and the ^{1}H NMR spectra were measured by means of FT techniques with a Bruker WP-60 spectrometer; an external ^{19}F lock was used. The rate data were determined from the line broadening of the two exchanging methoxy signals at δ 4.90 and 3.77 at 3.8 °C; the spectra were simulated between δ 3.5 and 5.2 by the use of Delpuech's method[13] (see Figure 1).

Results and Discussion

The atmospheric pressure results, measured both at Stony Brook and in Lausanne, agree very well with those reported by Nickon; they show (see Figure 2) that $\Delta H^{\ddagger} = 18.1 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = 14.8 \pm 1.2$ eu between −25 and +20 °C. The high-pressure data are shown in Table I. The rate at 3.7 °C is evidently strongly depressed by the application of hydrostatic pressures. The data can be fitted to $\Delta V^{\ddagger} = -RT\ \delta \ln k/\delta p$ by use of the linear approximation as shown in Figure 3, and this gives the result that $\Delta V^{\ddagger} = +8.7 \pm 0.5$ cm^3/mol.

This result demonstrates that the partial volume of the nonclassical structure is indeed larger than that of the limiting classical ions as postulated earlier. The numerical result is not directly comparable to the earlier difference $\Delta\Delta V^{\ddagger}$ of 3.5 cm^3/mol. It is tempting to ascribe the larger difference found in the present experiment to the facts that it presumably considers free and fully developed ions, whereas the solvolytic measurement dealt with transition states likely to resemble ion pairs, and that the charge in the transition state of the equilibration may be even more highly dispersed than that leading to the nonclassical 2-norbornyl ion because of the methoxy groups. The difference in medium renders the further pursuit of a *quantitative* comparison unprofitable at this stage; however, there can be little doubt about the *qualitative* conclusion that charge delocalization in the 2-norbornyl ion does indeed lead to an expansion in volume.

Acknowledgment. The authors express their gratitude for support by the U.S. National Science Foundation (Grant No. CHE7726634) and by the Swiss National Science Foundation (Grant No. 2.921-0.77). Professor Alex Nickon kindly provided us with unpublished details of his synthetic work.

Registry No. 1,2,2-Trimethoxynorborane, 26391-31-1; fluorosulfonic acid, 7789-21-1; methyl fluorosulfonate, 421-20-5; 1,2-dimethoxy-2-norbornyl cation, 26327-58-2.

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[12] A 1218 Special 2 resistor of 100 ω from Heraeus was used: F. K. Meyer and A. E. Merbach, *J. Phys. E*, in press.

[13] J. Chrisment, J. J. Delpuech, and P. Rubini, *Mol. Phys.*, 27, 1663 (1974).

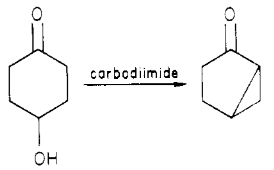
Synthesis of an Unusual Carbodiimide

R. R. Hiatt,* Min-Jen Shaio, and Fawzi Georges

Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1

Received January 30, 1979

The preparation of a series of cyclopropyl ketones by the reaction of keto alcohols with cyclohexylcarbodiimide[1] suggested the possibility of a novel asymmetric synthesis. Reaction, say, of 4-hydroxycyclohexanone with a chiral carbodiimide of known configuration might yield bicyclo[3.1.0]hexan-2-one with predictable geometry.



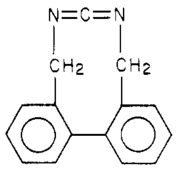
(1)

While preparation of a carbodiimide from an optically active amine presented no synthetic difficulties, models indicated that such a reagent would exhibit little steric control. A cyclic carbodiimide constructed from a restricted rotamer of biphenyl seemed to offer both more chance of success and more interesting chemistry. While carbodiimides have allene-like chirality, some structural constraint is necessary to prevent racemization by nitrogen inversion.

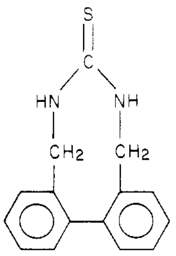
We report here on the feasibility of synthesis of such a carbodiimide, taking as a model an achiral analogue, and peripherally on the bicyclo ketone preparation using a chiral, but acylic, reagent.

Results

The key intermediate, 2,2′-bis(aminomethyl)biphenyl, in the projected synthesis of the nine-membered cyclic carbodiimide, a dibenzo[*e*,*g*](1,3)diazonine (I) was prepared from diphenic acid in fair yield by either of two routes: (1) reduction of diphenic acid diamide with an excess of boron hydride; (2) LiAlH$_4$ reduction of 2,2′-bis(azidomethyl)biphenyl, prepared conventionally from dimethyl diphenate.



I

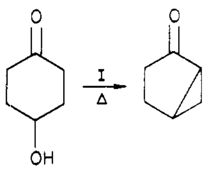


II

All attempts to prepare the cyclic urea from the diamine failed. Reaction of diamine with CS$_2$ proceeded smoothly, however, to yield the cyclic thiourea (II), which was fully characterized.

Dehydrosulfurization of II with mercuric oxide[2] gave I, albeit impure. IR and ^{1}H NMR gave spectra consistent with I, with no extraneous peaks. Mass spectrometric analysis showed the contaminant to be elemental sulfur (S$_8$). Attempts to remove this impurity were unsuccessful.

In addition to the spectral evidence, compound I, although not pure, gave chemical evidence of being a carbodiimide. In particular, it was used (1) to prepare an acyl anhydride, and (2) to prepare bicyclo[3.1.0]hexan-2-one from 4-hydroxycyclohexanone (eq 2) in fair yield. Thus



(2)

the feasibility of synthesis of a nine-membered ring cyclic carbodiimide has been established.

Our enthusiasm for repeating the synthesis with chiral starting material was dampened by concurrent results

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[1] P. C. Alexandre and F. Rouessac, *Bull. Soc. Chim. Fr.*, 5, 1837 (1971).

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using *N*,*N*′-bis[(*R*)-1-phenylethyl]carbodiimide. Dehydration of 4-hydroxycyclohexanone using this chiral carbodiimide exhibited no asymmetric induction whatever, giving only racemic bicyclo[3.1.0]hexan-2-one.

Experimental Section

Preparation of 2,2′-Bis(aminomethyl)biphenyl. Method I. Diphenic acid (0.02 mol) was converted to its acyl chloride ($SOCl_2$) and thence to the dicarboxamide with aqueous NH_3: yield 3.94 g (82%); mp 209–211 °C (lit.[3] 209 °C); IR and MS confirmed the structure.

2,2′-Diphenyldicarboxamide (0.02 mol), a slurry in THF, was refluxed with BH_3 (0.103 mol) for 18 h and worked up to yield 2.6 g (62%) of oil: ^1H NMR ($CDCl_3$) δ 1.57 (s, 4 H), 3.57 (s, 4 H), 7.3 (m, 8 H); IR (film) 3370, 3300, 1075 cm^{-1}; MS *m/e* 212 (M^+) were consistent with the structure 2,2′-bis(aminomethyl)biphenyl. A byproduct, 6,7-dihydro-5*H*-dibenz[*c*,*e*]azepin-7-one, mp 193–194 °C (lit.[4] 194–195 °C), was obtained in 30% yield.

Method II. Dimethyl diphenate (0.02 mol) was reduced to the diol with $LiAlH_4$, which on treatment with $HBr–H_2SO_4$ gave 2,2′-bis(bromomethyl)biphenyl: yield, 3.8 g (56% overall); mp 88–90 °C (lit.[5] 90 °C); MS *m/e* 340 (M^+). Heating (120 °C, 12 h) the dibromide (0.015 mol) in DMF with NaN_3 (0.04 mol), followed by column chromatography (silica gel), gave 2.9 g (73%) of 2,2′-bis(azidomethyl)biphenyl: IR 2475 cm^{-1} (N_3); MS *m/e* 208 ($M^+ - 2N_2$). Reduction of the diazide (H_2 (40 psi/Pd on carbon, 24 h, 22 °C) gave 2.1 g (90%) of the diamine previously described.

Preparation of 5,6,8,9-tetrahydro-7*H*-dibenzo[*e*,*g*](1,3)diazonine-7-thione (II). CS_2 (10 mL) was added dropwise to 2,2′-bis(aminomethyl)biphenyl (0.01 mol) in 5 mL of pyridine + 0.5 g of I_2 at 0 °C.[6] After 1 h the solution was evaporated and the residue was recrystallized from benzene to give 1.75 g (69%) of the thiourea (I): mp 254–255 °C; IR (KBr) 1204 cm^{-1} (C═S); MS *m/e* 254 (M^+); ^1H NMR (Me_2SO-d_6) δ 3.9 (t, 4 H), 7.4 (m, 8 H), 8.4 (t, 2 H). Saturation at δ 8.4 (h-N) gave the methylene protons as an AB quartet centered at δ 3.9, *J* = 14.9 Hz. Anal. Calcd for $C_{15}H_{14}N_2S$: C, 70.83; H, 5.55; N, 11.01. Found: C, 70.69; H, 5.63; N, 11.22.

Preparation of 7,8-Didehydro-8,9-dihydro-5*H*-dibenzo[*e*,*g*](1,3)diazonine (I). Thiourea (II) (0.067 mol), 2.5 g of yellow mercuric oxide,[2] and 3 g of anhydrous $MgSO_4$ were refluxed in 20 mL of benzene for 5 days. Filtration and evaporation of benzene gave 0.8 g of a solid residue which resisted attempts at crystallization: IR (KBr) 2097 cm^{-1} (N═C═N); ^1H NMR ($CDCl_3$) δ 4.31 (quartet, 4 H, *J* = 15.4 Hz), 7.37 (m, 8 H); MS *m/e* 220 (M^+), 256 (S_8^+).

Preparation of *N*,*N*′-Bis[(*R*)-1-phenylethyl]carbodiimide. (*R*)-1-Phenylethylamine (0.24 mol) (Aldrich) was refluxed with 6 g of urea and 40 mL of isoamyl alcohol to yield 23.7 g (75%) of *N*,*N*′-bis[(*R*)-1-phenylethyl]urea: mp 207–209 °C; MS *m/e* 268; $[\alpha]^{22}_D$ (ethanol) +51.7°. The substituted urea (0.03 mol) was refluxed with 36 g of P_2O_5 in pyridine for 1 h. Filtering and distillation gave 5 g (67%) of *N*,*N*′-bis[(*R*)-1-phenylethyl]carbodiimide: bp 105 °C (0.7 mm); IR (film) 2122 cm^{-1} (N═C═N); ^1H NMR ($CDCl_3$) δ 1.42 (d, 6 H), 4.5 (quartet, 2 H), 7.1 (m, 10 H); $[\alpha]^{22}_D$ ($CHCl_3$) + 2.19°.

Reactions of 7,8-Didehydro-8,9-dihydro-5*H*-dibenzo[*e*,*g*](1,3)diazonine (I). A. With Diphenic Acid. The acid (0.00066 mol) with 0.15 g of carbodiimide (I) was refluxed in 10 mL of benzene for 7 h. Evaporation and crystallization gave 0.8 g (53%) of diphenic anhydride: mp 217 °C (lit.[7] 217 °C).

B. With 4-Hydroxycyclohexanone. The hydroxy ketone (0.0038 mol) and 0.8 g of carbodiimide (II) were refluxed (heat, 110 °C) for 1.5 h. Extraction with ether followed by distillation yielded an oil which upon gas chromatographing (20% isodecyl phthalate on Cromosorb W) gave a peak corresponding to authentic bicyclo[3.1.0]hexanone. Response calibration indicated a yield of approximately 30%.

Reactions of 4-Hydroxycyclohexanone with *N*,*N*′-Bis[(*R*)-phenylethyl]carbodiimide. The hydroxy ketone (0.012 mol) plus the carbodiimide (0.010 mol) were refluxed (heat, 160 °C) under N_2 for 8 h. Ether extraction, distillation, and preparative GC (20% isodecyl phthalate on Chromosorb W) yielded 0.24 g (20%) of bicyclo[3.1.0]hexan-2-one. ORD (*c* 0.25, dioxane) (579-265 nm) showed no measurable rotation.

Acknowledgment. The authors respectively acknowledge the contributions of Dr. P. H. Bickart, who conceived the idea and offered many helpful suggestions during the course of the work. Gratitude is due the National Research Council of Canada for financial support.

Registry No. I, 70898-12-3; II, 70898-13-4; 2,2′-bis(aminomethyl)biphenyl, 70898-14-5; diphenic acid, 482-05-3; 2,2′-diphenyldicarbonyl chloride, 7535-15-1; 2,2′-diphenyldicarboxamide, 39950-05-5; 6,7-dihydro-5*H*-dibenz[*c*,*e*]azepin-7-one, 31638-37-6; dimethyl diphenate, 5807-64-7; 2,2′-diphenyldimethanol, 3594-90-9; 2,2′-bis(bromomethyl)biphenyl, 38274-14-5; 2,2′-bis(azidomethyl)biphenyl, 1924-80-7; *N*,*N*′-bis[(*R*)-1-phenylethyl]carbodiimide, 67277-79-6; (*R*)-1-phenylethylamine, 3886-69-9; urea, 57-13-6; *N*,*N*′-bis[(*R*)-1-phenylethyl]urea, 70954-01-7; diphenic anhydride, 6050-13-1; 4-hydroxycyclohexanone, 13482-22-9; (±)-bicyclo[3.1.0]hexan-2-one, 70954-02-8.

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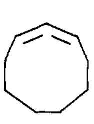
Classical Approach to 1,2,4,6,8-Cyclononapentaene

Edward E. Waali*[1] and Neil T. Allison

Departments of Chemistry, University of
Wisconsin-Whitewater, Whitewater, Wisconsin 53190, and
Georgia College, Milledgeville, Georgia 31061

Received November 7, 1978

The reaction of alkyllithiums with geminal dibromocyclopropanes represents an extremely valuable method for the preparation of allenes.[2] The procedure has found important applications in the generation of cyclic allenes of six,[3] eight,[4] nine,[5] and larger carbon atoms. The stability of these cyclic allenes is crucially dependent upon the ring size and the presence of additional unsaturation within the ring. 1,2-Cyclononadiene (1) is a well studied stable allene, but those of smaller size are strained and dimerize rapidly. Unsaturated derivatives of 1 are known (2,[5] 3,[6] and 4[6]) but the two additional double bonds in 4 substantially increase the ring strain resulting in its rapid dimerization at 0 °C ($t_{1/2}$ = 10–20 min in $CDCl_3$).[6] Perhaps the most interesting unsaturated derivative of 1 would be the fully conjugated allene, 1,2,4,6,8-cyclononapentaene (5). We would now like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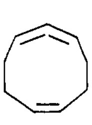
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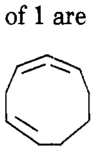
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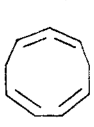
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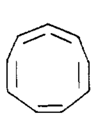
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[1] Address correspondence to author at the University of Montana, Missoula, Montana 59812.

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