cooled in an ice bath, and treated with 30 ml of 10% aqueous sulfuric acid. The benzene layer was washed with water and saturated salt solution, dried over magnesium sulfate and concentrated to dryness *in vacuo*. A small sample was dissolved in benzene and sampled by vpc. Three peaks were present in the following amounts and retention times: (a) 14.1%, 2 min; (b) 46%, 4.2 min; and (c) 39.8%, 6.7 min. The first peak represented unreacted 5-methoxyindanone-1; the remaining peaks (b and c) represented the *endo*- and *exo*-olefinic esters, **5a** and **5**, present in the ratio 54:46, respectively. The structural assignments were based on the uv and ir spectra (*cf*. Table I) of samples isolated by preparative vpc.

In another preparation the total Reformatsky product was distilled to yield 48% of crystalline *exo*-olefinic ester **5**, bp 134° (0.15 mm), which after recrystallization from hexane had mp 52–54° (lit.[5] mp 50–51°).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.39; H, 6.95.

Equilibration of Olefinic Ester Mixture (5 $\rightleftharpoons$ 5a).—A 212-mg sample of the total Reformatsky product described above was dissolved in 5 ml of absolute ethanol under a nitrogen atmosphere. A small precipitate formed after about 5–10 min and was then removed by filtration (2 mg). A vpc probe of the ethanol solution revealed three peaks as follows: 19.1%, 2.4 min (5-methoxy indanone-1); 16.6%, 5 min; and 64.1%, 7.7 min. Ethanol alone apparently shifts the *endo*/*exo* ratio to 20:80. A tiny speck of sodium metal was added and the solution stirred at room temperature. After 4 hr the reaction mixture was found by vpc to have three peaks as follows: 13.2%, 1.9 min; 9.5%, 3.9 min; and 77.2%, 6.1 min. The *endo*/*exo* ratio was now 10:90. Neither reflux nor extended (4 days) room temperature treatment changed this final ratio.

Saponification of Olefinic Ester Mixture.—The total product mixture from the above Reformatsky reaction (6.2 g, 0.027 mol) was dissolved in 50 ml of absolute ethanol and the system purged with nitrogen. Potassium hydroxide (2.64 g of 85% pellets, 0.04 mol) was added and the reaction mixture was stirred and refluxed for 3.5 hr. After cooling to room temperature the reaction mixture was diluted with 200 ml of water, the precipitated 5-methoxyindanone-1 removed by filtration, and the filtrate treated with charcoal and again filtered. The clear aqueous filtrate was chilled and acidified with 2.5 *N* hydrochloric acid and the resulting precipitate aged overnight at 0°. After filtering, washing with water, and drying, the acid product weighed 3.67 g (80% yield based on starting mixture containing 15% neutral indanone). The product was slurried at room temperature with 100 ml of ether, followed by filtration, and evaporation of the filtrate to yield two crystalline acids, 500 mg of ether-insoluble material, representing *ca*. 14% of the total acid, and 3.11 g of ether-soluble material, representing *ca*. 85% of the total acid. The ether insoluble acid, 5-methoxy-1-indanylideneacetic acid (**7**), was recrystallized from xylene to yield material with mp 192° dec (lit.[5] mp 192–196° dec).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.35; H, 6.07.

The ether-soluble acid, 5-methoxy-1-indenylacetic acid (**6**), was recrystallized from cyclohexane–benzene (6:1) to yield material with mp 95–100° (prisms formed from melt on continued heating melted at 185–190°).

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.71; H, 6.02.

Registry No.—**2**, 21779-31-7; **3**, 4709-56-2; **4**, 1620-00-4; **5**, 21779-34-0; **5a**, 21779-35-1; **6**, 21779-36-2; **7**, 21779-37-3.

A Simple Route to *cis*-Bicyclo[4.2.0]octan-2-one

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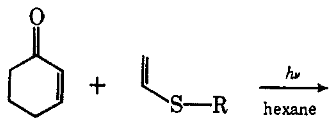
In the course of some related work, appreciable quantities of *cis*-bicyclo[4.2.0]octan-2-one (**1**) were needed. Although various procedures for the preparation of **1** from readily available starting materials had been reported,[1-3] they all involved many steps. Consequently, we felt the need for a shorter route to compound **1**.

We wish to report our results, which led to a convenient two-step process to *cis*-bicyclo[4.2.0]octan-2-one (**1**).

Recently, a general method for the preparation of cyclobutane derivatives was developed that involved the photochemical cycloaddition of olefins to α,β-unsaturated ketones.[3,4] Corey[5] reported that the photochemical reaction of 2-cyclohexen-1-one (**2**) with different olefins yielded various bicyclo[4.2.0]octan-2-one derivatives. However, the preparation of **1**, the parent member of this class of compounds, was not mentioned.

It has been postulated[5] that electron-releasing groups enhance the reactivity of the olefin in the photocycloaddition reaction with a cyclenone. Thus, it seemed probable that vinyl sulfides would behave accordingly. Irradiation of a hexane solution of 2-cyclohexen-1-one (**2**) and benzyl vinyl sulfide[6] (**3a**, R = CH_2Ph) and subsequent work-up yielded an adduct (**4a**, R = CH_2Ph). This adduct was assigned the "head-to-tail" structure **4** rather than the "head-to-head" structure **5** based on the analogous results with olefinic ethers obtained by Corey.[5] The correctness of this conclusion will not affect the utility of the synthetic route to **1**. Product **4a** exhibited two carbonyl frequencies in its



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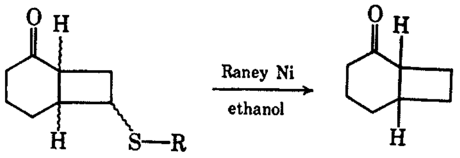
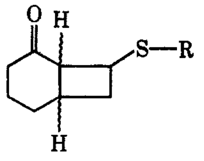
3a, R = CH_2Ph
b, R = n-C_4H_9
c, R = Ph



4a, R = CH_2Ph
b, R = n-C_4H_9
c, R = Ph
cis and *trans*

1, *cis*



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[1] A. C. Cope and R. W. Gleason, *J. Amer. Chem. Soc.*, **84**, 1928 (1962).

[2] G. Büchi and E. M. Burgess, *ibid.*, **84**, 3104 (1962).

[3] H. O. House and T. H. Cronin, *J. Org. Chem.* **30**, 1061 (1965).

[4] For an excellent review of this subject, see P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

[5] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

[6] H. J. Schneider, J. J. Bagnell, and G. C. Murdoch, *J. Org. Chem.*, **26**, 1980 (1961).

TABLE I

PHOTOLYSIS OF 2-CYCLOHEXEN-1-ONE (**2**) WITH VINYL SULFIDES (**3**)

Reactant, mmol **2**	Reactant, mmol **3**	Photolysis time, hr	Product, mmol **4**	Yield, %
51.0	**a**, 340	8[a]	**a**, 32.7	64
51.0	**b**, 339	5.5[a]	**b**, 31.7	62
51.1	**c**, 340	14.5[b]	**c**, 25.3	62[b,c]

[a] After this time, the photolysis was complete, as evidenced by the disappearance of the infrared band at 5.90 μ due to starting ketone **2**. [b] After this time, 20% of starting ketone **2** was still present (infrared). [c] Based on reacted ketone.

infrared spectrum, at 5.86 and 5.81 μ, due to the *cis* and *trans* fused isomers, respectively. Similar results were obtained with *n*-butyl vinyl sulfide[6] (**3b**, R = n-C_4H_9) and phenyl vinyl sulfide[7] (**3c**, R = Ph). The data are summarized in Table I.

Various workers[8] have reported successful desulfurization with Raney nickel[9] in the presence of carbonyl groups. Treatment of adduct **4a** with the moderately active W-2 catalyst[10] yielded a product consisting of one major component (75%) and three minor ones.[11] The major component was isolated by preparative vpc and its spectral characteristics were found to be identical with those of an authentic sample of *cis*-bicyclo[4.2.0]octan-2-one (**1**).[12] Isomerization had occurred prior to preparative vpc work, since the reaction product showed only one carbonyl band (5.85 μ), indicative of only one isomer, the more stable *cis* isomer. Corey[5] established that in the presence of either acid or base, the *trans* 6–4 fused ring juncture could be converted to the more stable *cis* form. In view of this and Fieser's observation[9] that traces of alkali remained adsorbed on the catalyst, the above result can be readily explained.

Based on the net amount of adduct **4a** used, the desulfurization step proceeded in 30% yield. In an effort to improve the yield, the following variations in the reaction conditions were studied (relative to the procedure described in the Experimental Section): reaction temperature, room temperature and 80–85°; reaction time, 0.25 and 1 hr; amount of catalyst, half and double amounts; type of catalyst, deactivated W-2,[13] Raney nickel Grade 28,[14] and Burgstahler's Raney nickel catalyst.[15] None of these variations resulted in an increase in the yield of **1**. Consequently, the above procedure was applied to adducts **4b** and **4c**. The results are tabulated in Table II. It is important to note that the optimum reaction conditions for the generation of the desired **1** are critical.[16]

TABLE II

RANEY NICKEL REDUCTION OF PHOTOADDUCTS (**4**)

Reactant	Mmol Start	Mmol Recovered	Mmol Net used	Product, mg	**1** in product (vpc),[a] %	Calcd yield of **1** (vpc), %
4a	16.26	3.90	12.36	630	75	30
4b	18.86	10.44	8.42	180	44	8.0
4c	16.83	4.40	12.43	690[b]	71[b]	32

[a] Calculated by area per cent. [b] This product showed an additional band at 5.96 μ (w) in the infrared. The apparent area per cent of the major peak was 79%, but, upon collection, the 5.96-μ band was still present. The impurity or impurities causing this band amounted to 10%, and consequently the "corrected" area per cent for **1** was 71%.

Since various workers[17] have reported that side reactions accompany desulfurization when other functional groups (such as the carbonyl moiety) are present, it was decided to protect the carbonyl group prior to the removal of the sulfide linkage. Treatment of adduct **4a** with ethylene glycol resulted in the formation of the ketal derivative (no ir absorption in the 3- or 5.8-μ region due to OH or C=O function, a multiplet centered at 3.8 ppm in the nmr spectrum attributable to the $-OCH_2CH_2O-$ group). Subsequent desulfurization with Raney nickel W-2 catalyst (no ir absorption in the 6.2–6.7- and 14.3-μ regions due to the phenyl group, no aromatic proton resonance in the nmr spectrum) was followed by regeneration of the carbonyl group by acid treatment. A product was obtained whose ir spectrum showed absorption at 5.83 μ (C=O) but whose nmr spectrum revealed the absence of the ethylenedioxy group. Vpc showed that this product consisted of 57% **1** and four other unidentified components. The overall yield of **1** from **4a** was not so good as that previously obtained.

Experimental Section

All boiling points are uncorrected. The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were taken on a Beckman IR-4 spectrophotometer. The nmr spectra were determined at 60 Mc with a Varian Model A-60 nmr spectrometer. The chemical-shift values are expressed relative to a TMS internal standard. The mass spectra were obtained with a CEC Model 21-103 mass spectrometer. Analyses by vpc were made using an F & M Model 810 gas chromatograph fitted with a 10 ft × 0.25 in. stainless steel column packed with 15.1% Apiezon M on Gas-Chrom P (the column had been cured at 280° for 72 hr). The preparative vpc work was carried out with an F & M Model 775 Prep Master instrument using an 8 ft × 0.75 in. stainless steel column packed with 15% Apiezon M on Gas-Chrom P.

General Procedure for Photochemical Reactions.—The apparatus consisted of a water-cooled Pyrex reaction vessel having a neck for a gas inlet tube and a neck to accommodate a quartz-jacketed, water-cooled immersion well with an Hanovia 450-W, high-pressure mercury vapor lamp surrounded by a Corex filter. An argon atmosphere was used.

A magnetically stirred solution of 2-cyclohexen-1-one (**2**) and vinyl sulfide (**3**) in 500 ml of *n*-hexane was irradiated (see Table I). The reaction was followed by removing an aliquot with a syringe and observing the disappearance of the infrared band at 5.90 μ (conjugated C=O) and the appearance of new peaks at 5.79 and 5.84 μ (nonconjugated C=O; these spectra were measured on the hexane solutions). Upon completion of the photolysis, the solvent was removed on a steam bath and the residue was distilled.

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[7] G. Pourcelot and P. Cadiot, *Bull. Soc. Chim. Fr.*, 3024 (1966).

[8] See, for example, S. Teich and D. Y. Curtin, *J. Amer. Chem. Soc.*, **72**, 2481 (1950); L. F. Fieser and W.-Y. Huang, *ibid.*, **75**, 5356 (1953); R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

[9] G. R. Pettit and E. E. van Tamelen, *Org. Reactions*, **12**, 356 (1962).

[10] R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N.Y., 1955, p 181.

[11] These have not been identified.

[12] We would like to express our thanks to Professor H. O. House, who provided us with the infrared, nmr, and mass spectra of authentic material.

[13] G. B. Spero, A. V. McIntosh, Jr., and R. H. Levin, *J. Amer. Chem. Soc.*, **70**, 1907 (1948); G. Rosenkranz, S. Kaufmann, and J. Romo, *ibid.*, **71**, 3689 (1949).

[14] Davison Chemical Division of W. R. Grace & Co., Baltimore, Md.

[15] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 729.

[16] Appreciable amounts of OH absorption and correspondingly decreased amounts of C=O absorption were observed with any of the following variations: higher temperature, longer reaction time, increased quantities of catalyst, or use of Burgstahler's catalyst.[15]

[17] See, for example, R. Mozingo, C. Spencer, and K. Folkers, *J. Amer. Chem. Soc.*, **66**, 1859 (1944).

Preparation of 4a.—A solution of 2-cyclohexen-1-one (**2**, 4.90 g, 51 mmol), benzyl vinyl sulfide[6] (**3a**, 51.00 g, 340 mmol), and hexane was irradiated for 8 hr. Solvent was removed and the unreacted **3a** (37 g) was recovered by distillation. The light yellow viscous residue was then distilled through a short-path still to give a light yellow forerun (0.85 g), bp 30–157° (0.03 mm), and a yellow main distillation fraction, **4a** (8.05 g, 64%), bp 157–162° (0.03 mm). The residue was a viscous orange oil (2.85 g). Adduct **4a** had ir (CCl_4) 5.81 and 5.86 μ; mass spectrum (70 eV) *m/e* 247 (strongest high mass peak due to a M + 1 species);[18] nmr (CCl_4) δ 7.18 (5 H, single aromatic proton peak), 3.20–3.80 (3 H, —CH_2SCH—), 2.50–3.20 (2 H, aliphatic CH at ring juncture), and 1.20–2.40 (8 H, aliphatic CH_2, complex multiplet).

Anal. Calcd for $C_{15}H_{18}OS$ (mol wt, 246.3): C, 73.13; H, 7.36; S, 13.01. Found: C, 72.93; H, 7.54; S, 13.21.

Preparation of 4b.—Adduct **4b** was made in the same way from 2 (4.90 g, 51 mmol) and *n*-butyl vinyl sulfide[6] (**3b**, 39.34 g, 339 mmol). Irradiation time was 5.5 hr. After recovery of **3b** (24 g), the yellow residue was distilled to give a forerun (0.96 g), bp 97–104° (0.01 mm), and a yellow main distillation fraction, **4b** (6.69 g, 62%), bp 104–107° (0.01 mm). The residue was a red oil (2.75 g). Adduct **4b** had ir (CCl_4) 5.81 and 5.86 μ; mass spectrum (70 eV) *m/e* 212 (M^+); nmr (CCl_4) δ 0.91 (CH_3, center of poorly resolved triplet), 2.46 (—CH_2S—, center of poorly resolved triplet), 1.18–2.30 (12 H, aliphatic CH_2), 2.50–3.20 (2 H, aliphatic CH at ring juncture), and 3.20–3.80 (—SCH<).

Anal. Calcd for $C_{12}H_{20}OS$ (mol wt, 212.3): C, 67.87; H, 9.49; S, 15.10. Found: C, 68.03; H, 9.75; S, 15.27.

Preparation of 4c.—Adduct **4c** was prepared in a similar fashion from **2** (4.91 g, 51 mmol) and phenyl vinyl sulfide[7] (**3c**, 46.24 g, 340 mmol). Irradiation time was 14.5 hr (see Table I, footnote *b*). After recovery of **3c** (36.5 g), the yellow residue was distilled to yield a forerun (0.61 g), bp 30–141° (0.02 mm), and a yellow main distillation fraction, **4c** (5.87 g, 62%, see Table I, footnote *c*), bp 141–147° (0.02 mm). The residue was a red oil (2.01 g). Adduct **4c** had ir (CCl_4) 5.81 and 5.86 μ; mass spectrum (70 eV) *m/e* 232 (M^+); nmr (CCl_4) δ 7.18 (5 H, complex multiplet, aryl CH), 3.20–4.15 (—SCH<, complex multiplet), 2.30–3.15 (2 H, aliphatic CH at ring juncture), and 1.30–2.30 (8 H, aliphatic CH_2).

Anal. Calcd for $C_{14}H_{16}OS$ (mol wt, 232.3): C, 72.38; H, 6.94; S, 13.80. Found: C, 72.37; H, 7.05; S, 14.06.

Bicyclo[4.2.0]octan-2-one (1). **A. By Desulfurization of Adduct 4a with Raney Nickel Catalyst.**—A solution of adduct **4a** (4.000 g, 16.26 mmol) in absolute ethanol (20 ml) was added to a suspension of W-2 Raney nickel catalyst[10] (20 g, decanted weight) in absolute ethanol (100 ml). The mixture was placed in an oil bath preheated to 65° and maintained at 62–67°, with stirring, for 0.5 hr. After cooling, the catalyst was removed by filtration and washed with an additional 50 ml of ethanol. The filtrates were combined and concentrated on a steam bath in order to remove the ethanol. Ether (100 ml) was added to the residue and the ethereal solution was washed with water (25 ml) and saturated NaCl solution (25 ml). After drying (Na_2SO_4), the ethereal solution was concentrated and the residue was distilled to give 630 mg of a colorless liquid, bp 67–71° (6 mm). The yellow residue (960 mg, 3.90 mmol) consisted entirely of recovered **4a**. The product exhibited four peaks on gas chromatography, one major (75%, area per cent) and three minor ones, and showed a single C=O band at 5.85 μ in the infrared spectrum. The major component (99.9% purity) was collected by preparative vpc (recovery yield was 86%) and its spectral characteristics were identical with those of an authentic sample of 1.[12]

B. By Desulfurization of Adducts 4b and 4c with Raney Nickel Catalyst.—Adducts **4b** and **4c** were treated in the same way as **4a**. The results are tabulated in Table II.

Registry No.—**1**, 21813-31-0; **4a**, 21779-15-7; **4b**, 21779-16-8; **4c**, 21779-17-9.

Acknowledgment.—The author wishes to thank Dr. Donald H. Wheeler for his helpful comments during the course of this work.

Heterolytic Fragmentation of 4-Substituted Decahydroquinolines

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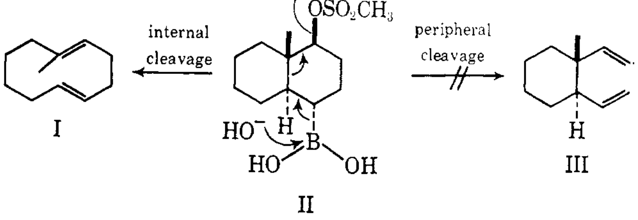
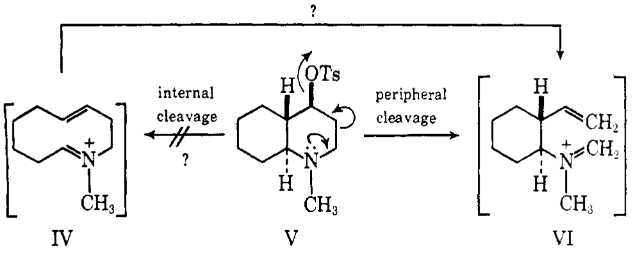
In the course of studies aimed at the development of new synthetic routes to medium ring compounds, we found that the boronate II underwent heterolytic fragmentation into 1-methyl-*trans,trans*-1,5-cyclodecadiene (I), the product of internal cleavage. None of the alternative (peripheral) cleavage product III could be detected.[1]



These findings contrast sharply with those of Grob and coworkers[2] who studied the seemingly analogous fragmentation reaction of the decahydroquinolyl tosylate V and concluded that the peripheral cleavage constituted the exclusive reaction pathway.



Since we could see no obvious basis for the divergent behavior of the two systems, we decided to explore fragmentations related to the amine system further. In particular, we wished to examine the possible isomerization of the medium-ring iminium salt IV into its cyclohexane counterpart VI, a reaction known to proceed with relative ease in related carbon systems.[3] Our findings, which we present at this time, show that the isomerization IV → VI is indeed facile, even at room temperature, and that the predominant, if not exclusive, fragmentation pathway of amine V must proceed by internal cleavage.

As our first objective we planned to study the solvolysis of the amine VII. We selected this amine in the hope that, if the medium-ring imine VIII was in fact a solvolysis product, it would show less tendency to rearrange to its isomer IX than the corresponding im-

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(18) This is not an uncommon occurrence. Cases have been reported where the M + 1 peak is stronger than the molecular ion peak (*e.g.*, oxonium ions). See K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 55–56.

(1) J. A. Marshall and G. L. Bundy, *Chem. Commun.*, 855 (1967).

(2) C. A. Grob, H. R. Kiefer, H. J. Lutz, and H. J. Wilkens, *Helv. Chim. Acta*, **50**, 416 (1967).

(3) *Cf.* C. A. Grob, H. Link, and P. W. Schiess, *ibid.*, **46**, 483 (1963).