,f] We here report determination of *exo*/*endo* ratios obtained during kinetically and non-kinetically controlled cycloadditions of cyclopenta- and cyclohexa-1,3-diene with various aldimines **1** under appropriate thermal or acid catalyzed conditions.

N-phenyl-5-methoxyhydantoin[2c,d] loses methanol either thermally or in the presence of trifluoroacetic acid to form a *Z*-aldimine. Under both sets of reaction conditions cycloaddition with cyclohexa-1,3-diene affords the *endo* stereoisomer **2**. Since the proton H_{3x} does not exhibit long-range W-plan coupling, it can be assigned the *exo* orientation,[1b] and the C-3 substituent the *endo* orientation.[2c,d] An *endo* assignment has previously been made for adduct **3** formed from cyclopentadiene.[2e]

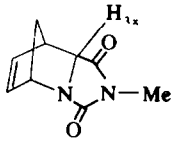
A number of acyclic aldimines, for which *Z*-*E* isomerism is possible,[3] were next investigated. N-carbethoxytrichloromethyl imine (anhydrochloralurethane) was reacted in refluxing benzene solution with cyclohexa-1,3-diene in the presence of catalytic boron trifluoride etherate to form **4** and **5** as a mixture of stereo-isomers. NMR integral analyses of **4** and **5** indicated 75 ± 5% *endo* trichloromethyl isomer **4** had been formed stereoselectively. A similar reaction in refluxing benzene without acid catalysis showed negligible product formation after one week. The ratio of a separate **4** and **5** mixture

R'CH = NR

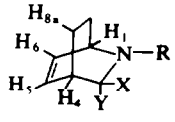
1



2



3



4: R = COOEt, X = H_{3x}, Y = CCl_3
5: R = COOEt, X = CCl_3, Y = H_{3n}
6: R = COOEt, X = H_{3x}, Y = Ph
7: R = COOEt, X = Ph, Y = H_{3n}
8: R = COOEt, X = H_{3x}, Y = $COCH_3$
9: R = COOEt, X = $COCH_3$, Y = H_{3n}
10: R = SO_2Ph–pMe, X = H_{3x}, Y = CF_3
11: R = SO_2Ph–pMe, X = CF_3, Y = H_{3n}

12: R = COOEt, X = H_{3x}, Y = CCl_3
13: R = COOEt, X = CCl_3, Y = H_{3n}
14: R = SO_2Ph–pMe, X = H_{3x}, Y = CCl_3
15: R = SO_2Ph–pMe, X = CCl_3, Y = H_{3n}
16: R = SO_2Ph–pMe, X = H_{3x}, Y = CF_3
17: R = SO_2Ph–pMe, X = CF_3, Y = H_{3n}

(62 ± 3% **4**) was unchanged by heating in benzene with boron trifluoride etherate, which indicates that the former stereoisomeric ratio represents the kinetically formed product mixture in acidic medium.

In order to determine stereochemical results under thermal conditions, N-carbethoxytrichloromethylimine and cyclohexa-1,3-diene were heated at 150° for 24 h in benzene in a sealed tube. NMR analysis of chromatographed **4** and **5** showed the cycloaddition product to be again predominantly *endo*-trichloromethyl adduct **4** (62 ± 3%). Continued heating resulted in no change. N-*p*-toluenesulfonyltrichloromethyl imine did not react with cyclohexa-1,3-diene to form bicyclic product even after 3 days at 150°. However, the more reactive aldimine, N-*p*-toluenesulfonyltrifluoromethylimine,[4] reacted completely during 2 h at 80° in benzene to form **10** and **11**. This reaction, which was monitored by NMR integration of the H_3 hydrogens, indicated a kinetic preference for the *endo*-CF_3 isomer **10** (56% *endo*[1a]).

In order to determine the effect of diene choice on stereochemistry, cycloadditions with cyclopentadiene, a more reactive diene, were investigated. Under kinetically controlled conditions, cyclopentadiene and N-carbethoxytrichloromeylimine[5] reacted for 2 days at 30° to form equal amounts of **12** and **13**.[1a] The same **12**–**13** mixture (50 ± 3% **12** by NMR) was formed after 3 days at 140° or after 3 h in refluxing benzene. The result using the latter conditions is contrary to an earlier report[2f] of 33% **12** based on isolated product ratios. N-*p*-toluenesulfonyltrichloromethylimine[4a] reacted during 2 h at 30° with cyclopentadiene to afford under kinetic conditions mainly *endo*-CCl_3 isomer **14** (78% *endo*).[1a] We have found that in refluxing benzene solution the *endo* isomer **14** both decomposes and rearranges to *exo* isomer **15**. This observation explains a recent report[2f] that only *exo* isomer **15** is formed if the original reaction conditions are 3 h in refluxing benzene. The reactive N-*p*-toluenesulfonyltrifluoromethylimine reacted immediately with cyclopentadiene in benzene to form mainly *exo*-CF_3 isomer **17** (57% *exo*).[1a] With time the *endo*-CF_3 isomer **16** preferentially decomposes at 30° in benzene solution as evidenced by integration of the total F^{19} spectrum. After one week the *exo*-CF_3 preference had risen to 71% *exo* **17**. Verification of the kinetic origin of the stereochemical results is described in the Experimental.

N-carbethoxy- and N-*p*-toluenesulfonyltrichloromethylimine failed to react with bicyclo[2.2.1]heptadiene during 3 days at 145°. N-*p*-toluenesulfonyl phenylimine[4b] failed to yield bicyclic products with either cyclopentadiene or cyclohexa-1,3-diene during 3 days at 145°.

DISCUSSION

Stereochemical results and reaction conditions for thermal and acid catalyzed cycloadditions of aldimines with cyclopenta- and cyclohexa-1,3-diene are summarized in Table 1. Firstly, it has been observed that Lewis acids notably increase the reactivity of N-carbethoxytrichloromethylimine with cyclohexa-1,3-diene. While the reaction to form **4** and **5** is complete at 30° in 3 days with boron trifluoride catalysis, without catalysis negligible reaction occurs after 6 weeks. The catalytic effect of Lewis acids implicates protonated or Lewis acid complexed imines* as reactive species in alkylidene

*In liquid SO_2 trifluorosulfonic acid protonates N-carbethoxyl and N-*p*-toluenesulfonyltrichloromethyl imines on nitrogen.

Table 1. Kinetic stereoselectivity in the synthesis of bicyclic heterocycles *via* aldimine cycloadditions[a]

Aldimine R′	(R′CH=NR) R	Diene I = cyclohexa-1,3-diene II = cyclopentadiene	Adduct 3-*endo*-R′	Selectivity (%)
CO—NPh —	CO	I	**2**	100[b]
CO—NMe —	CO	II	**3**	100[c]
CCl_3	CO_2Et	I	**4–5**	75[d]
CCl_3	CO_2Et	I	**4–5**	62[e]
Ph	CO_2Et	I	**6–7**	20[f]
$COCH_3$	CO_2Et	I	**8–9**	33[f]
CF_3	SO_2Ph-*p*-CH_3	I	**10–11**	57[g]
CCl_3	CO_2Et	II	**12–13**	50[h]
CCl_3	CO_2Et	II	**12–13**	50[i] (33)[j]
CCl_3	SO_2Ph-*p*-CH_3	II[k]	**14–15**	78[l,m]
CF_3	SO_2Ph-*p*-CH_3	II	**16–17**	43[n]

[a] Benzene; [b] 145°, sealed tube or *p*-toluenesulfonic acid, 80°; [c] 25°, 2 h, Ref 2*e*; [d] BF_3, 30°, 72 h; [e] 145°, sealed tube, 64 h; [f] BF_3, reflux, alkylidenebisurethane reactant, Ref 1*d*; [g] 2 h reflux; [h] 30°, 48 h or 145°, 3 days; [i] 3 h, reflux; [j] Ref 2*f*; [k] no bicyclic product with I after 3 days, 150°; [l] 30°, 2 h; [m] Ref 2*f*, 3 h, reflux, only *exo* CCl_3 **15** was reported. We have found (Ref 1*a*) that in refluxing benzene the *endo*-CCl_3 isomer **14** both decomposes and rearranges to the *exo*-CCl_3 isomer **15**; [n] 30°, immediate reaction.

bisurethane reactions[1b-d] with dienes to form compounds **6–9**. The catalytic effect of Lewis acids does not, however, necessitate stepwise reactions in Diels-Alder cycloadditions as pointed out recently by Houk.[7] The acid catalyzed reaction to form **4** and **5** (75% *endo* CCl_3) showed a slightly greater *endo* preference than the thermal reaction (62% *endo*-CCl_3).

Secondly, in agreement with precedent for the *endo* orientation in the reactions of *Z*-1,2-disubstituted olefins with cyclic dienes,[8] the *Z*-aldimines formed from N-phenyl and N-methyl dehydrohydantoins formed *endo* adducts **2** and **3**. Since the cyclic *Z*-aldimines give *endo* products, *E*-aldimines are implicated where major amounts of *exo* substitution at C-3 is observed. A preference for reaction via *E*-aldimines can be rationalized[9] by noting the increase in steric compression of *cis*-substituents in the *Z*-aldimine as the bond angle is gradually changed from 120° to 109° about the imine carbon and nitrogen in the transition state for product formation. The *E*-isomer is free from this disadvantage. Until better understanding is gained of substituent effects in these reactions, the relative roles of *Z* and *E* imines in cycloadditions will remain hazy.

As a result of our observations that both *exo* and *endo* substitutions at C-3 of bicyclic adducts are possible in aldimine cycloadditions, efforts are underway to control this stereochemistry. This should be possible by appropriate choices of substituents on nitrogen and by variation of solvent, reaction temperatures, and Lewis acid catalysts.

EXPERIMENTAL

The NMR spectra were determined with a Varian Associates XL-100-15 spectrometer in $CDCl_3$ solvent using TMS as internal standard and are summarized in Table 2. Structural assignments were made to adducts of cyclohexa-1,3-diene by observation of long-range W-plan coupling[1a] of H_{3endo} protons in the case of 3-*exo* substitution and by the absence of this coupling in the 3-*endo* substituted isomers. The H_{3endo} proton appears as a singlet in 3-*exo* substituted adducts formed from cyclopentadiene and aldimines, since a 90° dihedral angle between H_{3endo} and the adjacent bridgehead proton H_4 results in no observable coupling. In 3-*endo* substituted adducts from cyclopentadiene, the H_{3exo} and H_4 protons are coupled. Elemental analyses were performed by Micro-Analysis, Wilmington, Delaware.

5,6-*Dehydroisoquinuclidine* **2**. The reaction of 5-methoxyhydantoin with cyclohexa-1,3-diene was repeated according to a published procedure.[2c,d] The NMR spectrum is highlighted in Table 2.

Table 2. Major NMR peaks[a]

Compound	Spectrum
2	4·95 (m, H_1), 4·17 (d, H_{3x}, $J_{3x,4}$ = 1·6 Hz), 3·45 (m, H_4), 6·78 (m, $H_{5,6}$)
4	4·90 (m, H_1), 4·70 (d, H_{3x}, $J_{3x,4}$ = 2·8 Hz), 3·50 (m, H_4), 6·40 (m, $H_{5,6}$)
5	4·90 (m, H_1), 4·32 (dd, H_{3n}, $J_{3n,4}$ = 3·2 Hz, $J_{3n,8a}$ = 1·4 Hz),[b] 3·50 (m, H_4), 6·40 (m, $H_{5,6}$), 1·1 (m, H_{8a})
10	4·54 (m, H_1), 4·38 (dq, H_{3x}, $J_{3x,F}$ = 6·5 Hz, $J_{4,3x}$ = 2·5 Hz), 3·10 (m, H_4), 6·20 (m, $H_{5,6}$)[c]
11	4·54 (m, H_1), 3·86 (ddq, H_{3n}, $J_{3n,F}$ = 6·95 Hz, $J_{3n,4}$ = 3·0 Hz, $J_{3n,8a}$ = 1·3 Hz), 3·10 (m, H_4), 6·50 (m, H_6), 6·08 (m, H_5)[c]
12	5·08 (m, H_1), 4·86 (d, H_{3x}, $J_{3,4}$ = 3·5 Hz), 3·80 (m, H_4), 6·36 (m, H_5), 6·50 (m, H_6), 1·66 (br, H_7)
13	4·83 (br, H_1), 3·84 (s, H_{3n}), 3·55 (br, H_4), 2·68 (d, H_{7syn}, J = 9 Hz), 6·50 (m, $H_{5,6}$), 1·44 (d, H_{7anti}, J = 9 Hz)
14	4·94 (br, H_1), 4·78 (d, H_{3x}, $J_{3x,4}$ = 3·8 Hz), 3·18 (br, H_4), 6·0 (br, $H_{5,6}$), 1·10 and 1·32 (dd, $H_{7syn,anti}$, $J_{7syn,anti}$ = 9 Hz)[d]
15	4·78 (br, H_1), 4·18 (s, H_{3n}), 3·30 (br, H_4), 6·10 (br, $H_{5,6}$), 1·04 and 2·40 (dd, $H_{7syn,anti}$, J = 10 Hz)[d]
16	4·62 (br, H_1) 4·05 (dq, H_{3x}, $J_{3x,4}$ = 3·25 Hz, $J_{3x,F}$ = 6·6 Hz), 2·83 (br, H_4), 6·05 (m, H_6), 5·88 (m, H_5), 1·05 (m, $H_{7syn,anti}$)[d]
17	4·46 (br, H_1), 3·56 (m, H_{3n}, $J_{3n,7anti}$ < 0·5 Hz, $J_{3n,F}$ = 7·3 Hz, $J_{4,3n} \cong 0$ Hz), 2·83 (br, H_4), 6·35 (m, H_6), 5·80 (m, H_5), 1·68 (d, H_{7syn}), 0·96 (d, H_{7anti}, $J_{7syn,anti}$ = 10 Hz)[d]

[a] Reported in δ as ppm from TMS: s = singlet, d = doublet, tr = triplet, q = quartet, m = multiplet, br = broad; [b] 4·42 in benzene-d_6; [c] acetone-d_6; [d] benzene-d_6.

N - *carbethoxy* - 3 - (endo - **4** *and* exo - **5**) - *trichloromethyl* - 2 - *azabicyclo*[2.2.2]*oct* - 5 - *enes*

Acid catalysis. A soln of N-carbethoxytrichloromethylimine[5] (4·4 g, 20 mmol), cyclohexa-1,3-diene (1·6 g, 20 mmol) and BF_3-etherate (0·5 ml) in CCl_4 (200 ml) was stirred at 30° for 72 h. Periodic monitoring by NMR integration of the H_1, H_3, and ester methylene regions of **4** and **5** indicated relative percentage 75 ± 3% *endo* trichloromethyl isomer **4**. Removal of solvent and extraction of the residue with n-heptane afforded 4·27 g (71%) of crude oil. Distillation at 132–134°, 0·05 mm, afforded 2·0 g (33%) of the mixture of trichloromethyl stereoisomers, IR (CCl_4) 1710 cm^{-1}, NMR ($CDCl_3$) see Table 2. An analytical sample was obtained by VPC (2 m × 1/4", 5% DC 550 Chrom W, 190°, RT 27 min). The formation of 75 ± 3% *endo* trichloromethyl isomer also occurred in benzene and $DCCl_3$ solvents with BF_3 catalysis.

Thermal reaction. A soln of N-carbethoxytrichloromethylimine (1·1 g, 5 mmol), cyclohexa-1,3-diene (0·6 g, 7·5 mmol) in benzene (3 ml) was heated (sealed glass tube) at 140–145° for 64 h. At this time all the imine had reacted. Removal of solvent and chromatography on neutral alumina ($CHCl_3$/hexane 50/50, R_f = 8·38) afforded 0·42 g (28%) of a colorless liquid **4** (62 ± 3%) and **5**. Decomposition of **4** and **5** or change in the *exo*/*endo* trichloromethyl ratio did not occur during 24 h heating in benzene soln at 140–145° (sealed tube). Attempted repetition of the thermal reaction in refluxing benzene indicated by NMR only traces of peaks corresponding to bicyclic adduct formation after 3 weeks. (Found: C, 44·30; H, 4·93; N, 4·74. Calcd. for $C_{11}H_{14}NO_2Cl_3$: C, 44·22; H, 4·71; N, 4·71%).

N - p - *Toluenesulfonyl* - 3 - (endo - **10** - *and* exo - **11**) - *trifluoromethyl* - 2 - *azabicyclo*[2.2.2]*oct* - 5 - *enes*[4a]

Cyclohexa-1,3-diene (80 mg, 1·0 mmol) and N-*p*-toluenesulfonyltrifluoromethylimine[4a] (250 mg, 1·0 mmol) were refluxed for 2 h in d_6-benzene (1 ml). NMR integration of the H_3 protons adjacent to CF_3 (Table 2) indicated formation of 56% *endo*-CF_3 isomer **10**. Removal of solvent and recrystallization from 80:20 heptane/EtOH afforded a white solid, m.p. 95–97°, of an equimolar mixture of *endo*-**10** and *exo*-**11**-CF_3 isomers. Reflux in benzene for 8 days resulted in slight change in the isomer ratio to 52% *endo*-CF_3 **10** by decomposition of the *exo*-CF_3 isomer **11**.

N - *carbethoxy* - 3 - (endo - **12** *and* exo - **13**) - *trichloromethyl* - 2 - *azabicyclo*[2.2.1]*hept* - 5 - *enes*

A soln of N-carbethoxytrichloromethylimine[5] (1·1 g, 5 mmol) and cyclopentadiene (340 mg, 5 mmol) in benzene (30 ml) was stirred 48 h at 30°. NMR monitoring of protons H_1, H_3, and H_4, of a reaction run in d_6-benzene indicated kinetic formation of a 50:50 *exo*/*endo* trichloromethyl isomeric mixture of **12** and **13**. Removal of solvent afforded 1·25 g (87%) of the bicyclic adducts, IR (CCl_4) 1710 cm^{-1}, NMR (Table 2), as an oil which by elution through a silica gel column with 50:50 chloroform-n-heptane or ether afforded early cuts enriched in the *exo*-trichloromethyl isomer **13** and late cuts in the *endo* isomer **12**. Neither isomer was affected upon 4 h reflux in benzene soln. An analytical sample of the mixture of isomers was obtained by molecular distillation at 90–100° (bath temp), 0·05 mm, and preparative VPC (2 m × 1/4", 5% SE52 on Chrom G, 180°, *exo* isomer **13** RT = 5·2 min, *endo* isomer **12** RT = 6·3 min). Reactions at 145°, 3 days or 80°, 3 h, afforded the same **12**–**13** mixture (50 ± 3% **12**). A reaction run at 30°, but with one drop of BF_3-etherate added, formed only polymer. (Found: C, 42·18; H, 4·34; N, 4·84. Calcd. for $C_{10}H_{12}NO_2Cl_3$: C, 42·40; H, 4·24; N, 4·95%).

N - p - *Toluenesulfonyl* - 3 - (endo - **14** *and* exo - **15**) - *trichloromethyl* - 2 - *azabicyclo*[2.2.1]*hept* - 5 - *enes*

Cyclopentadiene (33 mg, 0·5 mmol) and N-*p*-toluenesulfonyltrichloromethylimine[4a] (150 mg, 0·5 mmol) were stirred in benzene-d_6 for 2 h at 30°. NMR integration of the H_3 protons indicated 78% *endo*-CCl_3 isomer **14**. Crystallization from 95:5 heptane/EtOH afforded crystals, m.p. 118–119°, 100% *endo*-CCl_3 **14**. When the original mixture (78% *endo* CCl_3) in benzene was heated to 80° for 17 h, the ratio of isomers changed in favor of the *exo*-CCl_3 isomer **15** (90% *exo* CCl_3). Decomposition to cyclopentadiene and starting imine also occurred under these conditions.

N - p - *Toluenesulfonyl* - 3 - (endo - **16** *and* exo - **17**) - *trifluoromethyl* - 2 - *azabicyclo*[2.2.1]*hept* - 5 - *enes*

Cyclopentadiene (200 mg, 3·0 mmol) and N-*p*-toluenesulfonyltrifluoromethylimine[4a] (625 mg, 2·5 mmol) reacted immediately when mixed in d_6-benzene (5 ml). NMR integration of the H_3 protons indicated 57% *exo*-CF_3 adduct **17**. Removal of solvent and crystallization from 95:5 heptane–EtOH afforded crop one (380 mg), m.p. 124–125°, enriched in *endo*-CF_3 isomer **16** (68% *endo*), and crop two (250 mg), m.p. 77–79°, enriched in the *exo* isomer **17** (75% *exo*). The 57% *exo* mixture after one week at 30° in benzene became further enriched in *exo*-CF_3 isomer **17** (71% *exo*). Monitoring of this change by integration of the total F_{19} resonances indicated preferential decomposition of *endo*-CF_3 isomer **16** was occurring. (Found: C, 52·87; H, 4·43; N, 4·35. Calcd. for $C_{14}H_{14}NO_2SF_3$: C, 52·99; H, 4·42; N, 4·42%).

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