sulfides, such as methyl, *n*-butyl and 2-phenylethyl, resulted in polymeric decompositions from which no products were isolated.

Potassium metal (8.7 g, 0.2 g-atom) was added in small pieces to a rapidly stirred solution of 0.5 g of ferric nitrate nonahydrate in 250 ml of condensed ammonia. After the blue color was discharged, 19 g (0.10 mole) of phenyl 3-chloropropyl sulfide in 250 ml of dry ether was slowly added. The ammonia was allowed to evaporate slowly from the solution, then the solution was refluxed for 3 hr. Upon cooling, the reaction mixture was hydrolyzed with water and filtered, and the ether layer was separated. The aqueous layer was extracted with ether; the ether solutions were combined, washed with water, dried ($CaCl_2$), and evaporated. The residue was distilled, yielding 11.7 g (79%) of phenyl cyclopropyl sulfide, bp 62–63° (1.0 mm), $n^{25}D$ 1.5801.

Anal. Calcd for $C_9H_{10}S$: C, 71.95; H, 6.71; S, 21.34. Found: C, 72.05; H, 6.75; S, 21.60.

A portion of this sulfide was oxidized to the known sulfone with 30% H_2O_2 in glacial acetic acid. The product melted at 35.5–36.5°, bp 129–131° (1.0 mm) (lit.[1,20] bp 130–135° (0.5 mm), mp 35–36°).

A similar cyclization procedure using *p*-tolyl 3-chloropropyl sulfide gave a 58% yield of *p*-tolyl cyclopropyl sulfide, bp 87° (2.3 mm), $n^{20}D$ 1.5713.

Anal. Calcd for $C_{10}H_{12}S$: C, 73.57; H, 6.79; S, 19.64. Found: C, 73.38; H, 6.54; S, 19.40.

α-Substituted Tetrahydrothiophenes by Cyclization.—Benzylic 3-chloropropyl sulfides undergo intramolecular alkylation to form 2-phenyltetrahydrothiophenes with potassium amide in ammonia–ether. The procedure above for preparation of aryl cyclopropyl sulfides by cyclization was used with the reflux period increased to 16 hr. In this manner 20.9 g of benzyl 3-chloropropyl sulfide was converted to 15.5 g of 2-phenyltetrahydrothiophene (95% yield), bp 118–120° (5 mm), $n^{25}D$ 1.5829 (lit.[12] bp 105–106° (3 mm), $n^{20}D$ 1.5839. A portion of this tetrahydrothiophene was oxidized to 2-phenyltetrahydrothiophene-1,1-dioxide with 30% H_2O_2 in glacial acetic acid, mp (methanol) 65–65.5°.

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.22; H, 6.12. Found: C, 61.03; H, 5.88.

Similarly 21.5 g (0.10 mole) of 1-phenethyl 3-chloropropyl sulfide was cyclized to give 13.6 g (76% yield) of 2-methyl-2-phenyltetrahydrothiophene, bp 90° (0.5 mm).

Anal. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.92; S, 17.99. Found: C, 73.99; H, 7.72; S, 17.98.

(20) H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **82**, 2505 (1960).

A portion of this 2,2-disubstituted tetrahydrothiophene was oxidized to 2-methyl-2-phenyltetrahydrothiophene-1,1-dioxide using 30% H_2O_2 in glacial acetic acid, mp 54–55°. 2-Phenyltetrahydrothiophene-1,1-dioxide was methylated to give the same compound, as follows: a solution of 0.80 g (0.004 mole) of 2-phenyltetrahydrothiophene-1,1-dioxide in 40 ml of anhydrous dimethylformamide was treated with 3.6 ml (0.008 mole) of sodium hydride–nujol dispersion. After 3.5 hr, 0.84 g (0.006 mole) of purified methyl iodide in anhydrous dimethylformamide was added to the reaction mixture. After 5 hr of additional stirring, the reaction was hydrolyzed with water and extracted with chloroform. The chloroform solution was washed with water, dried (Na_2SO_4), and evaporated. The residue was washed with ether, leaving 0.31 g (36% yield) of product, mp 53–55°, mmp 53–55°.

Registry No.—**1**, 14633-28-4; **2**, 14633-29-5; **3**, 14633-30-8; **4**, 14633-31-9; **5**, 14633-32-0; **7**, 4911-65-3; **8**, 3147-30-6; **9**, 14633-35-3; **10**, 14633-36-4; **11**, 14856-63-4; **12**, 13012-59-4; **13**, 14633-38-6; **14**, 14633-39-7; **15**, 14633-40-0; **16**, 14633-41-1; **17**, 14633-42-2; **18**, 14633-43-3; *n*-butyl 5-hydroxypentyl sulfide, 14633-44-4; *n*-butyl 5-hydroxypentyl sulfone, 14633-45-5; **19**, 14633-46-6; **20**, 14633-47-7; **21**, 14633-48-8; **22**, 14633-49-9; **23**, 14633-50-2; cyclopentyl sulfide, 1613-51-0; 2-phenyltetrahydrothiapyran 1,1-dioxide, 14856-64-5; 2-phenyltetrahydropyran, 4203-44-5; 2-phenyltetrahydrothiopyran, 1622-06-6; phenyl cyclopropyl sulfide, 14633-54-6; *p*-tolyl cyclopropyl sulfide, 14633-55-7; 2-phenyltetrahydrothiophene, 2060-65-3; 2-phenyltetrahydrothiophene 1,1-dioxide, 13557-28-3; 2-methyl-2-phenyltetrahydrothiophene, 14856-67-8; 2-methyl-2-phenyltetrahydrothiophene 1,1-dioxide, 14633-57-9.

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Perhydroindan Derivatives. VIII. Bridgehead Alkylation *via* Cyclopropane Intermediates[1a]

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The copper-catalyzed decomposition of ethyl diazoacetate in the presence of enol acetate **1**, allylic acetate **6c**, and olefin **12** has been investigated. The cyclopropyl ester adducts **2** (from **1**) and **7a** (from **6c**) were converted into derivatives of 3a-perhydroindanylacetic acid having a *cis* ring fusion. The reductive cleavage of the adducts **13c** (from **12**) with lithium and ammonia gave a mixture of perhydroindanylacetic acids **11** and **15** in which the isomer **15** with a *trans* ring fusion predominated.

Since the alkylations of the enolate anions (*e.g.*, **1b**) derived from perhydroindan-1-one and several derivatives yield predominantly *cis*-fused perhydroindanone products (*e.g.*, **3b**),[2] we were led to examine other synthetic routes which might be used to introduce a bridgehead substituent into a preformed perhydroindan derivative to form a *trans*-fused product (*e.g.*, **4**). The copper-catalyzed reaction of ethyl diazoacetate with olefins to form cyclopropane derivatives[3] was selected for study with the olefins **1a**, **6c**, and **12** because it seemed probable that each of the initial cyclopropane derivatives **2**, **7**, and **13** could be converted to a perhydroindane with a bridgehead substituent. This paper reports the results of this study and the determination of the stereochemistry for the major alkylated product in each case.

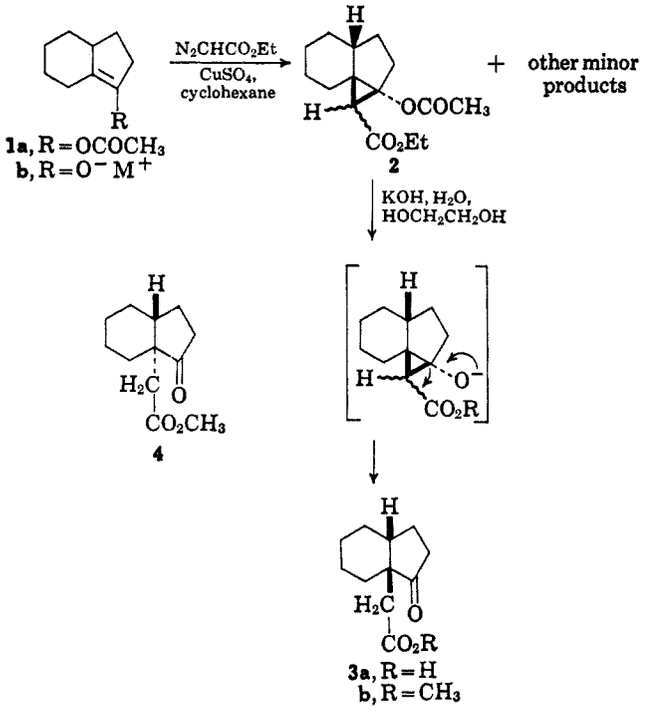
Reaction of the enol acetate **1a** (Scheme I) with

(1) (a) This research has been supported by a grant from the National Institutes of Health (No. GM-08761); (b) National Institutes of Health Predoctoral Fellow, 1964–1967.

(2) H. O. House and C. J. Blankley, *J. Org. Chem.*, **32**, 1741 (1967), and references cited therein.

(3) For general reviews of this reaction, see (a) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, pp 108–156; (b) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 95–143; (c) W. Ried and H. Mengler, *Fortschr. Chem. Forsch.*, **5**, 1 (1965).

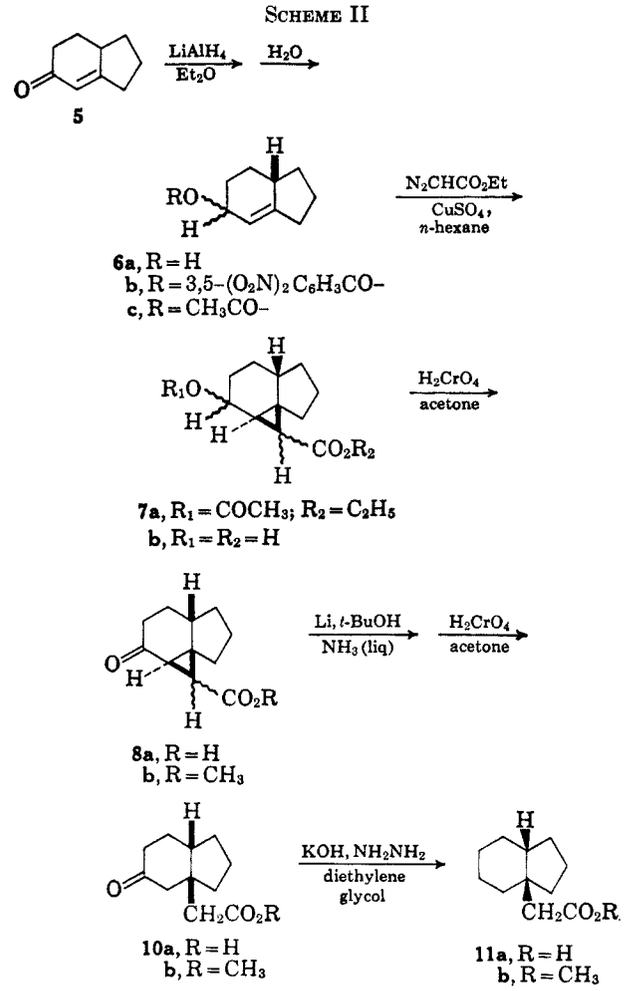
SCHEME I



ethyl diazoacetate in the presence of anhydrous copper(II) sulfate[4] yielded two major adducts, each of which when saponified with aqueous alkali[5] gave the known[2] *cis*-fused keto acid **3a**. We therefore conclude that the predominant stereoisomers of the cyclopropane intermediate are those indicated in structure **2** which have resulted from addition of the reactive intermediate, presumably either the copper derivative of a diazo compound[6] or an ethoxycarbonylcarbene complexed with a copper derivative,[7] to the less hindered side of the carbon–carbon double bond. This type of stereoselectivity has been observed previously in such reactions, particularly in cases where the reactive intermediate is generated in the presence of a copper catalyst.[3b,8]

Since our initial study of the reaction of ethyl diazoacetate with the unsaturated ketone **5** apparently led to a rather complex mixture of products as might be expected,[3b,4a,9] the ketone was converted into the allylic alcohols **6a** and then the corresponding allylic acetates **6c** (Scheme II) for further study.[10] The copper(II) sulfate

SCHEME II



catalyzed reaction of the allylic acetate **6c** with ethyl diazoacetate produced a mixture of stereoisomeric acetoxy esters **7a** which was saponified and oxidized to form one major keto acid **8a**. Reductive cleavage of the keto acid **8a** followed by oxidation of the intermediate hydroxy acid yielded the keto acid **10a** identified as the known[11] keto ester **10b**. The presence of a *cis* ring fusion in this material was further confirmed by the Wolff–Kishner reduction of the keto acid **10a** to form, after esterification, the known[2,11] *cis* ester **11b**. These transformations indicate that the predominant cyclopropyl ester products **7a** also have the indicated *cis*-fused perhydroindan ring, again suggesting attack of

(4) Earlier reports of the copper-catalyzed reaction of enol acetates with ethyl diazoacetate include (a) M. S. Kharasch, T. Rudy, W. Nudenberg, and G. Büchi, *J. Org. Chem.*, **18**, 1030 (1953); (b) K. B. Wiberg and R. K. Barnes, *ibid.*, **23**, 299 (1958); (c) B. R. Davis and P. D. Woodgate, *J. Chem. Soc., Sect. C*, 2006 (1966).

(5) The base-catalyzed opening of cyclopropanol derivatives has been discussed by (a) P. S. Wharton and T. I. Bair, *J. Org. Chem.*, **31**, 2480 (1966); (b) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Am. Chem. Soc.*, **88**, 3343 (1966); (c) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *ibid.*, **88**, 3354 (1966).

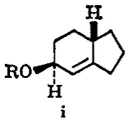
(6) *Cf.* (a) U. Schöllkopf and N. Rieber, *Angew. Chem. Intern. Ed. Engl.*, **6**, 261 (1967); (b) F. Gerhart, U. Schöllkopf, and H. Schumacher, *ibid.*, **6**, 74 (1967); (c) P. Yates and F. X. Garneau, *Tetrahedron Letters*, No. 1, 71 (1967); (d) H. Kwart and A. A. Kahn, *J. Am. Chem. Soc.*, **89**, 1950, 1951 (1967).

(7) See (a) D. O. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964); (b) R. Huisgen, G. Binsch, and L. Ghosez, *Chem. Ber.*, **97**, 2628 (1964); (c) I. Moritani and N. Obata, *Tetrahedron Letters*, No. 32, 2817 (1965); (d) H. Nozaki, S. Moriuti, H. Takaya, and R. Noyori, *ibid.*, No. 43, 5239 (1966); (e) R. K. Armstrong, *J. Org. Chem.*, **31**, 618 (1966).

(8) (a) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960); (b) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961); (c) R. R. Sauers and P. E. Sonnet, *Tetrahedron*, **20**, 1029 (1964); (d) K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Letters*, No. 21, 1553 (1965); (e) F. W. Breitbeil, J. J. McDonnell, T. A. Marolewski, and D. T. Dennerlein, *ibid.*, No. 51, 4627 (1965); (f) I. A. D'yakonov, V. V. Razin, and M. I. Komendantov, *ibid.*, No. 11, 1127 (1966); (g) J. A. Berson and E. S. Hand, *J. Am. Chem. Soc.*, **86**, 1978 (1964).

(9) (a) W. T. Tai and E. W. Warnhoff, *Can. J. Chem.*, **42**, 1333 (1964); (b) I. A. D'yakonov, I. N. Somin, and M. I. Komendantov, *J. Gen. Chem. USSR*, **23**, 1721 (1953).

(10) A mixture of alcohols **6a** containing a major and a minor stereoisomer was obtained in this reduction and converted into a comparable mixture of acetates **6c**. Although analogy with the previous reduction of the homologous octalones [J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964), and H. B. Henbest and J. McEntee, *J. Chem. Soc.*, 4478 (1961)] would suggest that the major alcohol and acetate used in our study have the stereochemistry indicated in formula i, we have no evidence to confirm this assignment and were not successful in separating each pure allylic acetate for study.

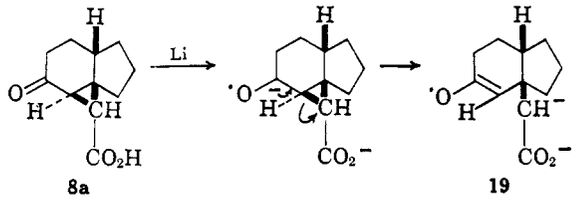


i

(11) H. O. House, S. G. Boots, and V. K. Jones, *J. Org. Chem.*, **30**, 2519 (1965).

the reactive intermediate from ethyl diazoacetate at the less hindered side of the carbon–carbon double bond in the allylic acetate **6c**.

It is of interest to note that the reductive cleavage[12] of the cyclopropyl ketone **8a** occurs in a single direction. This result may be attributable to the opening of the radical anion (or dianion) intermediate to form the anion **19** stabilized by an adjacent carboxylate function.[13a]



8a **19**

Alternatively, the direction of bring opening may be determined by cleavage of the cyclopropane carbon–carbon bond which is best situated to overlap with the π orbital of the carbonyl function.[12d]

Reaction of the tetrasubstituted olefin **12** (Scheme III) with ethyl diazoacetate in the presence of copper(II) sulfate yielded a mixture of the stereoisomeric cyclopropyl esters **13a** which was saponified to give the two acids **13b**. Reductive cleavage[12] of either of the corresponding methyl esters **13c** (the acids **13b** were inert) gave a crude mixture of alcohols **14** which was oxidized to a 4:1 mixture of the *trans* (**15**) and *cis* (**11**) acid derivatives. The stereochemistry of the previously unknown *trans* ester **15b** was established by the indicated Barbier–Wieland degradation to the known[13b] *trans* ester **17b**.

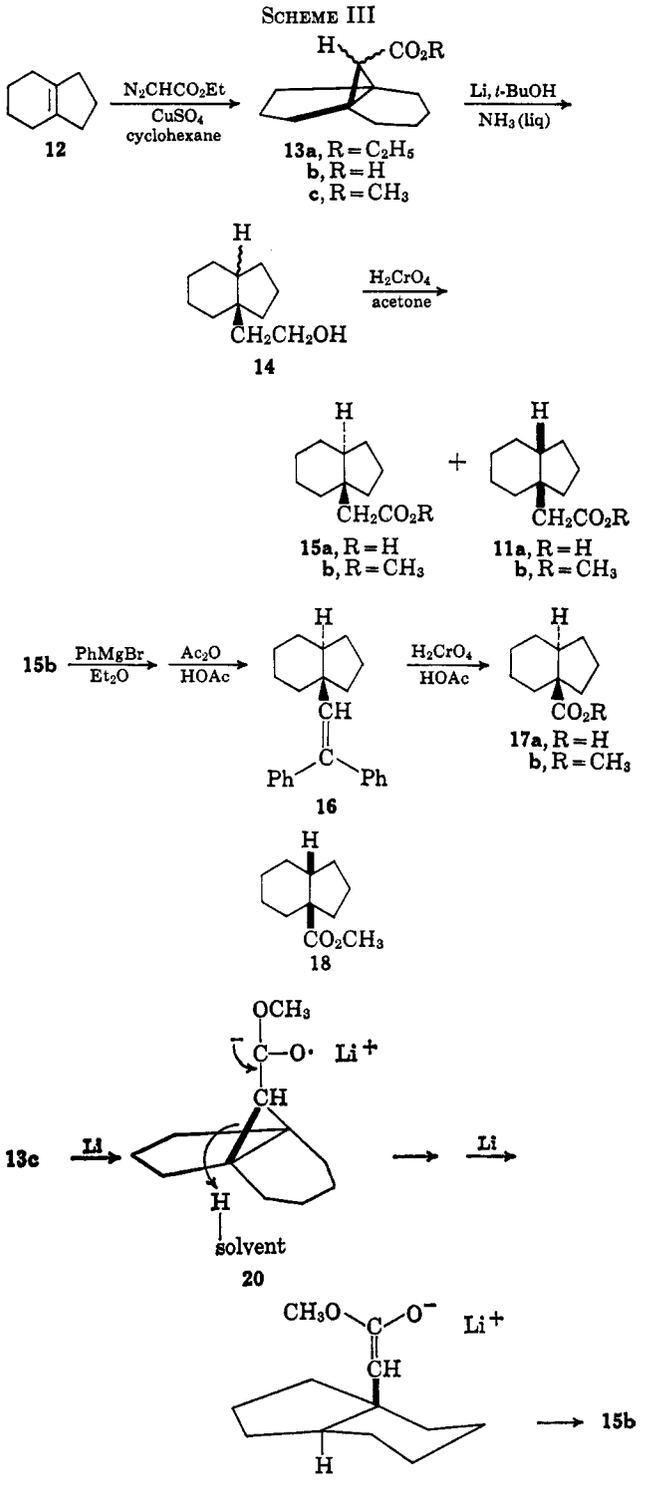
The over-all conversion **12** → **13** → **15** represents the most stereoselective process we have yet found for the introduction of a bridgehead substituent into a preformed perhydroindan derivative to form a *trans*-fused system. The sequence would appear to involve the transfer of hydrogen (either a hydrogen atom or a proton) to the backside of one of the cyclopropane carbon atoms (illustrated as **20** for a proton transfer) either concurrent with or possibly following cleavage of the cyclopropane carbon–carbon bond. Although there are examples of predominant inversion of configuration accompanying the protonation of carbanions generated in polar, protic media,[14] it is not clear at the present whether the process described here involves transfer of hydrogen to a developing carbanion or a developing carbon free radical. In a preliminary examination, we found the proportions of the two isomeric cleavage products **11** and **15** to be influenced little if at all by the presence of *t*-butyl alcohol in the reduction medium. However, no definitive answer to the mechanism of the cleavage process can be provided until more experimental data are available.

(12) For other examples of the reductive cleavage of cyclopropyl ketones with alkali metals in liquid ammonia, see ref 11 and (a) R. van Volkenburgh, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 3595 (1949); (b) N. A. LeBel and R. N. Liesemer, *ibid.*, **87**, 4301 (1965); (c) T. Norin, *Acta Chem. Scand.*, **19**, 1289 (1965); (d) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966); (e) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967).

(13) (a) Although early studies [R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953)] probably overestimated the acidity of the α proton of the acetate anion, it is clear from later work [*e.g.*, P. L. Creger, *ibid.*, **89**, 2500 (1967)] that the enolate anions derived from carboxylic acid salts have reasonable stability. (b) H. O. House and G. A. Frank, *J. Org. Chem.*, **30**, 2948 (1965).

(14) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, pp 137–173.

SCHEME III



Experimental Section[15]

Reaction of Ethyl Diazoacetate with the Enol Acetate 1a.—To a mixture of 2.12 g (11.8 mmoles) of the enol acetate **1a**,[3] 199 mg

(15) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 infrared recording spectrophotometer fitted with a grating. Unless otherwise stated the ultraviolet spectra were determined in 95% ethanol with a Cary recording spectrophotometer, Model 14. The nmr spectra were determined at 60 Mc with a Varian Model A-60 nmr spectrometer. The chemical-shift values are expressed either in cycles per second or δ values (parts per million) relative to a tetramethylsilane internal standard. The mass spectra were obtained with a CEC Model 21-130 or a Hitachi (Perkin-Elmer) mass spectrometer. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

of anhydrous $CuSO_4$,[16] and 5 ml of refluxing cyclohexane was added, dropwise and with strring over a 1.2-hr period, a solution of 4.71 g (41.3 mmoles) of ethyl diazoacetate in 30 ml of cyclohexane. After the addition was complete, refluxing and stirring were continued for an additional 1.5 hr and then the reaction mixture was filtered, dried, and concentrated under reduced pressure. Fractional distillation of the residual yellow liquid (5.10 g) separated 1.48 g of low-boiling products fractions (bp 50–106° (0.06–0.07 mm)) which contained[17] components with the retention times of diethyl fumarate, diethyl maleate, and the enol acetate **1a** and 1.90 g (61%) of fractions, bp 106–150° (0.08–0.2 mm), which partially solidified on standing and contained[17] primarily the two stereoisomers of the acetoxy ester **2** accompanied by 5% or less of several minor components. Fractional crystallization from methanol separated the major stereoisomer of ester **2** (eluted first) as colorless prisms: mp 98.5–100°; infrared (CCl_4), 1755 and 1730 cm^{-1} (two ester C=O); nmr (CCl_4), δ 4.00 (2 H quartet, J = 7 cps, OCH_2), 2.00 (3 H singlet, $OCOCH_3$), 1.21 (3 H triplet, J = 7 cps, CH_3C), and 1.0–2.7 (14 H multiplet, aliphatic CH); mass spectrum, no molecular ion peak, abundant fragment peaks at m/e 168, 151, 91, 55, 43, 41, and 39.

Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.42; H, 8.20.

The mother liquors remaining after separation of the crystalline isomer from several reactions were concentrated and chromatographed on neutral alumina (activity grade III). The early fractions, 1.50 g of colorless liquid eluted with benzene–hexane mixtures, contained[17] one major (eluted second) and two minor components. A collected[17] sample of the major component was a colorless liquid believed to be a second stereoisomer of the ester **2**: infrared (CCl_4), 1740 cm^{-1} (broad, ester C=O); nmr (CCl_4), δ 4.03 (2 H quartet, J = cps, $-OCH_2-$), 2.53 (3 H singlet, CH_3COO), 1.22 (3 H triplet, J = 7 cps, CH_3C), and 1.0–2.9 (14 H, multiplet, aliphatic CH).

After a mixture of 216 mg (0.81 mmole) of the crystalline ester **2** and 146 mg (2.6 mmoles) of potassium hydroxide in 10 ml of aqueous ethylene glycol (1:1 v/v) had been refluxed for 5 hr, the resulting solution was acidified and extracted with ether. The ethereal extract was washed with water and aqueous NaCl and then dried and concentrated to leave 146 mg (92%) of the crude acid **3a**, mp 95–99° (lit.[2] mp 100.5–102.5°). Esterification with excess ethereal diazomethane yielded 120 mg (70% over-all) of the keto ester **3b** as a pale yellow oil identified with an authentic sample[2] by comparison of infrared spectra and gas chromatographic retention times. The same saponification precedure was applied to 511 mg of the crude liquid product (presumably the second stereoisomer of **2**) separated by columu chromatography. The crude acidic product (402 mg of semisolid material) was esterified with excess ethereal diazomethane to yield 351 mg of liquid product which contained[18] *ca.* 83% of the keto ester **3b** (first eluted) accompanied by *ca.* 17% of an unknown component eluted second. A collected[18] sample of the major component was identified with the *cis*-keto ester **3b** by comparison of gas chromatographic retention times and infrared and mass spectra. The infrared and mass spectra of a collected[18] sample of the minor component differed from that obtained[2] for *trans*-keto ester **4**.

Preparation of the Tetrahydroindanol Derivatives 6.—The α,β-unsaturated ketone **5** was prepared as previously described.[19,20] A solution of 8.42 g (62 mmoles) of this ketone **5** in 20 ml of ether was added, dropwise and with stirring over a 30-min period, to a cold (0°) solution of 1.29 g (34 mmoles) of $LiAlH_4$ in 30 ml of ether and the resulting mixture was stirred at room temperature for 1 hr and then partitioned between ether and cold, dilute aqueous HCl. The ethereal layer was washed successively with aqueous $NaHCO_3$ and aqueous NaCl and then dried and concentrated. Distillation of the residual liquid separated 6.65 g (75%) of the alcohol **6a** (mixture of stereoisomers): bp 65–69° (0.28 mm); $n^{26}D$ 1.5130. A comparable sample, bp 63–65° (0.04 mm), was obtained in 57% yield by the reduction of the ketone **5** with lithium tri-*t*-butoxyaluminum hydride in tetrahydrofuran solution. Redistillation afforded the alcohol **6a** (mixture of stereoisomers) as a colorless liquid: bp 58° (0.08 mm); $n^{27}D$ 1.5138; infrared (CCl_4), 3590 and 3400 (free and associated OH) and 1665 cm^{-1} (C=C); nmr (CCl_4), δ 5.2–6.0 (1 H multiplet, vinyl CH), 3.4–4.7 (2 H multiplet, superimposed signals for >CHOH), and 0.9–2.9 (11 H multipet, aliphatic CH); mass spectrum, no molecular ion, abundant fragment peaks at m/e 121, 108, 105, 91, 92, 79, 77, 51, 41, and 39. Gas chromatographic analyses[18] indicated the presence of a minor stereoisomer (eluted first) and a major stereoisomer (eluted second); however, our efforts to obtain pure samples of each of the stereoisomeric alcohols **6a** were complicated by the thermal instability of these allylic alcohols.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.90; H, 9.94.

Reaction of 522 mg (3.8 mmoles) of the alcohol **6a** with 883 mg (4.16 mmoles) of 3,5-dinitrobenzoic acid and 1.609 g (8.44 mmoles) of *p*-toluenesulfonyl chloride in 25 ml of pyridine as previously described[21] afforded 732 mg (59%) of the crude crystalline 3,5-dinitrobenzoate **6b**. Recrystallization from methanol–acetone mixtures separated 575 mg of the ester **6b** as pale yellow prisms: mp 94 dec (dependent on rate of heating); infrared (CCl_4), 1730 cm^{-1} (ester C=O); ultraviolet maximum, 227 mμ (ϵ 22,200); nmr ($CDCl_3$), δ 9.0–9.4 (3 H multiplet, aryl CH), 5.2–6.0 (2 H multiplet, >CHO and vinyl CH), and 0.9–2.8 (11 H mulitplet, aliphatic CH).

Anal. Calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.85; N, 8.43. Found: 57.65; H, 4.71; N, 8.40.

After 4.27 g (31.4 mmoles) of the ketone **5** had been reduced with excess ethereal $LiAlH_4$ as described above, the resulting suspension of lithium and aluminum alkoxides in ether was treated with 10.01 g (98 mmoles) of acetic anhydride. The resulting mixture was stirred for 3 hr at room temperature and then partitioned between ether and aqueous $NaHCO_3$. The ethereal layer was washed with aqueous NaCl, dried, concentrated, and distilled to separate 3.63 g of colorless liquid, bp 103–109° (6 mm), which contained both the acetate **6c** and the alcohol (infrared analysis) **6a**. This crude acetate was combined with another comparable sample (total 5.15 g) and allowed to react with 5 ml of acetic anhydride and 20 ml of pyridine for 3 hr at room temperature. After repeating the same isolation procedure, the crude product was distilled to separate 3.76 g (34% based on the starting ketone **5**) of the acetate **6c**: bp 49–50° (0.03 mm); $n^{23.5}D$ 1.4881. Although the gas chromatogram[18] of this material indicated the presence of two components (presumably stereoisomers), a minor component eluted first and a major component eluted second, our efforts to separate the stereoisomers were complicated by the thermal instability of the acetates. A redistilled sample of the acetate **6c**, bp 64° (0.35 mm), $n^{27}D$ 1.4860, was employed for analysis: infrared (CCl_4), 1735 (ester C=O) and 1680 cm^{-1} (weak, C=C); nmr (CCl_4), δ 4.9–5.7 (2 H multiplet, vinyl CH and >CHO), 1.95 (3 H singlet, $OCOCH_3$), and 0.8–2.7 (11 H multiplet, aliphatic CH); mass spectrum, no molecular ion, abundant fragment peaks at m/e 120 115, 92, 91, 79, 77, 60, 45, 43, and 39.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.06; H, 8.97.

Reaction of Ethyl Diazoacetate with the Allylic Acetate 6c.—Although the copper-catalyzed decomposition of ethyl diazoacetate in the presence of the ketone **5** or the alcohol **6a** led to mixtures from which we were unsuccessful in isolating perhydroindane derivatives, reaction with the acetate **6c** was more satisfactory. To a mixture of 2.30 g (12.8 mmoles) of the acetate **6c** and 63 mg of anhydrous $CuSO_4$ in 5 ml of refluxing *n*-hexane was added, dropwise and with stirring over a 3-hr period,[22] a solution 5.51 g (48.3 mmoles) of ethyl diazoacetate in 45 ml of hexane. The resulting mixture was cooled, filtered, and concentrated to leave 5.7 g of yellow liquid which was distilled. After separation of the more volatile material, bp 45–70° (0.15 mm), which contained[17] components corresponding in retention time

(16) A series of trial experiments suggested that an anhydrous $CuSO_4$ catalyst gave higher yields of the desired product **2** than did untreated copper bronze, the acetylacetonate complex of copper(II), the tri-*n*-butylphosphine complex of copper(I) iodide, or the dimer of π-allylpalladium chloride. Although this latter catalyst[7e] would promote the decomposition of ethyl diazoacetate at 25°, the products were mainly low boiling and little, of any, of the desired product **2** was present.

(17) A gas chromatography column packed with a silicone gum, no. SE-30, suspended on Chromosorb P was employed for this analysis.

(18) A gas chromatography column packed with Carbowax 20M suspended on Chromosorb P was employed for this analysis.

(19) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(20) H. O. House, B. M. Trost, R. W. Magin, R. G. Carlson, R. W. Franck, and G. H. Rasmusson, *J. Org. Chem.*, **30**, 2513 (1965).

(21) (a) J. H. Brewster and C. J. Ciotti, *J. Am. Chem. Soc.*, **77**, 6214 (1955); (b) G. F. Hennion and S. O. Barrett, *ibid.*, **79**, 2146 (1957).

(22) An induction period of about 15–30 min was normally observed before decomposition of the diazo compound began.

to the starting acetate **6c**, ethyl fumarate, and ethyl maleate, the crude product was collected as 2.28 g (*ca.* 60%) of a pale yellow liquid, bp 70–122° (0.13 mm), which contained[17] the cyclopropyl ester **7a** (eluted first) accompanied by two minor components (*ca.* 25% of the mixture, eluted second and third). A sample of the ester **7a** was collected[17] for spectral data: infrared (CCl_4), 1735 cm^{-1} (ester C=O); nmr (CCl_4), δ 4.9–5.3 (1 H multiplet, >CHO), 4.05 (2 H quartet, J = 7 cps, CH_2O), and three overlapping absorptions (total 19 H) at 1.97 (singlet, $OCOCH_3$); 1.24 (triplet, J = 7 cps, CH_3C), and 0.8–2.5 (multiplet, aliphatic CH); mass spectrum, no molecular ion peak, abundant fragment peaks at m/e 206, 177, 133, 122, 91, 79, 67, 55, 43, 41, and 39.

A solution of the crude product and 2.2 g of potassium hydroxide in 50 ml of an ethylene glycol–water mixture (1:3 v/v) was refluxed for 5 hr and then partitioned between water and ether. The aqueous phase was acidified and extracted with ethyl acetate to separate, after the usual manipulations, 1.44 g of crude acidic product. Trituration with ethyl acetate and subsequent filtration separated 0.77 g of one or more stereoisomers of the hydroxy acid **7b** as white prisms, mp 185–189°. Additional recrystallization from ethyl acetate–methanol mixtures gave the acid **7b**: mp 185.5–188°; infrared (KBr pellet), 2800–3600 (broad, carboxyl OH) and 1690 cm^{-1} (carboxyl C=O).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.15; H, 8.19.

Preparation of the Keto Acid Derivatives 8.—A cold (0°) solution of 0.50 g (2.6 mmoles) of the hydroxy acid **7b** was treated with 1.0 ml of 8 N chromic acid solution.[23] After the resulting solution had been stirred for 10 min, the excess oxidant was destroyed with isopropyl alcohol and the solution was concentrated and the partitioned between water and ether. The ethereal solution was washed with aqueous sodium chloride, dried, and concentrated to leave 0.50 g of the crude keto acid as a white solid which was recrystallized from ether to separate 0.375 g (75%) of the keto acid **8a** as white prisms: mp 119–123°. (further recrystallization from ethyl acetate–petroleum ether (bp 30–60°) mixtures raised the melting point to 121–125°); infrared ($CHCl_3$), 2800–3500 (broad, carboxyl OH) and 1700 cm^{-1} (C=O); ultraviolet maximum, 279 mμ (ϵ 54).

Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27. Found: C, 67.88; H, 7.29.

A 0.3-g sample of the crude keto acid **8a** was esterified with excess ethereal diazomethane and the crude neutral product was distilled in a short-path still (0.2 mm and 122°) to separate 188 mg of the ester **8b** as a pale yellow liquid. This product[18] has one major component, the keto ester **8b** (eluted first), and one minor (*ca.* 5%) component (eluted second). A sample of the ester **8b** was collected[18] for characterization: infrared (CCl_4), 1740 (ester C=O) and 1710 cm^{-1} (ketone C=O); nmr (CCl_4), δ 3.63 (3 H singlet, OCH_3) and 1.1–2.4 (13 H multiplet, aliphatic CH).

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74; mol wt, 208. Found: C, 69.03; H, 7.76; mol wt, 208 (mass spectrum).

Reductive Cleavage of the Keto Acid 8a.—A solution of 502 mg (2.58 mmoles) of the crude keto acid **8a** (mp 113–118°) in 2 ml of *t*-butyl alcohol and 5 ml of tetrahydrofuran was added dropwise and with stirring over a 2-min period to a solution of 244 mg (33.5 mg-atoms) of lithium in 50 ml of liquid ammonia. After the resulting mixture had been stirred for 10 min, the unchanged lithium was consumed by the addition of excess solid NH_4Cl and then the ammonia was allowed to evaporate. The residue was partitioned between ether and dilute aqueous HCl and the organic layer was washed with aqueous NaCl, dried, and concentrated to leave a colorless oil which solidified on standing. Recrystallization from cyclohexane–ethyl acetate mixtures separated 308 mg (61%) of fractions of the crude hydroxy acid **9** melting within the range 82–105°. A solution of 300 mg (15. mmoles) of this crude acid **9** in 15 ml of acetone was oxidized with 1.0 ml of 8 N chromic acid solution[23] as previously described to give 283 mg of the crude keto acid **10a** as a colorless oil: infrared (CCl_4), 3500–2800 (carboxyl OH) and 1710 cm^{-1} (carboxyl and ketone C=O). In another experiment, 0.67 g (3.5 mmoles) of the cyclopropyl acid **8a** was reduced as described above and then, without purification, oxidized with chromic acid to yield 515 mg (76%) of the crude keto acid **10a**. Short-path distillation (0.25 mm and 185–192° bath) afforded 378 mg of the keto acid **10a** as a colorless liquid. This material was esterified with excess ethereal diazomethane to give, after short-path distillation (0.35 mm and 135–145° bath), 391 mg of the keto ester **10b** as a colorless liquid which exhibits one major peak on gas chromatography.[17] This material was identified with a previously described[11] sample of the keto ester **10b** by comparison of infrared, nmr, and mass spectra and by the subsequently described reduction.

A mixture of 0.25 g (1.3 mmoles) of the crude keto acid **10a**, 0.51 g of KOH, 1.0 ml of 85% hydrazine, and 13 ml of diethylene glycol was heated to reflux for 1 hr (170° bath) and then the bath temperature was raised to 215° for 1.5 hr while volatile components were allowed to distil from the reaction mixture. The resulting mixture was cooled and partitioned between ether and dilute aqueous HCl. The crude acid **11a** (179 mg of colorless oil) recovered from the ether phase was esterified with excess ethereal diazomethane to give, after short-path distillation (0.1 mm and 69–74° bath), 140 mg (56% over-all) of the crude ester **11b** as a colorless liquid which contained[24] the ester **11b** (*ca.* 80% eluted first) accompanied by two minor, unidentified components (*ca.* 20%, eluted second and third). A collected[24] sample of the ester **11b** was identified with an authentic sample[2,11] by comparison of infrared and nmr spectra and gas chromatographic retention times.

Reaction of Ethyl Diazoacetate with 4,5,6,7-Tetrahydroindane (12).—Following a previously described procedure,[25] 27.08 g (0.226 mole) of indan was reduced with 7.08 g (1.0 g-atom) of lithium in a mixture of 200 ml of dimethylamine and 200 ml of ethylamine. After the crude product had been partitioned between water and hexane, the organic solution was washed successively with dilute, aqueous HCl, and with aqueous NaCl and then dried and concentrated. Distillation of the residual pale yellow liquid separated 20.7 g (75%) of colorless liquid, bp 60–62° (17 mm), $n^{25}D$ 1.4880, which contained[17] the olefin **12** accompanied by two minor impurities which were eluted more rapidly. Fractional distillation through a 40-cm spinning-band column separated a pure[17] sample of the olefin: bp 70° (19 mm); $n^{24}D$ 1.4890; infrared (liquid film), 1665 cm^{-1} (weak, C=C); nmr (CCl_4), δ 1.3–2.5 multiplet (aliphatic CH); mass spectrum, moleclar ion, m/e 122, abundant fragment peaks, m/e 94, 93, 81, 80, 79, 41, and 39.[26]

To a mixture of 2.08 g (17.0 mmoles) of the olefin **12**, 1.00 g of anhydrous $CuSO_4$, and 5 ml of refluxing cyclohexane was added, dropwise with stirring and refluxing over a 2-hr period, a solution of 6.58 g (57.7 mmoles) of ethyl diazoacetate in 40 ml of cyclohexane. The resulting mixture was refluxed with stirring for an additional 15 min and then filtered and concentrated. The residual brown liquid (7.01 g) was subjected to a series of distillations to separate 1.16 g (32%) of a fraction, bp 60–65° (0.07 mm), which contained[17,18] primarily the stereoisomeric esters **13a** accompanied by a number of minor components. A collected[17] sample of the major components, a mixture of stereoisomers **13a**, had the following spectral properties: infrared (CCl_4) 1730 cm^{-1} (ester C=O); nmr (CCl_4), δ 3.99 (2 H quadruplet, J = 7 cps, $-CH_2O-$) and 1.23 (triplet, J = 7 cps, CH_3C) superimposed on 1.0–2.5 multiplet (aliphatic CH).

A mixture of 10.85 g (52 mmoles) of the ester **13a**, 5.30 g (81 mmoles) of potassium hydroxide, 10 ml of methanol, and 100 ml of water was refluxed with stirring for 4.5 days and then cooled, extracted with ether, acidified, and again extracted with ether. The crude semisolid acid **13b** (8.64 g of 91%) was recovered from the ether extract. This material was subjected to as series of fractional crystallizations from hexane and then from aqueous ethanol to separate two stereoisomeric acids **13b** which were further purified by sublimation under reduced pressure. The less soluble isomer A of acid **13b** was obtained as white needles: mp 146–148°; infrared (CCl_4), 3500–2800 (carboxyl OH) and 1700 cm^{-1} (carboxyl C=O); nmr ($CDCl_3$), δ 11.73 (1 H singlet, OH) and 0.8–2.7 (15 H multiplet, aliphatic CH). The isomer B of acid **13b** (more soluble in hexane) was obtained as white needles: mp 105–108°; infrared (CCl_4), 3500–2800 (carboxyl OH) and 1700 cm^{-1} (carboxyl C=O); nmr

(23) D. C. Kleinfelter and P. von R. Schleyer, *Org. Syn.*, **42**, 79 (1962).

(24) A gas chromatography column packed with tris(β-cyanoethoxy)propane (TCEP) suspended on Chromosorb P was employed for this analysis.

(25) R. A. Benkeser and E. M. Kaiser, *J. Org. Chem.*, **29**, 955 (1964).

(26) This procedure for the olefin **12** was found to be more satisfactory than reduction of indane to the 4,7-dihydroindane with lithium, ethanol, and ammonia followed by selective hydrogenation of the $\Delta^{5,6}$-double bond in the dihydro compound. The olefin **12** is reported to boil at 66° (18 mm): H. Christol, R. Jacquier, and M. Mousseron, *Bull. Soc. Chim. France*, 1027 (1957).

($CDCl_3$), δ 11.75 (OH) and 0.8–2.6 (15 H multiplet, aliphatic CH).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found for isomer A: C, 73.06; H, 9.10. Found for isomer B: C, 73.20; H, 9.08.

Samples of each of the crystalline acids **13b** were treated with excess ethereal diazomethne and the crude neutral product was distilled in a short-path still (0.1 mm and 63–72° bath). From 1.40 g of acid **13b**, isomer A (mp 146–148°), was obtained 1.33 g (80%) of ester **13c**, isomer A, $n^{28}D$ 1.4892, which contained[27] *ca.* 1% of the more slowly eluted isomer B: infrared (CCl_4), 1735 cm^{-1} (ester C=O); nmr (CCl_4), δ 3.57 (3 H singlet, OCH_3) and 0.9–2.4 (15 H multiplet, aliphatic CH). Methylation of 1.27 g of acid **13b**, isomer B (mp 105–108°), gave 1.12 g (82%) of ester **13c**, isomer B, $n^{28}D$ 1.4863, which contained[27] *ca.* 6% of the more rapidly eluted isomer A: infrared (CCl_4), 1735 cm^{-1} (ester C=O); nmr (CCl_4), δ 3.55 (3 H singlet, OCH_3) and 0.9–2.5 (15 H multiplet, aliphatic CH). Methylation of 3.03 g of the crude mixture of stereoisomeric acids **13b** gave 2.57 g (79%) of a mixture of esters **13c**, bp 64–66° (0.1–0.2 mm), $n^{27.5}D$ 1.4881, which contained[27] *ca.* 30% of isomer A (first eluted) and *ca.* 70% of isomer B (second eluted).

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34; mol wt, 194. Found for isomer A: C, 73.94; H, 9.32; mol wt, 194 (mass spectrum). Found for isomer B: C, 73.91; H, 9.41; mol wt, 194 (mass spectrum).

Reductive Cleavage of the Cyclopropane Ester 13c.—To a solution of 0.43 g (61 mg-atom) of lithium in 75 ml of liquid ammonia was added, dropwise and with stirring over a 5-min period, a solution of 1.13 g (5.8 mmoles) of the ester **13c** (mixture of stereoisomers) and 2.5 ml of *t*-butyl alcohol in 10 ml of tetrahydrofuran. The resulting mixture was refluxed with stirring for 15 min and then the unchanged lithium was consumed by the addition of excess solid NH_4Cl. The ammonia was allowed to evaporate and the residue was partitioned between ether and dilute aqueous HCl. After the ethereal layer had been washed with aqueous NaCl, dried, and concentrated, a solution of the residual colorless oil (964 mg with infrared absorption corresponding to the alcohol **14**) in 50 ml of cold (0°) acetone was oxidized with 2.0 ml of 8 *N* chromic acid solution[23] as previously described to yield 891 mg of crude acidic product as a colorless oil which partially solidified on standing. A portion of this crude acid (primarily a mixture of **15a** and **11a**) was esterified with ethereal diazomethane to yield a mixture of esters which contained[24] the *trans* ester **15b** (*ca.* 80%, eluted first) and the *cis* ester **11b** (*ca.* 20%, eluted second).

Recrystallization of the crude acid from petroleum ether (bp 30–60°) separated 122 mg of the crude *trans* acid **15a**, mp 77–88°. Repeated crystallization from petroleum ether separated the pure *trans* acid **15a** as white prisms: mp 88.5–89°; infrared (CCl_4), 3400–2700 (carboxyl OH) and 1705 cm^{-1} (carboxyl C=O); nmr ($CDCl_3$), δ 11.82 (1 H singlet, OH) and 0.8–2.7 (17 H multiplet, aliphatic CH).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.55; H, 9.97.

A 136-mg sample of the crystalline *trans* acid **15a** was methylated with excess ethereal diazomethane and the crude neutral product was distilled in a short-path still (0.17 mm and 69–74° bath) to separate 137 mg (94%) of the *trans* ester **15b** as a colorless liquid: infrared (CCl_4), 1375 cm^{-1} (ester C=O); nmr (CCl_4), δ 3.56 (3 H singlet, OCH_3) and 0.8–2.5 (17 H multiplet, aliphatic CH).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27; mol wt, 196. Found: C, 73.22; H, 10.26; mol wt, 196 (mass spectrum).

The crude mixture of acids **11a** and **15a** (866 mg) remaining after separation of the pure *trans* acid **15a** was esterified with ethereal diazomethane and the crude product was distilled in a short-path still (0.2 mm and 65–90° bath) to give 738 mg (79%) of a mixture of esters which contained[27] *ca.* 65% of the *trans* ester **15b** and *ca.* 35% of the *cis* ester **11b**. A collected[27] sample of the *cis* ester **11b** was identified with a previously described sample by comparison of infrared spectra and gas chromatographic retention times.

In subsequent experiments, samples of each of the pure cyclopropane esters **13c**, isomer A and isomer B, were reduced with lithium in ammonia. The crude products were oxidized with chromic acid, esterified with diazomethane, mixed with known amounts of an internal standard (pentamethylbenzene), and then analyzed by gas chromatography employing columns[24,27] calibrated with known mixtures of authentic samples. Isomer A (retention times 64.4 min[24] or 52.0 min[27]) is eluted more rapidly than isomer B (retention times 74.0 min[24] or 55 min[27]) on each column. Although the esters **11b** and **15b** are not resolved on one column (retention time 61.2 min[27]), on the other column the retention times are 73.8 min (**15b**) and 77.0 min (**11b**). In certain runs no *t*-butyl alcohol was added during the lithium ammonia reduction, while 1.5–1.8 equiv of *t*-butyl alcohol was added in other cases. Table I lists typical results for these reactions.

TABLE I
REDUCTION OF THE ISOMERIC CYCLOPROPANE ESTERS WITH LITHIUM AND AMMONIA

Reactants	Calculated yields, % Starting esters 13c	Product esters 11b + 15b	Product ratio *trans* ester 15b/*cis* ester 11b
13c, isomer A	3	70	4.2
13c, isomer A + *t*-BuOH	<1	70	4.1
13c, isomer B	<1	68	3.9
13c, isomer B + *t*-BuOH	<1	50	3.9

Degradation of the *trans* Ester 15b.—To a solution of 4.2 mmoles of phenylmagnesium bromide in 13 ml of ether was added, dropwise and with stirring under a nitrogen atmosphere, a solution of 327 mg of the *trans* ester **15b** (containing 1–2% of the *cis*-ester **11b** as an impurity) in 5 ml of ether. The resulting mixtue was refluxed for 2 hr and then washed successively with aqueous NH_4Cl, dilute aqueous HCl, and aqueous NaCl. The organic layer was dried and concentrated to leave 515 mg of the crude diphenylcarbinol: infrared (CCl_4) 3610 cm^{-1} (OH). A solution of the crude carbinol in 13 ml of acetic anhydride and 5 ml of acetic acid was refluxed for 5.5 hr and then concentrated and partitioned between ether and aqueous $NaHCO_3$. The ether layer was washed with aqueous NaCl, dried, and concentrated to leave 457 mg of a brown oil which was chromatographed on silicic acid. The crude olefin **16** was collected as 305 mg (61%) of colorless liquid in fractions eluted with 10% benzene in hexane. The sample was further purified by distillation in a short-path still (0.12 mm and 175–183° bath): infrared (CCl_4) no bands in the 3- or 6-μ region attributable to OH or C=O functions; ultraviolet maximum, 248 mμ (ϵ 15,600); nmr (CCl_4) δ 6.9–7.5 (10 H multiplet, aryl CH), 5.97 (1 H singlet, vinyl CH), and 0.8–2.1 (15 H multiplet, aliphatic CH).

Anal. Calcd for $C_{23}H_{26}$: C, 91.33; H, 8.67; mol wt, 302. Found: C, 91.09; H, 8.70; mol wt, 302 (mass spectrum).

To a warm (50°) solution of 263 mg (0.87 mmole) of the olefin **16** in 2 ml of acetic acid was added, dropwise and with stirring over a 10-min period, 5 ml of a solution prepared from 1.0 g CrO_3, 1 ml of water, and 10 ml of acetic acid.[28] The mixture was maintained at 50° for an additional 20 min and the excess oxidant was consumed with methanol. The mixture was concentrated under reduced pressure and then partitioned between dilute aqueous HCl and ether. The ethereal layer was washed with aqueous NaOH to leave 148 mg of crude neutral product in the ether layer. The aqueous phase was acidified and extracted with ether to separate, after the usual manipulations, 154 mg of the crude acid **17a** which crystallized on standing. Esterification of this crude acid with ethereal diazomethane gave 116 g (73%) of the crude ester **17b** which contained the *trans* ester **17b** (first eluted) accompanied by *ca.* 1% of a material with the retention time of the *cis* ester **18** (second eluted). Distillation in a short-path still (0.1 mm and 50–55° bath) afforded 83 mg of the *trans* ester **17b** as a colorless liquid which was identified with a previously described[13b] sample by comparison of gas chromatographic retention times and infrared, nmr, and mass spectra.

In a comparable experiment, 495 mg (2.52 mmoles) of a mixture of the *trans* ester **15b** (*ca.* 65%) and the *cis* ester **11b** (*ca.* 35%) was degraded to give 208 mg (45%) of the crude esters **17b** (*ca.* 64%)[18] and **18** (*ca.* 36%)[18] as a yellow liquid. Collected samples of each of the esters **17b** and **18** were identified with authentic samples[13] by comparison of infrared spectra and gas chromatographic retention times.

(27) A gas chromatography column packed with silicone gum XE-60 suspended on Chromsorb P was employed for this analysis.

(28) The procedure of B. Riegel, R. B. Moffett, and A. V. McIntosh, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 234.

Registry No.—**2**, 14885-98-4; **6a**, 14885-99-5; **6b**, 14886-00-1; **6c**, 14930-19-9; **7a**, 14886-01-2; **7b**, 14886-02-3; **8a**, 14886-03-4; **8b**, 14886-04-5; **10a**, 14886-05-6; **12**, 695-90-9; **13a**, 15007-59-7; **13b**, 14969-89-2; **13c**, 15007-58-6; **15a**, 14886-07-8; **15b**, 14886-08-9; **16**, 14886-09-0.

Preparation and Decomposition of Unsaturated Esters of Diazoacetic Acid[1a]

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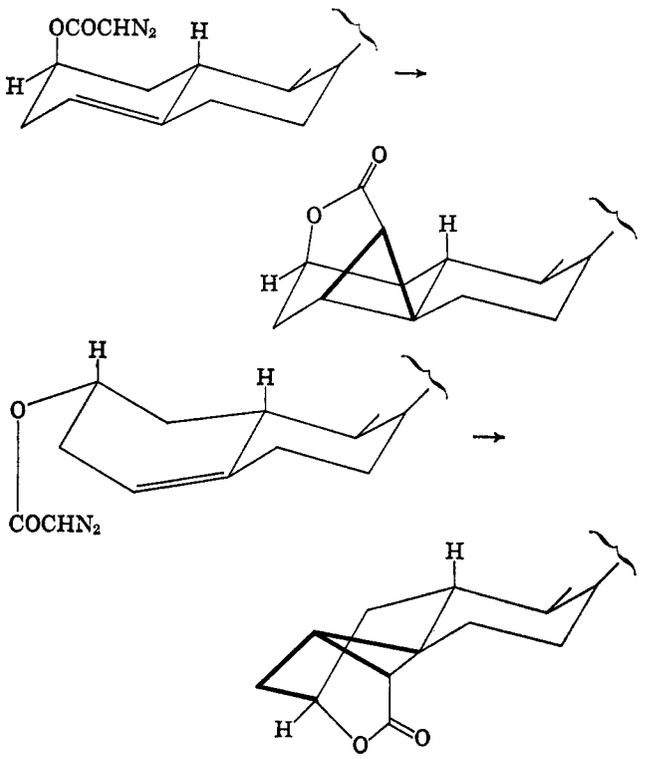
A general synthesis of diazoacetic esters (*e.g.*, **15**) is described which utilizes reaction of the corresponding alcohol with the acid chloride **14** in the presence of 2 equiv of triethylamine. The unsaturated diazo esters **15**, **19**, and **20** have been prepared and their copper-catalyzed decompositions have been studied. The reaction products include a lactone (*e.g.*, **26**) derived from intramolecular attack on the C–C double bond and ester by-products (*e.g.*, **23–25**) derived from dimerization or attack on the solvent.

The copper-catalyzed decomposition of unsaturated diazomethyl ketones to form polycyclic cyclopropyl ketones *via* an intramolecular C–C double-bond addition reaction has been used sufficiently that it may be considered as a standard synthetic operation.[2] However, the corresponding reaction with unsaturated esters of diazoacetic acid has been much less well explored[3] in spite of the synthetic potential which this latter reaction would appear to offer. The accompanying equations (Scheme I) illustrate the possibility that the choice of the stereochemistry for the starting unsaturated alcohol might serve to direct the entering carboalkoxy carbene (presumably complexed with the metal catalyst and possibly also with nitrogen) to attack only one side of the C–C double bond. Combined with further transformations, this scheme could offer a method for the introduction of an alkyl group in a stereoselective manner. To examine the utility of the ring closure step, we have examined the properties of diazoacetic esters of crotyl alcohol and the bicyclic alcohols **1–4** prepared as indicated in Scheme II.

For the present purpose, the usual preparative methods[4] for diazoacetic esters such as the diazotization of glycine esters,[5] the pyrolysis of N-acyl-N-nitrosoglycine esters,[6] the base-catalyzed cleavage of α-diazo-β-keto acetates,[7a,b] the reactions of carboalkoxymethylenephosphoranes with aryl sulfonyl azides,[7c] or the acid-catalyzed decomposition of acetic esters with aryltriazene substituents[7d] did not appear desirable because the unsaturated alcohol would need to be carried through intermediate synthetic steps prior to the formation of the diazo ester. Rather, we wished to find a method which would permit the unsaturated alcohol

SCHEME I



to be introduced in the final stage of the diazoacetic ester synthesis. Such an approach would be the most efficient in cases where the unsaturated alcohol was the limiting reactant or was sensitive to vigorous reaction conditions. Two general methods have been explored utilizing crotyl alcohol as the model substrate. In the first method (Scheme III), crotyl alcohol was converted to its chloroformate **16** by reaction with phosgene[8] and the chloroformate **16** was allowed to react with excess diazomethane in a reaction comparable to the conversion of acid chlorides to diazomethyl ketones.[4,9] Although this procedure permitted the preparation of the diazo ester **15** from the chloroformate in 49% yield, the reaction with diazomethane was very slow requiring more than 1 week to go to completion.

(1) (a) This research has been supported by a grant from the National Institutes of Health (No. GM-08761); (b) National Institutes of Health Predoctoral Fellow, 1964–1967.

(2) For examples and leading references, see (a) G. Stork and J. Ficini, *J. Am. Chem. Soc.*, **83**, 4678 (1961); (b) F. Medina and A. Manjarrez, *Tetrahedron*, **20**, 1807 (1964); (c) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *ibid.*, **21**, 25 (1965); (d) M. M. Fawzi and C. D. Gutsche, *J. Org. Chem.*, **31**, 1390 (1966).

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