that the reaction is indeed complex.[5,6] However, it was found that lower temperatures, longer reagent preparation time, and smaller reaction volumes enhanced the resultant rotatory power of the partially resolved *trans*-cyclooctene.[7]

The overall results of these experiments indicate that partial resolution of *trans*-cyclooctene by kinetic asymmetric destruction (*via* asymmetric hydroboration) can be a valuable alternate[8] path to the optical enrichment of this unique olefin.

Experimental Section

Instrumentation.—All gas chromatographic analyses were performed on a Varian Aerograph Model 90-P instrument. Optical rotations were measured with a Ruldolph Model 80 polarimeter.

Materials.—(+)-α-Pinene (Aldrich) was distilled from crushed calcium hydride and collected at 152–155° (670 mm) [lit.[9] bp 156.2° (760 mm)], $[\alpha]^{27}D$ +57.1 ± 0.4° (*c* 5, $CHCl_3$). Boron trifluoride etherate (Eastman) was purified by distillation at 73° (59 mm) [lit.[9] bp 67° (43 mm)]. Triglyme (Ansul) was distilled at 216–217° (670 mm) [lit.[9] bp 220° (760 mm)] from $LiAlH_4$.

Preparation of (±)-*trans*-Cyclooctene.—The racemic olefin was prepared according to Cope's procedure[10] except that the *N,N,N*-trimethylcyclooctylammonium iodide was synthesized in one step from cyclooctylamine (Aldrich) using excess methyl iodide and base. In a typical run cyclooctylamine (50 g, 0.394 mol) was reacted with methyl iodide (228 g, 1.6 mol) in 200 ml of methanol. After the initial reaction had subsided, potassium carbonate (55 g, 0.4 mol) was carefully added and the mixture refluxed for 24 hr. After filtering, partially stripping, and cooling, the solution yielded 112 g (0.376 mol, 96%) of the tetraalkylammonium iodide. Following Cope's procedure,[10] 50 g (0.168 mol) of the iodide yielded 14.1 g (0.128 mol, 76%) of a 3:2 mixture of *trans*- and *cis*-cyclooctene, respectively. Extraction of the mixture with a 20% silver nitrate solution[10] yielded 7.2 g (0.065 mol, 37% overall yield from cyclooctylamine) of >98% pure (gc, 20 ft × 3/8 in., 20% DEGS) *trans*-cyclooctene.

Partial Resolution of (±)-*trans*-Cyclooctene.—In a typical run, the asymmetric hydroborating reagent was prepared by mixing 0.379 g (0.01 mol) of $NaBH_4$ (12.0 ml of a 0.83 *M* solution in triglyme) and 2.68 g (0.197 mol) of (+)-α-pinene [$[\alpha]^{27}D$ +57.1 ± 0.4° (*c* 5, $CHCl_3$)] with 30 ml of dry triglyme. The solution was placed in a three-necked round-bottom flask, covered by N_2, and kept at −10°. Through a dropping funnel 1.39 g (0.0098 mol) of $BF_3 \cdot Et_2O$ (in 5 ml of triglyme) was slowly added to the rapidly stirred triglyme solution of $NaBH_4$ and α-pinene. After addition of the reagent was complete, the entire mixture was stirred an additional 30 hr at −10° after which 2.024 g (0.0184 mol) of (±)-*trans*-cyclooctene (containing 2.024 g of pentane as a gc standard) was added.

This mixture was stirred 4 hr at −10° and then flash distilled at 50° (5 mm) into a Dry Ice–acetone trap until no more cyclooctene (by gc) remained in the reaction pot. Gc analysis of the raw flash distillate showed the presence of 0.87 g (0.0079 mol) of *trans*-cyclooctene. This raw yield represents 92% of the theoretically recoverable trans olefin.[11] Some *cis*-cyclooctene[12] and α-pinene[13] was also observed in the flash distillate.

Finally, the *trans*-cyclooctene was recovered in pure form from the flash distillate by the usual 20% $AgNO_3$ extraction.[10] After destruction of the silver complex with ammonium hydroxide, 0.685 g (0.0062 mol, 72%[10]) of *trans*-cyclooctene was obtained as a pentane solution. Removal of the pentane by distillation gave the pure trans olefin with $[\alpha]^{25}D$ −95.5 ± 0.5° (*c* 7, $CHCl_3$). Comparing the rotation in CH_2Cl_2 with that of Cope's[9] gives an optical purity of 20.8% for the partially resolved olefin.

Registry No.—(±)-*trans*-cyclooctene, 28541-65-3; (−)-*trans*-cyclooctene, 22770-27-0.

(5) As with some of the more hindered olefins of Brown's, there is some ambiguity as to the exact nature of the asymmetric hydroborating species. See ref 6 and 7.

(6) D. J. Pasto, V. Balasubramaniyan, and P. W. Wojtkowski, *Inorg. Chem.*, **8**, 594 (1969). The authors proved that five different disproportionating equilibrium reactions exist simultaneously in certain alkylborane solutions.

(7) H. C. Brown and G. J. Klender, *ibid.*, **1**, 204 (1962). The authors showed that an appreciable equilibrium exists between tetraisopinocampheylditborane and triisopinocampheylditborane when the reagent is prepared in tetrahydrofuran. The trialkylditborane is thought to be the cause of the reduced degree of resolution in the case of certain sterically hindered olefins. See H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 1071 (1964). In diglyme the tetraalkylditborane appears to precipitate, thereby shifting the equilibrium toward the more highly substituted diborane. Results in this lab indicate that this borane is more soluble in triglyme than in diglyme and that a more concentrated solution is required to effect precipitation.

(8) Since the synthesis of *dl-trans*-cyclooctene is relatively simple and inexpensive, loss of part of the trans olefin should not be objectionable. Moreover, the amount of the olefin "lost" can be reduced by the use of less hydroborating reagent. Of course, this would also result in lowered optical activity of the resolved *trans*-cyclooctene.

(9) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, New York City, N. Y., 1966.

(10) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953). The near-quantitative extraction procedure described by Cope has not yet been reproduced in this laboratory. Recovery of *ca.* 80% *trans*-cyclooctene by the $AgNO_3$ method represents this laboratory's best efforts.

(11) Generally, half of the *trans*-cyclooctene should have been returned unreacted.

(12) The exact origin of the cis olefin is unknown. However, gc analysis of the reaction mixture immediately after addition of the racemic olefin indicated almost immediate formation of this less strained alkene.

(13) α-Pinene has been found in varying amounts as a side product from the asymmetric hydroboration of bulky olefins, thereby inferring a preequilibrium between tetraisopinocampheylditborane and triisopinocampheylditborane plus α-pinene. See ref 7.

Catalysis by Molecular Sieves in the Preparation of Ketimines and Enamines[1]

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Ketimines and enamines can conveniently be prepared in high yield by the reaction of the appropriate ketones and amines in the presence of molecular sieves. The method is quite general and can be applied successfully even to medium-sized ring ketones and camphor, which are rather hindered. Since the method is so mild, it might be employed where more vigorous reagents (such as zinc chloride,[2a] titanium tetrachloride,[2b] or aluminum chloride[3]) may cause side reactions; since it is so simple, it may prove preferable to the use of acetals,[4] 1-amino-1-cyanoalkanes,[5] thioketones,[6] gem dichlorides,[7] or iminophosphorus compounds,[8] etc.,[9]

(1) After this note had been submitted for publication, the authors saw the paper by E. P. Kyba, *Org. Prep. Proced.*, **2**, 149 (1970), on "An Improved Synthesis of Ketimines." Dr. Kyba used molecular sieves to shift the equilibrium in favor of the formation of six ketimines, three from acetone with various amines and three from methylamine with various methyl ketones. The present work extends that of Kyba to hindered ketones and further, in particular, reports the catalytic effects of molecular sieves in the formation of ketimines.

(2) (a) J. H. Billman and K. M. Tai, *J. Org. Chem.*, **23**, 535 (1958); (b) W. A. White and H. Weingarten, *ibid.*, **32**, 213 (1967).

(3) K. Taguchi, unpublished results.

(4) J. Claisen, *Ber.*, **29**, 2931 (1926); J. Hoch, *C. R. Acad. Sci., Ser. C*, 199, 1428 (1934).

(5) W. C. Bain, P. D. Richie, and A. E. Wright, *J. Chem. Soc.*, 1454 (1964); J. S. Walia, L. Heindl, H. Lader, and P. S. Walia, *Chem. Ind. (London)*, 155 (1968).

(6) A. Schoenberg and W. Urban, *J. Chem. Soc.*, 530 (1935).

(7) M. Pauly, *Justus Liebigs Ann. Chem.*, **187**, 196 (1877); D. Y. Curtin and J. W. Hausser, *J. Amer. Chem. Soc.*, **83**, 3474 (1961).

(8) R. Appel and A. Hauss, *Ber.*, **93**, 405 (1960); W. S. Wadsworth and W. D. Emmons, *J. Amer. Chem. Soc.*, **84**, 1316 (1962).

(9) P. A. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. I, W. A. Benjamin, New York, N. Y., 1965, p 295.

TABLE I
IMINES AND ENAMINES[a]

Ketone	Amine	Yield, %	Mp or bp, °C (mm)	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
Cyclooctanone	Aniline	88	107–108 (0.25)	83.53	9.51	6.96	83.47	9.47	6.96
Cycloheptanone	Aniline	85	97–98 (0.4)	83.37	9.15	7.48	83.00	9.12	7.53
Cyclohexanone	Aniline	74	85–86 (0.4)						
Cyclohexanone	*m*-Toluidine	77	90–92 (0.25)	83.37	9.15	7.48	83.36	9.00	7.22
Camphor-*d*	Aniline	81	17	84.53	9.31	6.16	84.66	9.36	6.19
Benzophenone	Aniline	85	114–115						
Acetophenone	Aniline	75	40–41						
Acetophenone	*m*-Toluidine	78	124–126 (0.4)						
Cyclooctanone	Pyrrolidine[a]	82	79–81 (0.25)						
Cyclooctanone	Morpholine[a]	88	90–92 (0.4)	73.80	10.84	7.17	73.72	10.93	7.14
Cycloheptanone	Pyrrolidine[a]	80	64–65 (0.4)						
Cycloheptanone	Morpholine[a]	87	75–76 (0.25)						
Cyclohexanone	Diethylamine[a]	78	52.5–53.5 (1.25)						
Acetophenone	Pyrrolidine[a]	77	75–76 (0.25)						
Bicyclo[4.3.1]decan-10-one	Aniline	81	48.5–49.5	84.53	9.31	6.16	84.70	9.36	5.88
Ketopinic acid	Aniline	70	130–131	74.68	7.44	5.44	74.54	7.44	5.26
Bicyclo[4.2.1]nonan-9-one-1-carboxylic acid[b]	Aniline	41	119.5–121.0	74.68	7.44	5.44	74.68	7.56	5.29
Bicyclo[3.3.1]nonan-9-one-1-carboxylic acid[c]	Aniline	64	174–175.5	74.68	7.44	5.44	74.44	7.61	5.19

[a] The product is an enamine. In all other cases, the product is an imine (see Table II). [b] J. R. Wiseman, H. F. Chan, and C. J. Ahola, *J. Amer. Chem. Soc.*, **91**, 2812 (1969). [c] E. W. Colvin and W. Parker, *J. Chem. Soc.*, 5764 (1965).

as intermediates or as special reagents. Ketimines and enamines are frequently prepared by azeotropic distillation of a mixture of ketone and amine with benzene or toluene; further, in some instances the distillate has been dried effectively with molecular sieves.[10] Bonnett and Emerson[11] previously used the method discussed in this note for the preparation of the *n*-butylketimine at the 17 position of androsterone, but they did not report that the sieves serve as catalyst as well as dehydrating agent. The generality of the method and especially its application to hindered ketones are reported here. The method is of interest in this laboratory for the preparation of ketimines in connection with researches on these compounds as intermediates in enzymic decarboxylation.[12]

Results

The half-time for the condensation of aniline and acetophenone, in the presence of molecular sieves under the conditions described in the Experimental Section (about 0.15 *M* reagents in benzene at room temperature), is about 15 min. In the absence of molecular sieves or other catalyst, the reaction is quite slow, with no detectable formation of ketimine in 50 hr.

Catalysis by aniline hydrochloride is ineffective in benzene as solvent because of the insolubility of the salt, but the reaction can be strongly catalyzed by soluble acids, such as acetic acid. However, in the absence of a dehydrating agent, the reaction is incomplete, with yields of less than 10%. Molecular sieves serve simultaneously as a dehydrating agent and as a catalyst that can be removed at the end of the reaction simply by filtration.

(10) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 217 (1965).
(11) R. Bonnett and T. R. Emerson, *J. Chem. Soc.*, 4508 (1965).
(12) F. H. Westheimer, *Proc. Chem. Soc.*, 253 (1963); *Search*, **1**, 34 (1970).

The anils and enamines, prepared by the method here described, are reported in Table I. Particular attention is directed to the anils of camphor and of cyclooctanone, which are not easily prepared in such high yields by other methods. On the other hand, the anils of the keto acids could be prepared in the absence of molecular sieves; apparently carboxyl groups supply the needed acid catalysis, although the preparation of the anil from ketopinic acid gave a slightly better yield, and in less time, in the presence of molecular sieves.

Experimental Section

General Procedure.—About 40 g of molecular sieves (Linde 5A) are added to 0.10 mol of ketone and 0.12 mol of aromatic amine in 40 ml of benzene or ether. The reaction mixture is shaken until almost no free ketone can be detected in the supernatant liquid by ir or nmr spectroscopy (1–30 hr at room temperature for unhindered ketones), and the corresponding absorption for the ketimine is maximized. The mixture is then filtered from the molecular sieves which are washed with solvent. Solvent is removed from the filtrate and washings by rotary evaporation, and the product purified by vacuum distillation or crystallization.

Cyclooctanone anil, cycloheptanone anil, cyclohexanone-*m*-toluid, and acetophenone-*m*-toluid were prepared in the above-described manner, employing benzene as solvent. The anil of benzophenone was prepared in this way in benzene as solvent except that the crude imine was crystallized from ethanol rather than subjected to distillation; the anil from acetophenone was crystallized from petroleum ether (bp 37–49°). The enamines from cyclooctanone and from cycloheptanone with pyrrolidine, the enamine from cyclohexanone with diethylamine, and that from cycloheptanone with morpholine were prepared by the standard procedure, using ether rather than benzene as solvent. The enamine from cyclooctanone and morpholine, prepared in ether as solvent, required 4 days at room temperature until the ir band of the ketone had nearly disappeared.

Camphor-*d* anil was prepared similarly, but the reaction is slow, with a half-time in benzene solution at room temperature of 2 days; to obtain a good yield, the reaction required 2 weeks at room temperature or 10 hr of refluxing. Similarly, the anil of

TABLE II

Compd	Registry no.	Ir, C=N or =C—N, μ[a]	Nmr, δ in ppm relative to TMS[b,c]	Ref
N-Cyclooctylideneaniline	13683-44-8	6.06	1.0–2.7 (m, 14 H), 6.4–7.3 (m, 5 H)	
N-Cycloheptylideneaniline	13683-43-7	6.08	1.3–2.2 (m, 12 H), 6.4–7.3 (m, 5 H)	5
N-Cyclohexylideneaniline	1132-38-3	6.01	1.3–2.5 (m, 10 H), 6.4–7.3 (m, 5 H)	*d*
N-Cyclohexylidene-*m*-toluidine	28627-51-2	6.01	1.3–2.5 (m, 10 H), 2.25 (s, 3 H), 6.2–7.2 (m, 5 H)	
Camphor-*d* anil	28627-52-3	5.94	0.81 (s, 3 H), 0.91 (s, 3 H), 1.05 (s, 3 H), 1.1–2.4 (m, 7 H), 6.5–7.2 (m, 5 H)	*d*
Benzophenone anil	574-45-8	6.20[e]	6.5–7.8 (m, 15 H)	*d*
Acetophenone anil	1749-19-5	6.14[e]	2.10 (s, 3 H), 6.5–8.0 (m, 10 H)	*d*
N-(1-Methylbenzylidene)-*m*-toluidine	28627-55-6	6.13	2.15 (s, 3 H), 6.5–8.0 (m, 10 H)	*d*
1-Pyrrolidenyl-1-cyclooctane	28627-56-7	6.14	1.2–3.2 (m, 20 H), 4.08 (t, 1 H, J = 8 Hz)	*f*
1-Morpholinyl-1-cyclooctene	17344-01-3	6.21	1.45 (br, 8 H), 1.8–2.4 (br, 4 H), 2.5–2.8 (m, 4 H), 3.4–3.7 (m, 4 H) 4.50 (t, 1 H, J = 8 Hz)	*g*
1-Pyrrolidenyl-1-cycloheptene	28627-58-9	6.12	1.2–3.2 (m, 18 H), 4.37 (t, 1 H, J = 7 Hz)	*f*
1-Morpholinyl-1-cycloheptene	7182-08-3	6.09	1.2–2.3 (m, 10 H), 2.5–2.7 (m, 4 H), 3.5–3.7 (m, 4 H), 4.08 (t, 1 H, J = 8 Hz)	10
1-Diethylamino-1-cyclohexene	10468-24-3	6.10	0.95 (t, 3 H, J = 8 Hz), 1.2–2.3 (m, 8 H), 2.90 (q, 2 H, J = 7 Hz), 4.40 (t, 1 H, J = 3 Hz)	*h*
α-Pyrrolidinyl styrene	3433-56-5	6.21	1.5–2.0 (m, 4 H), 2.2–3.1 (m, 4 H), 3.80 (s, 1 H), 3.87 (s, 1 H), 7.0–7.5 (m, 5 H)	*i*
10-Phenyliminobicyclo[4.3.1]decane	28627-61-4	6.14[e]	1.1–2.2 (m, 14 H, 2.85 (br, 2 H), 6.4–7.3 (m, 5 H)[j]	
2-Phenylimino-7,7-dimethylbicyclo-[2.2.1]heptane-11-carboxylic acid	28627-62-5	6.00[e]	1.20 (s, 3 H), 1.33 (s, 3 H), 1.5–2.5 (m, 12 H), 2.6 (br, 1 H), 6.8–7.6 (m, 5 H), 14.03 (s, 1 H)[j]	
9-Phenyliminobicyclo[4.2.1]nonane-1-carboxylic acid	28627-63-6	6.00[e]	1.0–2.7 (m, 12 H), 3.00 (br, 1 H), 6.7–7.7 (m, 5 H), 13.45 (s, 1 H)[j]	
9-Phenyliminobicyclo[3.3.1]nonane-1-carboxylic acid	28627-64-7	6.07[e]	1.0–2.8 (m, 12 H), 2.90 (br, 1 H), 6.7–7.6 (m, 5 H), 14.90 (s, 1 H)[j]	

[a] Infracord ($\pm$0.02 μ); liquid film unless otherwise noted. [b] In CCl_4 unless otherwise noted. [c] s, singlet; t, triplet; q, quartet; m, multiplet; br, broad. [d] G. Reddelien, *Ber.*, **42**, 4759 (1909); *ibid.*, **43**, 2476 (1910); *ibid.*, **46**, 2712 (1913); G. Reddelien and O. Meyn, *Ber. Deut. Chem. Gesell. B*, **53**, 345 (1920); *Justus Liebigs Ann. Chem.*, **388**, 187 (1912). [e] In KBr. [f] M. E. Kuhne, *J. Amer. Chem. Soc.*, **81**, 5400 (1959). [g] G. Opitz and A. Griesinger, *Justus Liebigs Ann. Chem.*, **665**, 101 (1965). [h] E. P. Blanchard, Jr., *J. Org. Chem.*, **28**, 1397 (1963). [i] P. Nelson and A. Pelter, *J. Chem. Soc.*, 5142 (1965). [j] Approximately 15% solution in $CDCl_3$.

ketopinic acid was prepared by refluxing the acid and aniline in chloroform solution in the presence of molecular sieves for 15 hr. The anils of the other keto acids here reported (bicyclo[4.2.1]- and bicyclo[3.3.1]nonan-9-one-1-carboxylic acids) are formed with 3 hr of refluxing and with 3 hr of shaking at room temperature, respectively.

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