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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[6] H. S. Fry, *J. Am. Chem. Soc.*, **35**, 1539 (1913).

[7] R. C. Roberts and T. B. Johnson, *J. Am. Chem. Soc.*, **47**, 1396 (1925).

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

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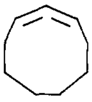
The reaction of alkyllithiums with geminal dibromocyclopropanes represents an extremely valuable method for the preparation of allenes.[2] The procedure has found important applications in the generation of cyclic allenes of six,[3] eight,[4] nine,[5] and larger carbon atoms. The stability of these cyclic 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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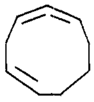
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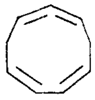
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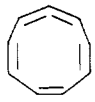
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[1] Address correspondence to author at the University of Montana, Missoula, Montana 59812.

[2] W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958).

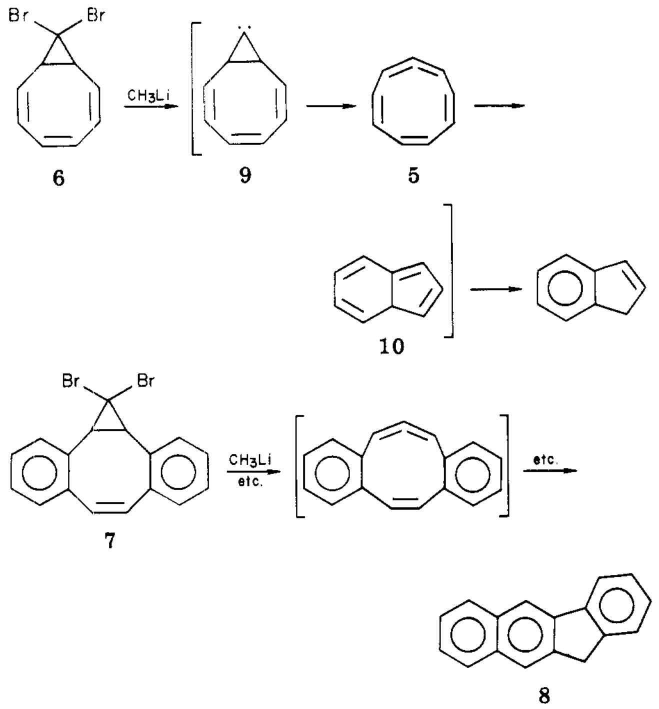
[3] W. R. Moore and W. R. Moser, *J. Am. Chem. Soc.*, **92**, 5469 (1970).

[4] E. T. Marquis and P. D. Gardner, *Tetrahedron Lett.*, 2793 (1966).

[5] (a) L. Skattebol, *Tetrahedron Lett.*, 167 (1961); L. Skattebol, *Acta Chem. Scand.*, **17**, 1683 (1963). (b) Although **1** has little ring strain implying a linear allene linkage, it is drawn as a nonagon for easier comparison with the other allenes, some of which may have nonlinear allene linkages.

[6] M. S. Baird and C. B. Reese, *Tetrahedron*, **32**, 2153 (1976).

Scheme I

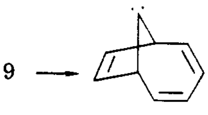


to report the application of the classical dibromocyclopropane synthetic approach to **5** and one of its dibenzo analogues.[7]

Although the reaction of 9,9-dibromobicyclo[6.1.0]nona-2,4,6-triene (**6**) with *n*-butyllithium (initially at −95 °C) was reported to give an indiscernible mixture of products,[8] we find that at an initial temperature of −78 °C a 10% yield of indene is formed (based on NMR analysis using toluene as an internal standard). If methyllithium is used instead in a reaction with **6** at 0 °C indene can be isolated in 36% yield. When the dibromide **7** is treated with methyllithium at −5 °C, a 35% yield of 2,3-benzofluorene (**8**) is recovered. The products in these reactions were identified by comparison of their NMR and IR spectra with published data.[9]

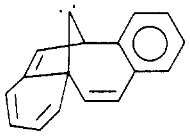
The formation of indene from **6** can be readily explained using Scheme I. Each step has ample precedence. As previously mentioned, the formation of allenes, including the smaller strained cyclic allenes, from dibromocyclopropanes (presumably via cyclopropylidene carbenes or carbenoids) is well known.[2-6] Rapid electrocyclic ring closures in nine-membered cyclic polyenes are also well established.[10] The isomerization of **10** to indene, although a thermally allowed 1,5-sigmatropic hydrogen shift,[11] could easily be a base-catalyzed reaction considering the nature of the reaction medium. Individual attempts to trap any intermediates with 1,3-pentadiene, 2-methyl-2-butene, and furan (as the solvent in this case) were unsuccessful. In each case the indene formation was essentially unaffected.[12,13]

A second possible mechanism could involve a vinylcyclopropylidene–cyclopentenylidene rearrangement,[14] yielding bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene (**11**). The



11

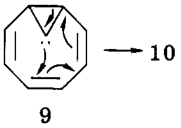
carbene **11** has been generated by Shechter and co-workers using a Bamford–Stevens reaction at 190 °C and does indeed yield indene (42%) in addition to 7-ethynyl-1,3,5-cycloheptatriene (**12**, 2%).[15] The involvement of a **9** to **11** rearrangement in the present work is less attractive, though, when one considers the formation of **8** from **7**. Assuming analogous pathways for **6** and **7**, a similar rearrangement would convert **7** to **13**, requiring the loss of



13

the aromaticity of one ring while maintaining the high energy carbene character of the intermediate. An intermediate such as **13** is unfavorable considering the relatively low temperature of the reaction.

If indeed **5** is an intermediate in the above reaction, one may wonder about its extreme lability. The construction of a Dreiding model of **5** shows that considerable ring strain has been introduced by the additional double bonds. In addition, one sees that C_2 and C_7 are rather close and that their π systems are pointing nearly directly at one another. This would greatly facilitate the symmetry allowed, thermal, disrotatory ring closure.[11] Thus **5** would be thermodynamically unstable and would have a *kinetically favorable, unimolecular* pathway to relieve its strain. It



9

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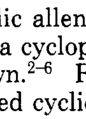
(7) (a) A partial account of this work has been previously presented: E. E. Waali and N. T. Allison, Southeast Regional American Chemical Society Meeting, Norfolk, Virginia, October, 1974. (b) A cyclic, completely conjugated allene, e.g. **5**, is theoretically interesting since it has a valence isomeric carbene form, e.g. i.



i

A preliminary attempt at the generation of i has been reported: see E. E. Waali, J. L. Taylor, and N. T. Allison, *Tetrahedron Lett.*, 3873 (1977).

(8) H. J. Loozen, W. A. Castenmiller, E. J. M. Bater, and H. M. Back, *J. Org. Chem.*, 41, 2965 (1976).

(9) C. J. Pouchert and J. R. Campbell, "The Aldrich Library of NMR Spectra", Aldrich Chemical Co., Milwaukee, Wisconsin, 1974; C. J. Pouchert, "The Aldrich Library of Infrared Spectra", Aldrich Chemical Co., Milwaukee, Wisconsin, 1970.

(10) For instance, see P. Radlick and G. Alford, *J. Am. Chem. Soc.*, 91, 6529 (1969).

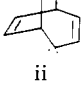
(11) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., W. Germany, 1970.

(12) Rapid infrared analysis of the reaction mixture failed to give evidence of any allenic intermediates.

(13) The starting material **7** was prepared via the extremely inefficient addition of dibromocarbene to *sym*-dibenzocyclooctatetraene (2.4% yield). Due to the limited quantity of **7** trapping experiments have yet to be performed.

(14) L. Skattebol, *Tetrahedron Lett.*, 2361 (1970).

(15) (a) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Am. Chem. Soc.* **94**, 5366 (1972); T. V. Rajan Babu and H. Shechter, *ibid.*, **98**, 8261 (1976). (b) Another C_9H_8 carbene, ii, has been reported to yield indene (14%) and **12** (8%): P. K. Freeman and K. E. Swenson, Northwest Regional American Chemical Society Meeting, Seattle, June, 1978.



ii

is quite possible that a structure such as **5** is not even an energy minimum on the reaction surface, making it virtually impossible to trap. In this extreme, the conversion of **9** to **10** might be written as follows.[16] A theoretical investigation of the rearrangement surface would be instructive.

Experimental Section

NMR spectra were recorded on Varian T-60 or A-60 spectrometers. Polystyrene calibrated IR spectra were taken on a Beckman Acculab 6 instrument. High-resolution mass measurements were made at the University of Florida. Analytical and preparative thin-layer chromatography employed Merck Silica Gel 60 PF-254 + 366 in 0.25- and 1.0-mm layers.

9,9-Dibromobicyclo[6.1.0]nona-2,4,6-triene (6).[17] To a well-stirred mixture of 48.5 g of bromoform (0.192 mol), 10.0 g of 1,3,5,7-cyclooctatetraene (0.096 mol), 0.10 g of triethylbenzylammonium chloride, and 0.20 mL of ethanol, 24 mL of 50% aqueous sodium hydroxide was added over a 10-min period while cooling the mixture in a water bath. The mixture was stirred overnight with cooling. After the addition of 200 mL of water, the mixture was extracted thrice with 50-mL portions of dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulfate and filtered through glass wool. The dichloromethane was removed under vacuum, followed by the removal of the excess cyclooctatetraene and bromoform by distillation at 0.4 mmHg (room temperature). The residue was chromatographed (silica gel/petroleum ether), resulting in 8.5 g of **6** (32%).

Reaction of 6 with Methyllithium. To an ice cold solution of 2.01 g of **6** (7.61 mmol) in 15 mL of anhydrous ether was added 9.12 mmol of methyllithium (2 M in ether) over a 20-min period. After an additional 30 min at 0 °C, 30 mL of water was added. The organic layer was separated and the aqueous layer was washed with additional ether. After drying the combined extracts, the ether was removed under vacuum on the rotary evaporator. Distillation of the residue resulted in 0.32 g of indene [42 °C (0.8 mmHg), 36%].

Reaction of 6 with *n*-Butyllithium. A flask containing 1.12 g of **6** (4.1 mmol) and 10 mL of dry THF was cooled to −78 °C in a dry ice–acetone bath. A dry nitrogen atmosphere was maintained on the system. To this was added 6.9 mL of 1.58 M *n*-butyllithium (4.4 mmol) over a 15-min period. The temperature was maintained between −75 and −70 °C. The solution was stirred for an additional period of 45 min. After allowing the solution to warm to room temperatures 60 mL of water was added. The mixture was extracted with two 30-mL portions of petroleum ether. The organic extracts were dried over $MgSO_4$ and the solvent was removed under slight vacuum. The residue, 0.569 g, was diluted to 3 mL with $CDCl_3$. A 0.6-mL aliquot of this solution was added to 0.016 g of toluene in an NMR tube. Integration of the indene CH_2 and the toluene CH_3 gave an *area* ratio of 3:9.5. From this it was calculated that indene was produced in this reaction in a yield of 10%.

2,3:6,7-Dibenzo-9,9-dibromobicyclo[6.1.0]nona-2,4,6-triene (7).[17] A 1-L three-neck flask was equipped with a mechanical stirrer, reflux condenser, and a dropping funnel and flushed with nitrogen. To this was added 5.3 g of *sym*-dibenzocyclooctatetraene (26 mmol), 528 g of bromoform (2.09 mol), 2 mL of ethanol, and 1.0 g of triethylbenzylammonium chloride. The solution was warmed to 40 °C and 300 mL of 50% aqueous NaOH was added very slowly over a 10-h period with stirring. The temperature was maintained at 40–45 °C. The mixture was then stirred at room temperature for an additional 15 h. Water (200 mL) was then added and the lower organic layer was removed. The aqueous layer was washed twice with 100 mL of dichloromethane. The combined organic extracts were dried over $MgSO_4$ and filtered through glass wool. The dichloromethane was removed under vacuum using a rotary evaporator. Most of the bromoform was removed by vacuum distillation. The residue was chromatographed through a large alumina column (petroleum ether) to remove polymer. The remaining bromoform (and tetrabromoethylene) was removed by additional vacuum distillation. This residue was chromatographed through silica gel (1 × 40 cm, petroleum ether). After ca. 550 mL of solvent eluted, three 50-mL fractions were collected. The first contained mostly starting material, but the second and third contained starting material and **7** in 1:1 and 1:3 ratios, respectively. The last two fractions were subjected to preparative thin-layer chromatography (1.0 mm silica gel, 5% CH_2Cl_2/petroleum ether). A total of 0.238 g of **7** was isolated (2.4% conversion). In addition, 1.56 g of *sym*-dibenzocyclooctatetraene was recovered. For **7**: mp 198–201 °C; IR (KBr pellet) ν_{max} 3100 (w), 3065 (w), 3055 (w), 3025 (w), 3000 (w), 1491 (m), 1440 (m), 1396 (m), 765 (s), 574 (m), and 498 cm^{-1} (m); NMR ($CDCl_3$) δ 3.20 (s, 2 H, cyclopropyl), 6.66 (s, 2 H, olefinic), 7.13 (m, 6 H, aromatic), and 7.67 (m, 2 H, aromatic); high-resolution mass spectrum *m/e* 373.9321 (M), 375.9280 (M + 2), 377.9279 (M + 4) [calcd for $C_{16}H_{12}Br_2$: 373.9305, 375.9285, and 377.9264, respectively].

Reaction of 7 with Methyllithium. To a solution of 0.179 g of **7** (0.477 mmol) in 5 mL of dry THF was added 0.85 mL of 1.77 M methyllithium (0.477 mmol) at −5 °C over a 2-min period. The solution was stirred for 60 min at −5 °C. The solution was allowed to warm to room temperature and 20 mL of water was added. The solution was extracted with three 30-mL portions of dichloromethane. After drying over $MgSO_4$ the solvent was removed under vacuum. The residue was subjected to thin-layer chromatography. An NMR spectrum of the leading band was shown to be that of 2,3-benzofluorene[9] (0.036 g, 35%). The sample was recrystallized from chloroform with cooling in a freezer: mp 192–198 °C.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. Gratitude is also expressed to Dr. W. M. Jones for helpful discussions. Appreciation is also expressed to the Department of Chemistry at the University of Florida for mass spectral data.

Registry No. 6, 70813-87-5; **7**, 70813-88-6; 1,3,5,7-cyclooctatetraene, 629-20-9; indene, 95-13-6; *sym*-dibenzocyclooctatetraene, 262-89-5; 2,3-benzofluorene, 243-17-4.

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[16] The conversion of **9** to indene represents an "electron pusher's delight." Considering the high degree of unsaturation in **9** and the necessity of at least one ring opening, one ring closure and one hydrogen shift, a number of other less attractive mechanisms can be proposed.

[17] The general procedure of M. Makosza and M. Fedorynski, *Synth. Commun.*, **3**, 305 (1973), was followed.

Catalytic Reduction of Trifluoroacetic Acid under Mild Conditions

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Received March 13, 1979

It has been previously recognized that activated carbonyl compounds, such as α-keto esters[1] or trifluoromethyl ketones,[2] can be hydrogenated more readily than their nonactivated derivatives. Similar behavior has, however, not yet been observed for activated carboxylic acids. Previous studies[3] have indicated that trifluoroacetic acid can only be reduced to 2,2,2-trifluoroethanol in the presence of rhenium blacks under rather vigorous conditions [207 °C (300 atm)]. Higher perfluoroalkanoic acids can be reduced under somewhat milder conditions

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