vinylethylene oxide along with their implications concerning the conformations of this molecule.

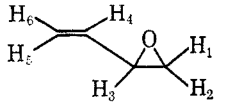
Spectra were analyzed in terms of chemical shifts and coupling constants with the aid of the computer program LAOCN3.[8] Results obtained from the analysis of vinylethyleneoxide (I) are given in Table I. Assuming I to be similar to vinylcyclopropane, the likely conformers of I are the *s-trans* and two *gauche* forms. Over the temperature range studied, there is rapid equilibrium between all the possible conformers, and a mean value for J_{34} is observed. This mean value of J_{34} is given by eq 1, where J_t and J_g are the *trans* and *gauche* coupling constants in individual conformers and p is the population of the *s-trans* conformer. If one assumes reasonable values for the individual coupling

$$J_{34} = pJ_t + J_t + (1 - p)J_g \qquad (1)$$

constants[6] and that the conformers are of equal energy, a value of 6.3 Hz is obtained for J_{34}.[9] The observed value of J_{34} indicates that $p > 0.33$, and furthermore, the increase in J_{34} on lowering the temperature also suggests that the *s-trans* conformer is the lower energy form. Using reasonable values for the individual couplings,[9] p is calculated to be 0.49 with an energy difference between the rotamers of 400 cal/mol.

TABLE I

NMR PARAMETERS FOR VINYLETHYLENE OXIDE AT VARIOUS TEMPERATURES



	+45[a]	+27	+16	−17	−45
V_1[b]	2.619	2.635	2.653	2.697	2.744
V_2	2.932	2.946	2.962	2.999	3.040
V_3	3.319	3.332	3.345	3.376	3.410
V_4	5.544	5.538	5.530	5.515	5.502
V_5	5.492	5.503	5.517	5.549	5.584
V_6	5.274	5.285	5.298	5.329	5.361
J_{12}[c]	5.36	5.28	5.29	5.12	5.08
J_{13}	2.60	2.63	2.62	2.67	2.67
J_{23}	4.09	4.01	4.09	4.08	4.13
J_{34}	7.58	7.69	7.83	8.06	8.40
J_{35}	−0.64	−0.62	−0.63	−0.55	−0.46
J_{36}	−0.61	−0.63	−0.59	−0.58	−0.64
J_{45}	17.24	17.17	17.22	17.11	17.06
J_{46}	10.54	10.40	10.42	10.44	10.30
J_{56}	1.28	1.22	1.28	1.28	1.30

[a] Temperature, °C. [b] In parts per million downfield from TMS. [c] In hertz.

In the vinyl coupling, the existence of a relationship between the coupling constants and substituent electronegativity has been adequately demonstrated.[10] All three couplings exhibit an approximately linear decrease as the electronegativity increases. Therefore, in I, as the population of the *s-trans* conformer increases, the electron-withdrawing effect of the ethylene oxide substituent should increase and the vinyl coupling should decrease. Examination of Table I shows that J_{45} and J_{46} do indeed decrease by 0.2 Hz, indicating a slightly greater electron-withdrawing effect of the ethylene oxide ring at lower temperatures (*i.e.*, an increased population of the *s-trans* conformer).

All chemical shifts are deshielded at lower temperatures, with the expection of V_4, which shows increased shielding (Table I). Similar results have been reported for vinylcyclopropane[5] and were interpreted in terms of the anisotropic diamagnetic polarizability of the cyclopropane ring, which has the large component normal to the ring. It has been suggested that the factors influencing the shifts in epoxides are similar to those in cyclopropane.[11,12] Therefore, the higher shielding of H_4 at low temperatures suggests that the location of H_4 is near the symmetry axis of the ring polarizability tensor (*i.e.*, the *s-trans* conformation). Therefore, the temperature variation of both chemical shifts and coupling constants indicates that the *s-trans* conformer is the lower energy conformation of vinylethylene oxide.

Experimental Section

Vinylethylene oxide, of commercial origin, was used without further purification. Samples were made up gravimetrically to 10 mol % in chloroform-*d* solution containing *ca.* 3% TMS as internal reference and lock signal source. Samples were degassed and sealed under vacuum.

Proton spectra were obtained using a Varian Associates HA-100 spectrometer with a probe temperature of 29°. Calibration of spectra was by the usual frequency difference technique. Line positions were obtained by averaging the results of two upfield and two downfield scans with a scan rate of 0.05 Hz/sec. Temperatures for the variable-temperature experiments were calibrated using the standard methanol and ethylene glycol samples.

Registry No.—Vinylethylene oxide, 930-22-3.

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[8] A. A. Bothner-By and S. M. Castellano, Mellon Institute, Pittsburgh, Pa., 1966.

[9] Calculated assuming J_t = 12.0 Hz and J_g = 3.5 Hz. The value of J_{34} will change slightly depending upon the values choosen for J_t and J_g.

[10] C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

[11] C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **32**, 1378 (1960).

[12] B. P. Dailey, A. Gawer, and W. C. Neikam, *Discussions Faraday Soc.*, **34**, 18 (1962).

Structure of the Indenylacetic Acids

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The reported literature on the 1-indenylacetic acids and their esters is ambiguous with regard to the α,β *vs.* β,γ position of the double bond in the various synthetic species prepared. The earlier workers[1,2] were not in a position to make completely unequivocal assignments, whereas in more recent times an incomplete analysis of the pertinent systems has left uncertainty in this area.[3-5] Since these systems provide intermediates of potential synthetic consequence, we undertook a clarification of the question of the relative double-bond position.

Ahmed and Campbell[3] had described the structure of the unsaturated acid derived from Reformatsky reaction of indanone-1 (**1**) with ethyl bromoacetate followed by saponification to be entirely the *endo* product,

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[1] J. Thiele and M. Ruediger, *Ann. Chem.*, **347**, 282 (1906).

[2] J. von Braun, E. Danziger, and Z. Koehler, *Ber.*, **50**, 56 (1917).

[3] H. Ahmed and N. Campbell, *J. Chem. Soc.*, 4115 (1960).

[4] D. A. H. Taylor, *ibid.*, 2805 (1960).

[5] L. Novak and M. Protiva, *Collect. Czech. Chem. Commun.*, **23**, 663 (1958).

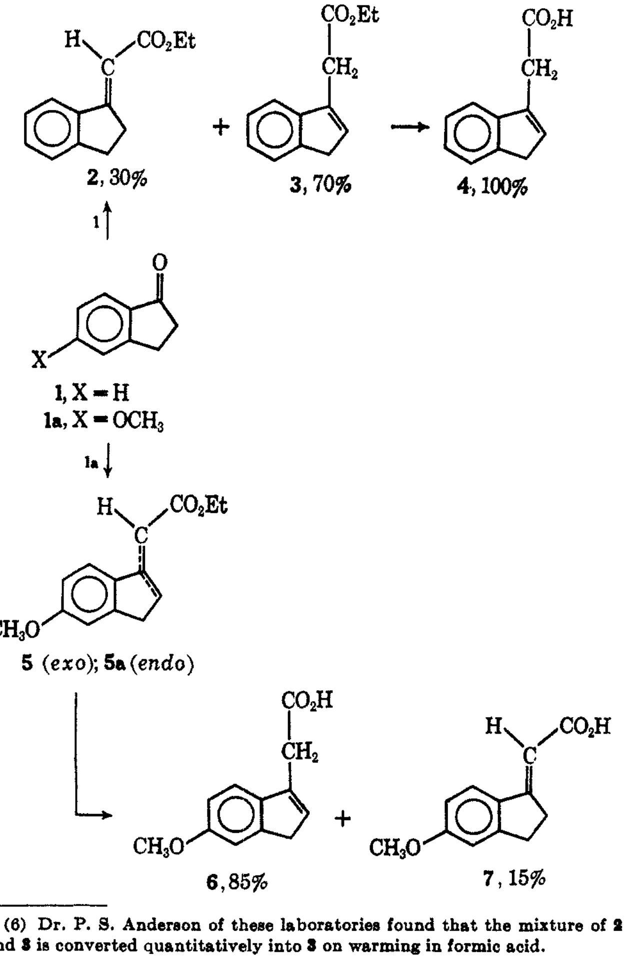
namely, 1-indenylacetic acid (**4**). We have confirmed this observation but in addition have established that the precursor ester, in fact, is a 30:70 kinetic[6] mixture of *exo* and *endo* isomers **2** and **3**. These esters were isolated in pure form by preparative vpc and characterized by their distinctive infrared C═O absorptions at 5.90 and 5.78 μ as well as their respective ultraviolet spectra (*cf.* Table 1).

TABLE I[a]

Compound	Uv (CH_3OH), λ_{max}, mμ (ε, mol)	Ir ($CHCl_3$), λ_{max}, μ
2 (*exo*)	285 (16,100)	5.90
3 (*endo*)	253 (9,820)	5.78
4 (*endo*)	253 (9,720)	5.82
5 (*exo*)	321 (25,715)	5.91
5a (*endo*)	262.5	5.80
6 (*endo*)	262.5 (12,420)	5.84
7 (*exo*)	320 (19,200)	5.99[b]

[a] Comparison of the λ_{max} and ε (mol) values of the *exo* compounds with those reported by E. Havinga and R. J. F. Nivard [*Rec. Trav. Chim. Pays-Bas* **67**, 846 (1948)] for the corresponding *cis*- and *trans*-tetralideneacetic acids makes it apparent that the former systems possess *trans* structures as formulated. [b] Nujol mull.

Novak and Protiva[5] in a similar manner isolated a crystalline unsaturated ester, mp 50–51°, in 50% yield from 5-methoxyindanone-1, to which they correctly assigned the *exo* structure **5** in agreement with our findings. This assignment, however, was based on earlier work by von Braun, *et al.*,[2] in the demethoxy series which in the meantime has been shown to be incorrect.[3] We have found the total unsaturated ester product derived directly from **1a** to be a nearly 50:50 mixture of *exo* (**5**) and *endo* (**5a**) isomers characterized by their infrared C═O absorptions at 5.92 and 5.80 μ, respectively (*cf.* Table I). That this mixture represents a kinetic product was demonstrated by isomerization into a 90:10 (*exo–endo*) product with ethanolic sodium ethoxide. The functional role in this case of the methoxyl group in providing an extended conjugated system is consonant with these results. Saponification of ester **5** yielded a mixture of crystalline acids **6** and **7** in an approximate ratio of 85:15. These acids were readily separated on the basis of the ether solubility of **6** and the virtually complete insolubility of **7** in the same solvent. By contrast Novak and Protiva reported only one acid from the saponification which is, in fact, the less soluble minor component, 5-methoxy-1-indanylideneacetic acid (**7**), of the actual mixture.



It is apparent from the foregoing that the position of the double bond (α,β or β,γ) in the 1-indenylacetic acid systems is a logical if not qualitatively predictable function of both the character of the carboxylate group as well as the substitution in the aromatic ring.

Experimental Section

All melting points, except where otherwise indicated, are capillary melting points and are uncorrected. Vapor phase chromatography was carried out on a Varian Aerograph (series 200) instrument using a 5 ft × 0.25 in. column with 20% SE-30/Chrom W packing at a column temperature of 200° for the unmethoxylated series and 255° for the methoxylated series.

Reformatsky Reaction on Indanone-1.—Granular zinc metal (2.4 g), activated by washing with 2% aqueous HCl followed by water, ethanol, acetone, and ether and drying, was covered with 10 ml of dry benzene under nitrogen. A solution of 4.0 g (0.030 mol) of indanone-1 and 6.0 g (0.036 mol) of ethyl bromoacetate in 40 ml of dry benzene was added over 30 min with warming. The mixture was stirred and refluxed for 2 hr. It was then 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 *in vacuo* to an orange oil which was distilled to yield 4.12 g (68%), bp 130–140° (4 mm). This product was shown by vpc analysis to consist of two components, in the ratio of 70:30, respectively. Thin layer chromatography did not resolve this mixture; however, by using preparative vpc technique, a pure sample of each component was obtained for physical measurements. Component A (retention time 8.5 min) was the *endo* isomer **3** (*cf.* Table I). Component B (retention time 10.8 min) was the *exo* isomer **2** (*cf.* Table I). The mixture consisted therefore of 70% *endo* ester **3** and 30% *exo* ester **2**.

Saponification of the Olefinic Ester Mixture (2 + 3 → 4).—The total distilled mixture of **2** and **3** (4.12 g, 0.0203 mol) was dissolved in 30 ml of absolute ethanol and treated with solid potassium hydroxide (1.97 g, 0.03 mol). The reaction mixture was then refluxed with stirring, under nitrogen, for 2.5 hr. During the last 15 min of reflux about 15 ml of ethanol was removed by distillation. The reaction mixture was then cooled to room temperature, diluted with 130 ml of water, treated with charcoal, and filtered through Celite. The combined filtrate and water washes were chilled to 10–15°, acidified with 2.5 *N* hydrochloric acid, and kept overnight at 0°. The precipitated acid was filtered, washed with water, and dried under vacuum at 55° to yield 2.85 g (80%) of crude crystalline 1-indenylacetic acid (**4**), mp 80–83° (micro hot stage). A 200-mg sample was recrystallized from hexane to yield 154 mg, mp 88–90° (lit.[3] mp 95–96°). The mother liquors (crystalline) were identical in their ir spectrum with the first crop, exhibiting no conjugate C═O and, hence, only *endo* acid **4** was produced.

Reformatsky Reaction on 5-Methoxy Indanone-1.—Granular zinc metal (2.46 g, 0.0376 g-atom), activated as reported above, was covered with 5 ml of dry benzene under nitrogen. A solution of 4.97 g (0.0306 mol) of 5-methoxyindanone-1 and 6.15 g (0.0368 mol) ethyl bromoacetate in 45 ml of dry benzene was added as described above, to the stirred suspension of zinc metal. The reaction mixture was stirred and refluxed for an additional 2 hr,

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[6] Dr. P. S. Anderson of these laboratories found that the mixture of **2** and **3** is converted quantitatively into **3** on warming in formic acid.

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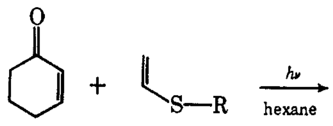
In the course of some related work, appreciable quantities of *cis*-bicyclo[4.2.0]octan-2-one (**1**) were needed. Although various procedures for the preparation of **1** from readily available starting materials had been reported,[1–3] they all involved many steps. Consequently, we felt the need for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

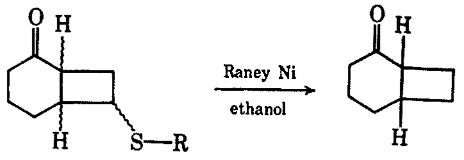
Recently, a general method for the preparation of cyclobutane derivatives was developed that involved the photochemical cycloaddition of olefins to α,β-unsaturated ketones.[3,4] Corey[5] reported that the photochemical reaction of 2-cyclohexen-1-one (**2**) with different olefins yielded various bicyclo[4.2.0]octan-2-one 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



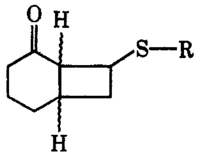
2

3a, R = CH_2Ph
b, R = $n\text{-}C_4H_9$
c, R = Ph



4a, R = CH_2Ph
b, R = $n\text{-}C_4H_9$
c, R = Ph
cis and *trans*

1, *cis*



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[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).

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