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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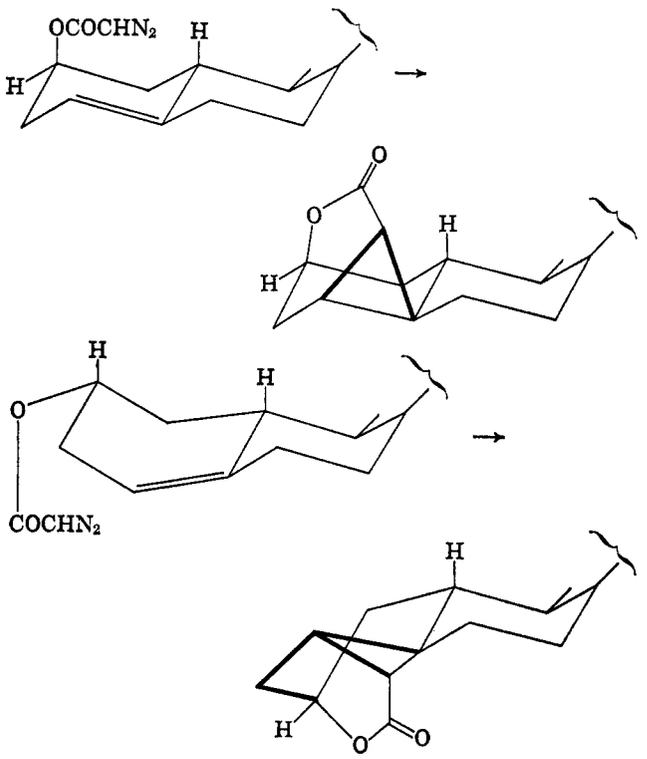
A general synthesis of diazoacetic esters (*e.g.*, **15**) is described which utilizes reaction of the corresponding alcohol with the acid chloride **14** in the presence of 2 equiv of triethylamine. The unsaturated diazo esters **15**, **19**, and **20** have been prepared and their copper-catalyzed 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).

(3) (a) W. Kirmse and H. Dietrich, *Chem. Ber.*, **98**, 4027 (1965). (b) L. Solomon, Ph.D. Dissertation, Columbia University, 1964; *Dissertation Abstr.*, **26**, 101 (1965).

(4) W. Reid and H. Mengler, *Fortschr. Chem. Forsch.*, **5**, 1 (1965).

(5) (a) E. B. Womack and A. B. Nelson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 392; (b) N. E. Searle, Coll. Vol. IV, 1963, p 424.

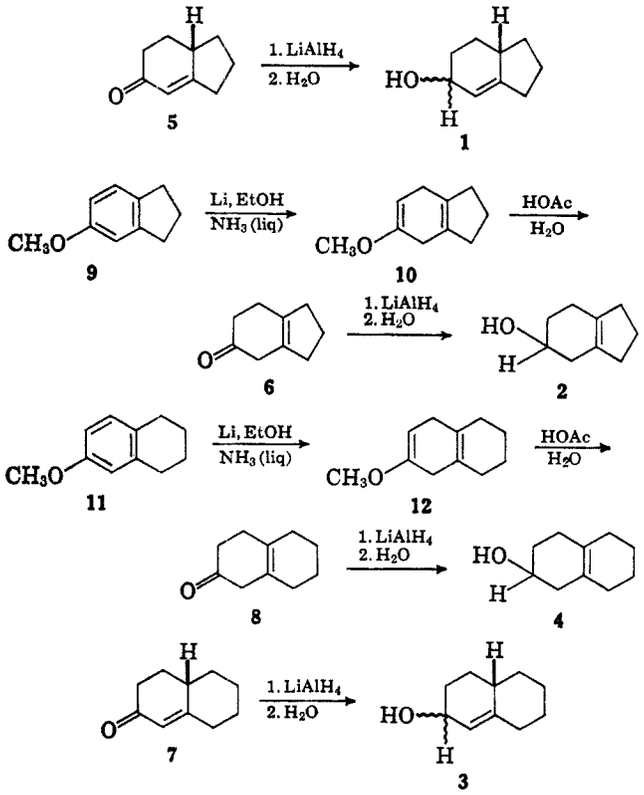
(6) (a) E. H. White and R. J. Baumgarten, *J. Org. Chem.*, **29**, 2070 (1964); (b) H. Reimlinger, *Angew. Chem.*, **72**, 33 (1960).

(7) (a) M. Regitz, *Chem. Ber.*, **98**, 1210 (1965); (b) M. Regitz, F. Menz, and J. Rüter, *Tetrahedron Letters*, No. 8, 739 (1967); (c) G. Harvey, *J. Org. Chem.*, **31**, 1587 (1966); (d) R. J. Baumgarten, *ibid.*, **32**, 484 (1967).

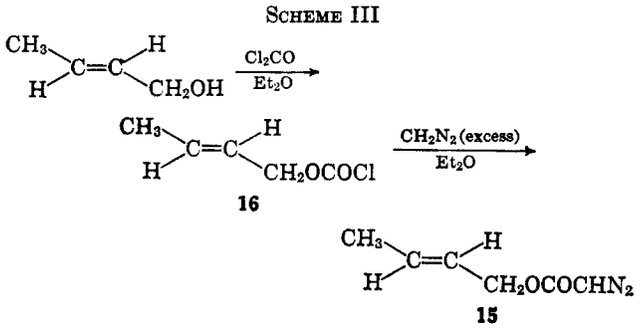
(8) K. L. Oliver and W. G. Young, *J. Am. Chem. Soc.*, **81**, 5811 (1959).

(9) (a) B. Eistert in "Newer Preparative Methods of Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1948, pp 537–551; (b) F. Weygand and H. J. Bestmann in "Newer Methods of Preparative Organic Chemistry," Vol. 3, W. Foerst, Ed., Academic Press Inc., New York, N. Y., 1964, pp 451–508; (c) the reaction of ethyl fluoroformate with diazoalkanes to form ethyl α-fluoro esters has been reported by E. D. Bergmann and I. Shahak, *Israel J. Chem.*, **3**, 73 (1965).

SCHEME II



SCHEME III



We therefore explored an alternative route based on the observation[10] that the benzenesulfonylhydrazones of certain α-ketoamides were converted to α-diazoamides by reaction with sodium hydride. As illustrated in Scheme IV, glyoxylic acid was converted into the sulfonylhydrazone **13** and then into the corresponding acid chloride **14** which could be isolated and purified as a mixture of geometrical isomers. Reaction of this acid chloride **14** with crotyl alcohol in the presence of sodium bicarbonate or 1 equiv of triethylamine afforded the two stereoisomeric esters **17** which could be isolated and characterized. Reaction of either isomer with 1 equiv of triethylamine in methylene chloride at room temperature yielded the diazo ester **15**. The reaction was significantly more rapid with the *trans* isomer, presumably because of a smaller degree of steric interference to incipient *p*-orbital overlap during the proton removal. The over-all conversion was more efficiently accomplished by direct reaction of the alcohol with the acid chloride in the presence of 2 equiv of triethylamine. After the crude reaction mixture had been filtered through a Florisil column to remove polar impurities, distillation afforded the pure diazo ester **15** in 54% yield.[11]

The same reaction procedure was used to prepare the diazo esters **19** (75% yield) and **20** (89% yield) (Scheme V) which could be further purified by low temperature crystallization. In one case, one stereoisomer (believed to be the *trans* isomer) of the intermediate ester **18** was also isolated. Although each of the secondary allylic alcohols **1** and **3** could be converted by this procedure into crude products which had spectroscopic properties consistent with the diazo-ester formulations **21** and **22**, we were unable to isolate pure diazo esters in these cases. These crude esters, like the acetates and 3,5-dinitrobenzoates of these allylic alcohols **1** and **3**,[12] were very unstable to heat, apparently undergoing elimination to form dienes. As a result it was not practical either to distil the crude esters **21** and **22** or to study the thermal decomposition of the diazo function in these materials.

Trial decompositions of the diazo ester **15** with copper catalysts led us to select a suspension of copper(I) oxide in refluxing cyclohexane for further work.[13] The product of this reaction (Scheme VI) was the desired lactone **26** from an intramolecular addition reaction accompanied by the dimeric esters **23** and **24** and the ester **25** apparently formed by attack of the carboalkoxycarbene on a C–H bond of the solvent. Although the carbene intermediates derived from photolysis or pyrolysis of diazoacetic esters have been observed to undergo both intramolecular and intermolecular attack on C–H bonds,[14] the reactive species derived from copper-catalyzed decomposition of diazo ketones or diazo esters has been considered to be sufficiently less reactive that it does not insert into C–H bonds.[15] The reactive species for C–C double-bond additions in the copper-catalyzed reactions has been regarded as a carbene complexed to a copper compound,[15,16] although other species involving more conventional organocopper compounds are clearly worthy of consideration. Whether the C–H insertion products we have observed from diazo ester **15** and the subsequently discussed decompositions of diazo ester **19** are derived from a slow competing reaction of a

(10) (a) E. J. Corey and A. M. Felix, *J. Am. Chem. Soc.*, **87**, 2518 (1965). (b) More recently, J. M. Muchowski [*Tetrahedron Letters*, No. 16, 1773 (1966)] has found that related sulfonylhydrazone derivatives can be converted into diazo compounds by treatment with a suspension of basic alumina in an inert solvent.

(11) We have considered the possibility that direct reaction of the acid chloride **14** might lead to the formation of the rather novel diazo ketene structure i. However, experiments in which the course of the alcohol–acid chloride–triethylamine reaction has followed spectroscopically and chromatographically indicated that the esters **17** were formed more rapidly than diazo functions. Our efforts to trap such an intermediate as i by forming cycloaddition products with olefins also did not lead to the isolation of characterizable substances.

$$N\equiv\overset{+}{N}-\bar{C}=C=O$$
i

(12) See the Experimental Section and H. O. House and C. J. Blankley, *J. Org. Chem.*, **33**, 47 (1968).

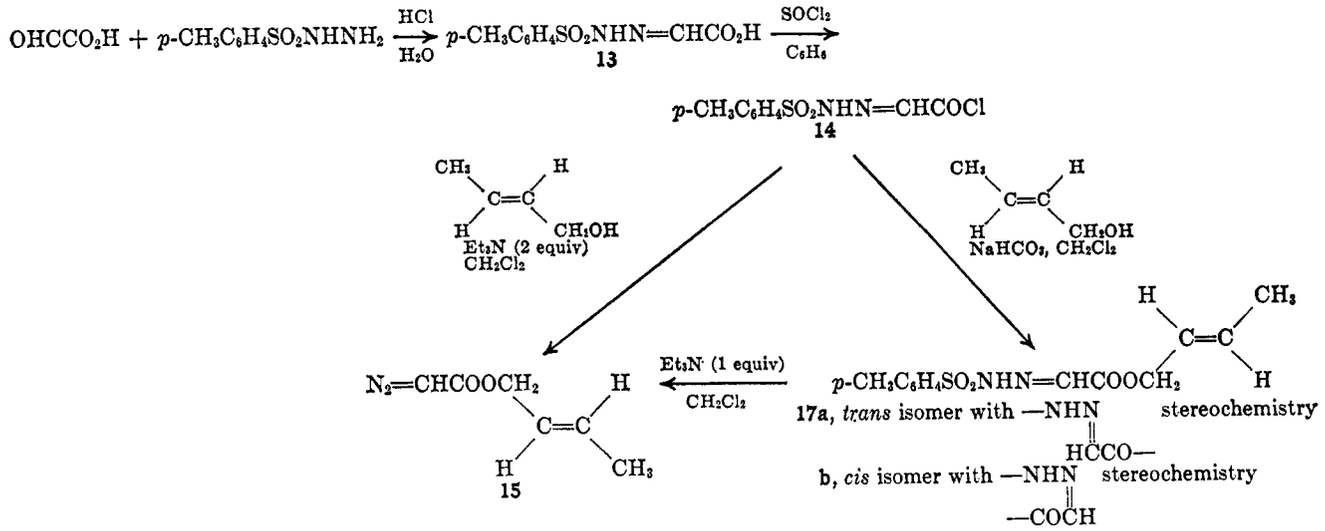
(13) As noted elsewhere,[12] these copper-catalyzed decompositions exhibit an induction period during which it appears that the actual catalyst for the decomposition is produced. It seems probable that once the nature of this actual catalyst has been determined, it will provide a more efficient method for the catalysis of the reactions being studied.

(14) (a) W. Kirmse, H. Dietrich, and H. W. Bücking, *Tetrahedron Letters*, No. 19, 1833 (1967); (b) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **78**, 4947 (1956).

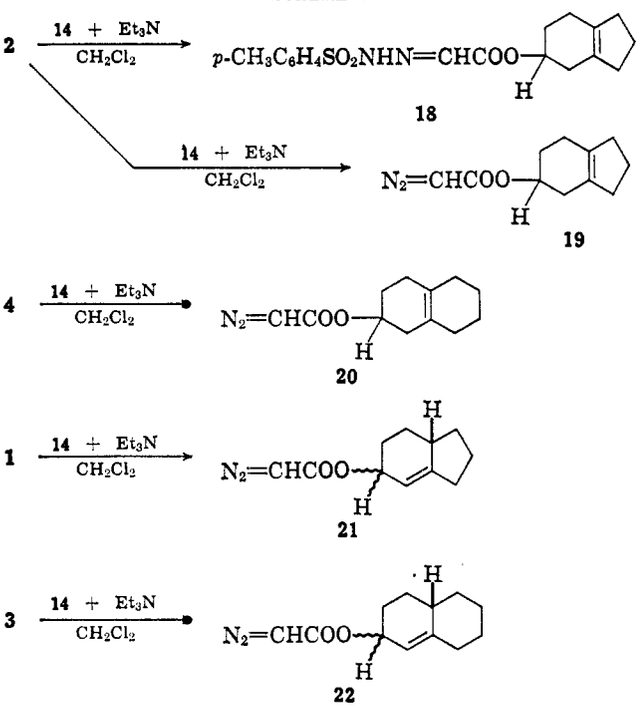
(15) (a) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961); (b) D. O. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964).

(16) (a) H. Nozaki, S. Moriuti, M. Yamabe, and R. Noyori, *Tetrahedron Letters*, No. 1, 59 (1966); (b) H. Nozaki, S. Moriuti, H. Takaya, and R. Noyori, *ibid.*, No. 43, 5239 (1966).

SCHEME IV



SCHEME V



"complexed carbene" with the solvent or from a reaction of a free carbene generated in an independent thermal process or from dissociation of a "complexed carbene" cannot be answered from our present data. If the latter possibility is the case, presumably this by-product can be eliminated by use of a more efficient catalyst.[18]

The structure and stereochemistry of the lactone **26** were verified by the degradation to the known diacid **27**[17] indicated in Scheme VII. Similarly, the copper-catalyzed decomposition of the diazo ester **19** yielded the lactone **30** and ester products **28** and **29** in Scheme VIII and an analogous lactone **33** was obtained from the catalyzed decomposition of the diazo ester **20**. As had been the case in an earlier study of the allyl diazoacetate,[3a] the yields of the lactone derived from intramolecular addition to the C–C double bond ranged from 20 to 45% with the major by-products being the indicated maleate and fumarate esters. Since the reverse situation has frequently been observed in the copper-catalyzed decompositions of diazomethyl ketones where yields of intramolecular insertion products may exceed 50%, it is possible that the reactive intermediates derived from diazo esters are less selective in their reactions than the corresponding intermediates from diazomethyl ketones. In any case, it is clear that for this reaction to become a good synthetic method, some method must be found to increase the amount of intramolecular reaction at the expense of the fumarate and maleate ester by-products.

(17) (a) G. Bonavent, M. Causse, M. Guitard, and R. Faisse-Jullien, *Bull. Soc. Chim. France*, 2462 (1964); (b) M. G. Ettlinger, S. H. Harper, and F. Kennedy, *J. Chem. Soc.*, 922 (1957).

Experimental Section[18]

Preparation of the Unsaturated Alcohols 1–4.—Each of the unsaturated ketones **5–8** was reduced with ethereal $LiAlH_4$ following the procedure described[12] for the alcohol **1**. In the reduction of $\Delta^{1,9}$-octal-2-one (**7**), prepared and purified as described elsewhere,[19] the isolation procedure of Marshall and Fanta[20] was followed. The octalol **3** was obtained in 93.5% yield as a colorless, viscous liquid: bp 68–75° (0.15–0.25 mm); $n^{25}D$ 1.5162 (lit.[20] bp 68° (0.3 mm)). The gas chromatogram[21] of the material exhibited two major peaks, component A (*ca.* 40%, first eluted) and component B (*ca.* 60% second eluted) which we presume are the two stereoisomers of the octalol **3**. Separation of these two components was complicated by the thermal instability of these allylic alcohols. A comparable product, bp 60–71° (0.15 mm), $n^{24}D$ 1.5167, was obtained in 91% yield by reduction of the octalone **7** with lithium tri-*t*-butoxyaluminum hydride in tetrahydrofuran solution. Reaction of 5.71 g (37.5 mmoles) of the alcohol **3** with 14.42 g (76 mmoles) of *p*-toluenesulfonyl chloride and 8.03 g (37.9 mmoles) of 3,5-dinitro-

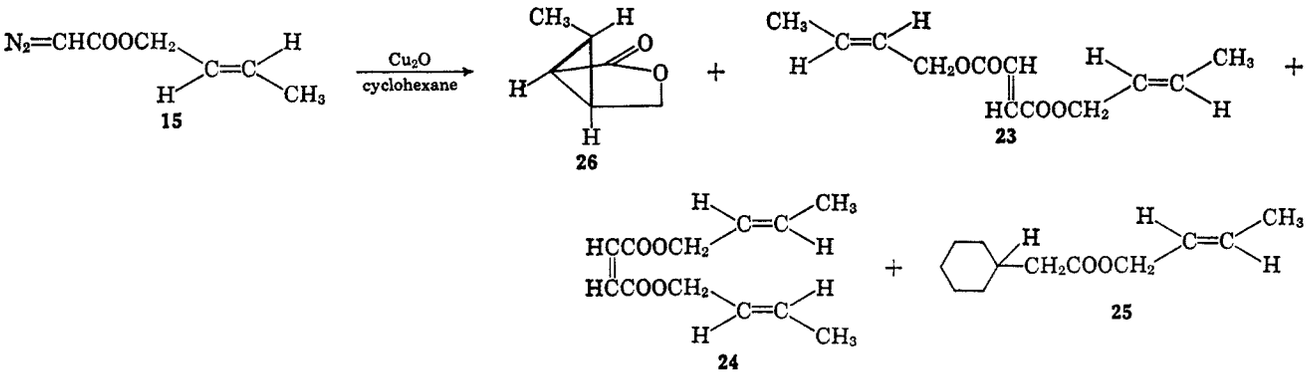
(18) All melting points are corrected and all boiling points are uncorrected. Unless otherwise stated magnesium sulfate was employed as a drying agent. The infrared spectra were determined with a Perkin-Elmer Model 237 infrared recording spectrophotometer fitted with a grating. Unless otherwise stated 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.

(19) (a) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963); (b) R. L. Augustine and J. A. Caputo, *Org. Syn.*, **45**, 80 (1965).

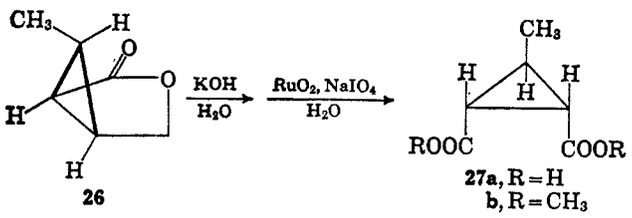
(20) J. A. Marshall and W. I. Fanta, *J. Org. Chem.*, **29**, 2501 (1964).

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

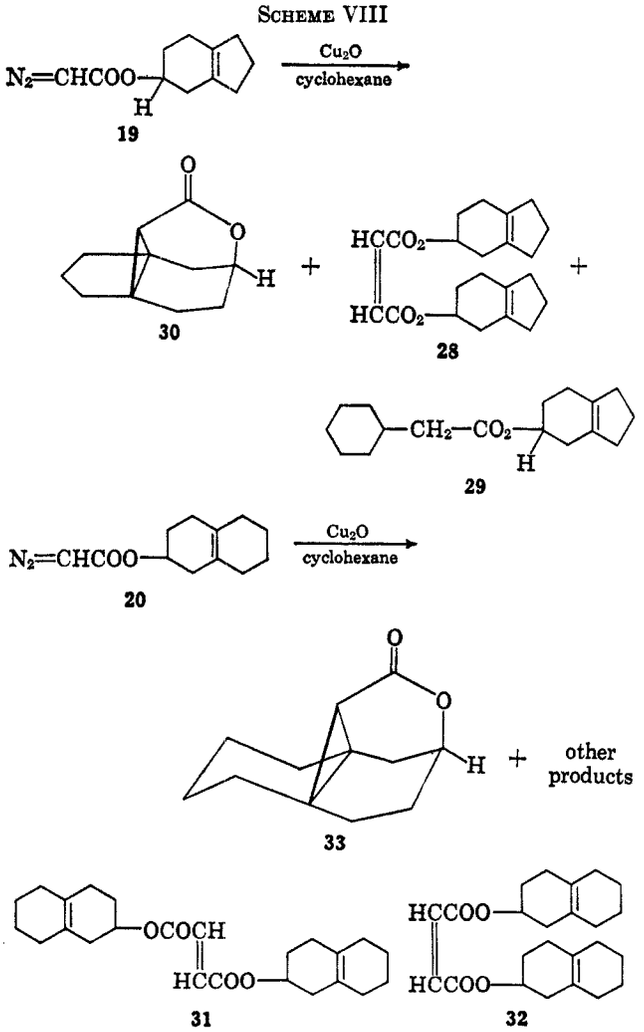
SCHEME VI



SCHEME VII



SCHEME VIII



benzoic acid in 140 ml of pyridine as previously described[22] yielded 13.5 g of the crude solid 3,5-dinitrobenzoate. Recrystallization from an acetone–methanol mixture separated 7.63 g of the derivative as pale yellow needles, mp 101–107°. Several additional recrystallizations from a benzene–petroleum ether (bp 30–60°) mixture gave material, mp 101.5–103.5°, which appears to be a single stereoisomer[23] of the 3,5-dinitrobenzoate of the alcohol **3**: infrared (CCl_4), 1735 cm^{-1} (ester C=O); ultraviolet maximum, 228 mμ (ϵ 26,800); nmr ($CDCl_3$), δ 9.13 (3 H partially resolved multiplet, aryl CH), 5.2–5.8 (2 H multiplet, >CHO and vinyl CH), and 1.0–2.5 (13 H multiplet, aliphatic CH).

To a warm (40°) solution of 50.0 g (0.373 mole) of 5-indanol in 205 ml of aqueous 2 *M* NaOH was added, dropwise and with stirring over a 1-hr period, 46 g (0.38 mole) of dimethyl sulfate while the reaction mixture was maintained at 43–46°. An additional 130 ml of aqueous 2 *M* NaOH was added followed by 25 g (0.18 mole) of dimethyl sulfate and the mixture was heated to 45–55° for 3 hr. The ethereal extract of the resulting mixture was washed with aqueous NaCl, dried, concentrated, and distilled to separate 50.5 g (92%) of 5-methoxyindan (**9**) as a colorless liquid, bp 101–107° (10 mm), $n^{26.3}D$ 1.5413, which exhibited a single peak on gas chromatography.[24] A collected[24] sample was used for characterization: ultraviolet maxima, 218 mμ (ϵ 7410), 280 (3060), and 288 (2640); nmr (CCl_4), δ 6.80 (1 H doublet, J = 7.5 cps, C-7 aryl CH), 6.2–6.6 (2 H multiplet, C-4 and C-6 aryl CH), 3.56 (3 H singlet, OCH_3), 2.5–3.0 (4 H multiplet, benzylic CH), 1.7–2.2 (2 H multiplet, aliphatic CH).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16; mol wt, 148. Found: C, 81.27; H, 8.18; mol wt (mass spectrum), 148.

To a cold (−78°) mixture of 30.0 g (0.202 mole) of the methoxyindane **9**, 100 ml of 1,2-dimethoxyethane, and 400 ml of liquid ammonia was added, rapidly and with stirring, 7.15 g (1.02 g-atoms) of lithium (wire cut into small pieces). The cooling bath was removed, the blue solution was refluxed with stirring for 20 min, and then 110.8 g of absolute ethanol was added, dropwise and with stirring, to discharge the blue color of the solution. After the ammonia had been allowed to evaporate, the residue was partitioned between ether and water and the ethereal layer was washed with aqueous NaCl, dried over K_2CO_3, and concentrated. Distillation separated 28.03 g (93%) of the dihydro ether **10**, bp 91–100° (10 mm), $n^{27.5}D$ 1.5060, which contained[24] the ether **10** accompanied by minor amounts of a more rapidly eluted and a more slowly eluted impurity. Redistillation afforded a pure sample of the dihydro ether, **10**: bp 92.5° (7 mm); $n^{23}D$ 1.5080; infrared (CCl_4), 1700 and 1660 cm^{-1} (C=C of olefin and enol ether); nmr (CCl_4), δ 4.42 (1 H, broad, vinyl CH), 3.38 (3 H singlet OCH_3), and 1.4–2.8 (10 H multiplet, aliphatic CH).

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.16; H, 9.62.

A mixture of 20.07 g (0.133 mole) of the enol ether **10**, 200 ml of 1,2-dimethoxyethane, and 200 ml of aqueous acetic acid (1:1 v/v) was stirred at room temperature for 5 hr and then poured into excess aqueous $NaHCO_3$. The ethereal extract of the resulting mixture was washed with aqueous NaCl, dried, concentrated, and distilled to separate 16.57 g (87%) of the unsaturated ketone **6**, bp 92–97° (10 mm), $n^{26.3}D$ 1.5019, which contained[24] a minor impurity eluted before the ketone **6** but exhibited no peak corresponding in retention time to the conjugated isomer **5**. A collected[24] sample of the ketone **6** was used for characterization: infrared (CCl_4), 1720 cm^{-1} (C=O); ultra-

(22) (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).

(23) S. Julia, M. Julia, and L. Brasseux [*Bull. Soc. Chim. France*, 374 (1962)] have reported obtaining this derivative (stereochemistry not stated) melting at 110°.

(24) A gas chromatography column packed with silicone fluid, no. 710, suspended on Chromosorb P was employed for this analysis.

violet maxima, 232 mμ (shoulder, ε 600) and 287 (102); nmr (CCl_4), δ 1.5–2.9 (multiplet, aliphatic CH).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88; mol wt, 136. Found: C, 79.26; H, 8.93; mol wt (mass spectrum), 136.

The reduction of 10.00 g (73.6 mmoles) of the ketone **6** with 1.90 g (50 mmoles) of $LiAlH_4$ in 110 ml of ether was effected following previously described procedures. The product **2** was separated by distillation as 8.89 g (88%) of a colorless viscous liquid: bp 110–115° (10 mm); $n^{27}D$ 1.5129 (lit.[25] bp 65–68° (3 mm)). A collected[24] sample of the alcohol **2** was used for characterization: infrared (CCl_4), 3600 and 3320 cm^{-1} (free and associated OH); nmr (CCl_4) δ 3.4–4.0 (2 H multiplet, >CHOH) and 1.2–2.5 (12 H multiplet, aliphatic CH).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21; mol wt, 138. Found: C, 77.96; H, 10.12; mol wt (mass spectrum), 138.

The hydrogenation of a solution of 18.26 g (0.104 mole) of 6-methoxy-1-tetralone in 100 ml of ethanol at room temperature and atmospheric pressure over 1.51 g of a 5% palladium on carbon catalyst resulted in the uptake of 4.65 l. (0.91 equiv) of hydrogen over a 14-hr period. The resulting mixture was filtered, concentrated, and distilled to separate 14.64 g (87%) of 6-methoxytetralin (**11**) as a colorless liquid, bp 118–130° (7 mm), $n^{24}D$ 1.5431 (lit.[26] bp 128–130° (13 mm), $n^{22}D$ 1.5449), which contained[24] the ether **11** accompanied by *ca.* 10% of a more slowly eluted impurity: ultraviolet maxima, 220 mμ (ε 7540), 279 (2430), and 288 (2020); nmr (CCl_4), δ 6.75 (1 H doublet, J = 9 cps, aryl CH at C-8), 6.2–6.6 (2 H multiplet, aryl CH at C-5 and C-7), 3.58 (3 H singlet, OCH_3), 2.2–2.9 (4 H multiplet, benzylic CH), and 1.5–2.0 (4 H multiplet, aliphatic CH).

Following the procedure described above, 27.85 g (0.172 mole) of the ether **11** was reduced with 6.5 g (0.93 g-atom) of lithium, 100 ml of 1,2-dimethoxyethane, 400 ml of liquid ammonia, and 111.5 g of absolute ethanol. The crude enol ether **12** (29.78 g, infrared (CCl_4), 1700 and 1670 cm^{-1} (enol ether and olefin C=C)) was hydrolyzed with 200 ml of 1,2-dimethoxyethane and 200 ml of aqueous acetic acid (1:1 v/v) as described above. Distillation separated 22.83 g (88%) of the octalone **8**, bp 55–65° (0.02 mm), $n^{26.3}D$ 1.5078, which contained[24] the unconjugated keton **8** accompanied by *ca.* 5% of a more rapidly eluted component; none of the conjugated ketone **7** was detected: infrared (CCl_4), 1720 cm^{-1} (C=O). A 20.15-g (0.134 mole) sample of the octalone **8** was reduced with 2.83 g (0.074 mole) of $LiAlH_4$ in 225 ml of ether as previously described. Distillation separated 17.95 g (89%) of the alcohol **4** as a viscous, colorless liquid, bp 81–86° (0.2–0.5 mm), $n^{26.7}D$ 1.5180 (lit. bp 72° (2 mm),[25] 83–88° (4 mm),[27] $n^{19}D$ 1.5220[27]), which contained[24] several minor impurities eluted before and after the major component. A sample of the alcohol **4** was collected[24] for characterization: infrared (CCl_4), 3600 and 3320 cm^{-1} (free and associated OH); nmr (CCl_4), δ 3.57 (1 H singlet, OH), 3.4–4.0 (1 H multiplet >CHO), and 1.0–2.5 (14 H multiplet, aliphatic CH).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59; mol wt, 152. Found: C, 78.90; H, 10.62; mol wt (mass spectrum), 152.

Preparation of the Sulfonylhydrazone Derivatives 13 and 14.—To a warm (steam bath) solution of 45.45 g (0.50 mole) of commercial glyoxylic acid (containing 80% of the pure acid) in 500 ml of water was added a solution of 93.26 g (0.50 mole) of *p*-toluenesulfonyl hydrazide in 250 ml of aqueous 2.5 *M* HCl. The mixture was heated on a steam bath with vigorous stirring until all the derivative, which initially separated as an oil, had crystallized and then the mixture was cooled and filtered. After the residue had been washed with cold water and air dried for 2 days, the crude hydrazone **13**, mp 145–149° dec, amounted to 115.5 g. The crude, dry hydrazone was recrystallized from a carbon tetrachloride–ethyl acetate mixture to separate 96.5 g (80%) of the acid hydrazone **13** as white prisms, mp 148–154° dec, which are presumably a mixture of stereoisomeric forms. Recrystallization gave material melting at 149.5–152° dec: infared (KBr pellet), 1710 cm^{-1} (carboxyl C=O); ultraviolet maxima, 223.5 mμ (ε 13,600) and 252 (10,200); nmr (CD_3SOCD_3), δ 7.0–8.0 (6 H multiplet, aryl CH, vinyl CH, and NH) and 2.37 (3 H singlet, aryl CH_3).

Anal. Calcd for $C_9H_{10}N_2O_4S$: C, 44.63; H, 4.16; N, 11.57; S, 13.21. Found: C, 44.47; H, 4.04; N, 11.54; S, 13.45.

A suspension of 20.00 g (82.5 mmoles) of the acid **13** in a mixture of 110 ml of benzene and 24.0 g (0.206 mole) of thionyl chloride was refluxed with stirring for 1.5–2.5 hr at which time the mixture had attained a distinct yellow color and only a small amount of fine, suspended insoluble material remained.[28] The mixture was cooled, treated with Celite, and filtered to give a light yellow solution which was concentrated under reduced pressure. The residual solid was triturated with a few milliliters of warm benzene, filtered, washed with cold benzene to remove colored impurities, and then dissolved in a minimum quantity of warm benzene, diluted with petroleum ether, and cooled. The acid chloride **14** separated as 12.79 g (60%) of pale yellow prisms, mp 102–111° dec (sealed tube), which is presumably a mixture of stereoisomers. Recrystallization from benzene gave a sample of the acid chloride **14** as white prisms, mp 103–110° dec (sealed tube), used for characterization: infrared (Nujol mull), 1775 (shoulder) and 1740 cm^{-1} (C=O); ultraviolet maxima (CH_3CN), 224.5 mμ (ε 14,300) and 252 (12,600); nmr (CH_3CN), δ 7.2–8.0 (multiplet, aryl CH, vinyl CH, and, possibly NH) with higher field absorption obscured by the solvent.

Anal. Calcd for $C_9H_9ClN_2O_3S$: C, 41.46; H, 3.48; N, 10.75; S, 12.30; Cl, 13.60. Found: C, 41.59; H, 3.60; N, 10.71; S, 12.43; Cl, 13.90.

Preparation of Crotyl Diazoacetate (15). A. From the Chloroformate 16.—Following previous directions,[8] 21.3 g (0.30 mole) of crotyl alcohol was added, dropwise and with stirring over a 1.2-hr period, to a solution of 37 g (0.38 mole) of phosgene in 100 ml of ether while the temperature of the reaction mixture was maintained at −8 ± 5°. After the mixture had been stirred for 1 additional hr at −8 to +7°, the low-boiling components were removed under reduced pressure and the residue was distilled to separate 36.1 g (91%) of the chloroformate **16** as a colorless liquid: bp 28–34° (6 mm); $n^{26.5}D$ 1.4323 (lit.[8] bp 33° (10 mm), $n^{25}D$ 1.4327); infrared (CCl_4), 1780 (acid chloride C=O), 1675 (C=C) and 970 cm^{-1} (*trans*-CH=CH); nmr (CCl_4), δ 5.3–6.3 (2 H multiplet, vinyl CH), 4.66 (2 H doublet, J = 5.5 cps, $-CH_2O$), and 1.77 (3 H doublet, J = 5.5 cps, CH_3C).

To a cold (0°) solution of *ca.* 80 mmoles of diazomethane in 350 ml of ether was added 2.59 g (19.3 mmoles) of crotyl chloroformate (**16**) and the resulting solution was allowed to stand at 0° for 44 hr. Since an infrared analysis of the solution indicated that the reaction was approximately half complete, an additional *ca.* 80-mmole portion of diazomethane was added along with a 5.0-g portion of solid sodium bicarbonate. After 11 days the infrared spectrum of the crude product indicated complete consumption of the acid chloride. The solution was dried, filtered, and concentrated to leave 3.58 g of the crude diazoacetate **15** as a yellow liquid. This product was passed through a column containing 100 g of Florisil to separate 1.35 g (49%) of the diazo ester **15** in the fraction eluted with an ether–hexane mixture (1:4 v/v). This material was identified by comparison of its infrared spectrum with the spectrum of a subsequently described sample.

B. From the Hydrazone Esters 17.—To a mixture of 5.01 g (19.4 mmoles) of the acid chloride **14**, 3.30 g (39.3 mmoles) of $NaHCO_3$, and 50 ml of methylene chloride was added 1.41 g (19.6 mmoles) of crotyl alcohol. The resulting mixture was stirred at room temperature for 3 hr (during which time some gas evolution was apparent) and then filtered and concentrated. The residual light orange oil (4.67 g) was chromatographed on 100 g of silicic acid to separate 2.35 g (41%) of the crude *cis* isomer **17b** in fractions eluted with 5% ether in benzene and 0.91 g (16%) of the crude *trans* isomer **17a** in subsequent fractions eluted with 10% ether in benzene. The crude *cis* isomer was crystallized from an ethyl acetate–cyclohexane mixture to separate 1.91 g of ester **17b** as white prisms, mp 62–68°; purification of this isomer was complicated by the tendency of this material to change to the higher melting isomer **17a** when solutions were allowed to stand. Additional recrystallizations from ethyl acetate–petroleum ether (bp 30–60°) mixtures gave a sample of the ester **17b**: mp 69–70°; infrared ($CHCl_3$), 3200 (NH), 1700 (ester C=O), and 965 cm^{-1} (*trans*-CH=CH); ultraviolet maxima, 225 mμ (ε 7180) and 251 (6280); nmr ($CDCl_3$), δ 11.84 (1 H broad, NH), 7.69 and 7.18 (two 2 H doublets, J = 8 for each, aryl CH), 6.68 (1 H singlet, −N=CH−), 5.3–6.1 (2 H multiplet vinyl CH), 4.52 (2 H doublet, J = 5.5 cps, CH_2O),

(25) J. Fried, N. A. Abraham, and T. S. Santhanakrishnan, *J. Am. Chem. Soc.*, **89**, 1044 (1967).

(26) A. J. Birch, E. M. A. Shoukry, and F. Stansfield, *J. Chem. Soc.*, 5376 (1961).

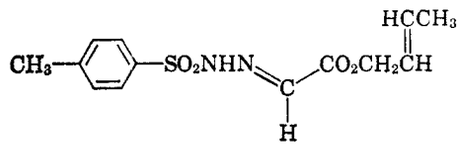
(27) R. H. Eastman and J. E. Starr, *J. Org. Chem.*, **31**, 1393 (1966).

(28) If heating is continued beyond this stage, the product is contaminated with a dark-colored impurity which is difficult to remove.

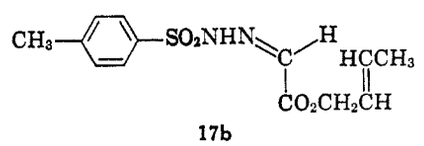
2.37 (3 H singlet, aryl CH_3), and 1.69 (3 H doublet, J = 5.5 cps, CH_3C).

Anal. Calcd for $C_{13}H_{16}N_2O_4S$: C, 52.70; H, 5.44; N, 9.46; S, 10.80. Found: C, 52.83; H, 5.55; N, 9.43; S, 10.86.

The crude *trans* isomer was crystallized from an ethyl acetate–cyclohexane mixture to separate 0.60 g of the *trans* ester **17a** as white needles: mp 101–105° dec (recrystallization raised the melting point of the ester **17a** to 105–106.5° dec); infrared (KBr pellet), 1720 (ester C=O) and 975 cm^{-1} (*trans*-CH=CH); ultraviolet maxima, 222 mμ (ε 17,450) and 250 (14,500); nmr ($CDCl_3$), δ 9.51 (1 H, NH), 7.67 and 7.13 (two 2 H doublets, J = 8 cps for each, aryl CH), 7.10 (1 H singlet, N=CH–), 5.2–6.1 (2 H multiplet, vinyl CH), 4.49 (2 H doublet, J = 5 cps, CH_2O), 2.35 (3 H singlet, aryl CH_3), and 1.67 (3 H doublet, J = 5.5 cps, CH_3C). This higher melting isomer is assigned the *trans* configuration **17a** because its ultraviolet absorption



17a



17b

is significantly more intense than the absorption of the *cis* isomer **17b** and because the nmr signal for proton α to the carbonyl group is shifted by 0.42 ppm to lower field in the *trans* isomer **17a** where deshielding by the adjacent arylsulfonyl function would be expected.

Anal. Calcd for $C_{13}H_{16}N_2O_4S$: C, 52.70; H, 5.44; N, 9.46; S, 10.80. Found: C, 52.89; H, 5.52; N, 9.33; S, 10.84.

A solution of 403 mg (1.3 mmoles) of each of the isomeric esters **17** in 10 ml of methylene chloride was treated with 113 mg (1.1 mmoles) of triethylamine and the progress of the reaction at room temperature was followed by thin layer chromatography.[29] The conversion of the *trans* isomer **17a** to the diazo ester **15** was more rapid than the corresponding conversion of the *cis* isomer **17b**. After reaction was complete (15–60 min), each reaction mixture was concentrated and chromatographed on 6 g of Florisil. The diazo ester **15**, eluted with benzene and identified by its infrared absorption in each case, amounted to 144 mg (88%) from the *trans* ester **17a** and 143 mg (87%) from the *cis* isomer **17b**.

The diazo ester **15** could be prepared more efficiently by the direct reaction of the acid chloride **14** with the alcohol in the presence of 2 equiv of triethylamine. A cold (0°) solution of 10.0 g (38 mmoles) of the acid chloride **14** in 100 ml of methylene chloride was treated with 2.80 g (38 mmoles) of crotyl alcohol and then a solution of 7.80 g (77 mmoles) of freshly distilled triethylamine in 25 ml of methylene chloride was added dropwise and with stirring over a 20-min period. After the resulting mixture had been stirred for 1 hr at 0°, the solvent was concentrated under reduced pressure and a mixture of the dark residual oil with benzene was slurried with 100 g of Florisil. The Florisil, which adsorbed the bulk of the dark impurities, was collected on a filter and washed with several portions of benzene. The combined benzene filtrates were concentrated under reduced pressure and the residual yellow oil was distilled to separate 2.94 g (54%) of the diazo ester **15** as a yellow liquid: bp 30–33° (0.15 mm); $n^{24}D$ 1.4856; infrared (CCl_4), 2110 (C=N=N), 1715 (diazo ester C=O), and 965 cm^{-1} *trans*-CH=CH); ultraviolet maxima (*n*-hexane), 225 mμ (shoulder, ε 7570) and 245 (12,300); ultraviolet maxima (95% ethanol), 213 mμ (ε 4860) and 248 (16,200); nmr (CCl_4), δ 5.2–6.1 (2 H multiplet, vinyl CH), 4.67 (1 singlet, –CH=N), 4.49 (2 H doublet, J = 5 cps, $-CH_2O-$), and 1.70 (3 H doublet, J = 5 cps, CH_3C); mass spectrum, no molecular ion, abundant fragment peaks at *m/e* 112, 82, 68, 55, 54, 53, 41, and 39.

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.42; H, 5.75; N, 19.99. Found: C, 51.65; H, 5.92; N, 19.80.

(29) A plate coated with silicic acid and eluted with an ethyl acetate–cyclohexane mixture was employed for this analysis.

Preparation of the Diazo Ester 19.—To a cold (0°) solution of 1.00 g (3.84 mmoles) of the acid chloride **14** in 10 ml of methylene chloride was added a solution of 516 mg (3.74 mmoles) of the alcohol **2** and 387 mg (3.84 mmoles) of triethylamine in 2 ml of methylene chloride. The resulting mixture was stirred for 2 hr while it was allowed to warm to room temperature and then the solvent was removed under reduced pressure and the residue was chromatographed on 20 g of silicic acid. The early fractions, eluted with 2% ether in benzene contained 208 mg (15%) of a pale yellow oil believed to be primarily the *cis* isomer of the ester **18**: infrared ($CHCl_3$), 3200 (NH) and 1695 cm^{-1} (conjugated ester C=O). Later fractions, 834 mg (62%) of an oil eluted with 8% ether in benzene, solidified on standing. Recrystallization of these later fractions from an ethyl acetate–petroleum ether (bp 30–60°) mixture separated the ester **18** (presumably the *trans* isomer) as a light tan solid, mp 123–125° dec. Additional recrystallizations afforded the ester **18** as white plates: mp 130–131° dec; infrared ($CHCl_3$), 3160, 3260 (NH), and 1735 (shoulder) and 1710 cm^{-1} (conjugated ester C=O); ultraviolet maximum, 222 mμ (ε 16,670) and 252 (12,600); nmr ($CDCl_3$), δ 7.87 (2 H doublet, J = 8 cps, aryl CH), 7.35 (2 H doublet, J = 8 cps, aryl CH), 4.9–5.5 (1 H multiplet, >CHO), 2.45 (3 H singlet, aryl CH_3), and 1.4–2.6 (12 H multiplet, aliphatic CH). In addition the spectrum has two sharp singlets at δ 6.83 and 7.29 together corresponding in area to 1 H (–CH=N–) which vary in intensity as the solution is allowed to stand. Considering the earlier specta of the esters **17** suggests that the initially more intense peak at δ 7.29 should be assigned to the *trans* isomer of ester **18** while the peak at δ 6.83 which is the more intense after 40 min should be assigned to the *cis* isomer of ester **18**.

Anal. Calcd for $C_{18}H_{22}N_2O_4S$: C, 59.66; H, 6.12; N, 7.73; S, 8.83. Found: C, 59.77; H, 6.32; N, 7.83; S, 8.85.

To a cold (0°) solution of 1.01 g (3.88 mmoles) of the acid chloride **14** in 10 ml of methylene chloride was added a solution of 521 mg (3.77 mmoles) of the alcohol **2** and 391 mg (3.88 mmoles) of triethylamine in 2 ml of methylene chloride. After the solution had been stirred and allowed to warm to room temperature over a 1-hr period, an additional 435 mg (4.31 mmoles) of triethylamine was added and the resulting solution was stirred for 1 hr at room temperature and then concentrated under reduced pressure. The residual oil was chromatographed on 12 g of Florisil to separate 585 mg (75%) of the diazo ester **19** as a yellow liquid in the fractions eluted with benzene. Crystallization of this material from a hexane solution at Dry Ice temperatures separated the diazo ester **19** as yellow prisms: mp 29–36°; infrared (CCl_4), 2100 (C=N=N) and 1700 cm^{-1} (diazo ester C=O); ultraviolet maxima (*n*-hexane), 220 mμ (ε 7850) and 245 (12,650); nmr (CCl_4), δ 4.7–5.3 (1 H multiplet, >CHO), 4.63 (1 H singlet, N=CH–), and 1.3–2.6 (12 H multiplet, aliphatic CH); mass spectrum, no molecular ion peak, abundant fragment peaks at *m/e* 178, 134, 91, 89, 87, 56, 45, 43, 41, and 39.

Anal. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.58. Found: C, 63.81; H, 7.05; N, 13.49.

Preparation of the Diazo Ester 20.—Following the previously described directions, a cold (0°) solution of 1.01 g (3.89 mmoles) of the acid chloride **14** in 10 ml of methylene chloride was treated successively with 577 mg (3.79 mmoles) of the alcohol **4** and with a solution of 397 mg (3.95 mmoles) of triethylamine in 2 ml of methylene chloride and the resulting solution was stirred for 30 min at room temperature. After a second 404-mg (3.98 mmoles) portion of triethylamine had been added, the mixture was stirred for 1 hr at room temperature and then concentrated under reduced pressure. A solution of the residue in benzene was filtered through a column containing 12 g of Florisil; concentration of the filtrate left 783 mg (89%) of the crude diazo ester **20** as a yellow oil. A solution of this material in hexane, when cooled to Dry Ice temperatures, deposited the diazo ester **20** as yellow prisms: mp 29–32° (recrystallization raised the melting point to 31–33°); infrared (CCl_4), 2100 (C=N=N) and 1700 cm^{-1} (diazo ester C=O); ultraviolet maxima (*n*-hexane), 217 mμ (ε 8100) and 245 (12,700); nmr (CCl_4), δ 4.7–5.3 (1 H multiplet, >CHO), 4.64 (1 H singlet, –CH=N) and 1.2–2.5 (14 H multiplet, aliphatic CH); mass spectrum, no molecular ion, abundant fragment peaks at *m/e* 192, 134, 105, 93, 92, 91, 79, 77, 41, and 39.

Anal. Calcd for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.66; H, 7.38; N, 12.88.

Attempts to apply this procedure to the alcohols **1** and **3** led to the formation of crude products (yellow liquids after filtration through a Florisil column) which had infrared absorption compati-

ble with structures **21** and **22**. However, our efforts to obtain pure samples of these diazo esters resulted in partial or complete decomposition of the products during the attempted purification.

The Copper-Catalyzed Decomposition of Crotyl Diazoacetate (15).—A solution of 1.66 g (7.57 mmoles) of the diazo ester **15** in 75 ml of cyclohexane was added, dropwise and with stirring over a 9.5-hr period, to a suspension of 1.35 g of copper(I) oxide in 75 ml of refluxing cyclohexane. The resulting mixture was refluxed with stirring for an additional 20 min and then cooled, filtered, and concentrated. The residual yellow oil (0.79 g) was distilled in a short-path still (0.12 mm and 40–140° bath) to separate 685 mg (80%) of the crude product as a colorless oil, $n^{27}D$ 1.4642. The gas chromatogram[21] of this product indicated the presence of the lactone **26** (*ca.* 82%, 5.9 min), an unidentified component (*ca.* 3%, 18.0 min), the fumarate ester **23** (*ca.* 9%, 22.5 min), and the maleate ester **24** (*ca.* 6%, 26.3 min). Subsequent work established that a small amount of the cyclohexylacetic ester **25** was also present but was not resolved from the gas chromatographic peak for the lactone **26** in this analysis. On a longer column[21] the retention times of the ester **25** and the lactone **26** were 12.0 and 12.8 min, respectively. To select a catalyst system for the catalyzed decomposition, a number of runs were made in which solutions containing a given weight of the diazo ester **15** in cyclohexane were added to a suspension of catalyst in refluxing cyclohexane as described above. The crude products were distilled in a short-path still to separate a crude lactone fraction, bp 40–55° (0.1 mm), and a crude dimer fraction, bp 55–100° (0.1 mm). The following yields, expressed as per cent yields of the pure lactone **26** and the pure dimers **23** and **24** for comparison, were obtained with various catalysts: Cu_2O, 39% lactone and 27% dimer; $CuSO_4$, 31% lactone and 14% dimer; Cu (untreated), 20% lactone and 19% dimer; Cu (washed with methanol), 30% lactone and 36% dimer; Cu (washed with aqueous solution of the disodium salt of ethylenediaminetetraacetic acid),[30] 37% lactone and 31% dimer; Cu (from the thermal decomposition of a slurry of methylcopper in cyclohexane under a nitrogen atmosphere), 24% lactone and 16% dimer.

To separate the products for identification, the crude distilled products from various runs were chromatographed on silicic acid. Chromatography of the 685 mg of crude product described above separated the following fractions: (1) 48 mg (3%) of the cyclohexylacetic ester **25** eluted with 2% ether in hexane and identified with a subsequently described sample by comparison of infrared and mass spectra; (2) 71 mg (8%) of dicrotyl fumarate (**23**) eluted with 5% ether in hexane and identified with a subsequently described sample by comparison of infrared spectra and thin layer chromatographic behavior;[29] (3) 58 mg (7%) of dicrotyl maleate (**24**) eluted with 10% ether in hexane and identified with a subsequently described sample by comparison of infrared spectra and thin layer chromatographic behavior;[29] and (4) 381 mg (45%) of the lactone **26** in fractions eluted with 20–50% ether in hexane. Distillation of this fraction in a short-path still (0.05 mm and 43–53° bath) afforded the lactone **26** as a colorless liquid: $n^{27.8}D$ 1.4602; infrared (CCl_4), 1815 (shoulder), 1780, and 1745 (shoulder) (lactone C=O); ultraviolet maximum, 215 mμ (shoulder, ε 246); nmr (CCl_4), δ 3.8–4.5 (2 H multiplet, CH_2O), 1.6–2.3 (2 H multiplet, bridgehead CH), and 1.18 (4 H singlet, superimposed peaks for both types of protons in the $CH_3CH<$ function; these signals were also not resolved when the spectrum was determined in benzene solution); mass spectrum, molecular ion at *m/e* 112, abundant fragment peaks at *m/e* 82, 68, 67, 55, 54, 53, 41, 40, and 39.

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.49; H, 7.24.

After a mixture of 656 mg (5.8 mmoles) of the lactone **26**, 0.45 g (6.8 mmoles) of 85% KOH, and 10 ml of water had been stirred at room temperature for 6.5 hr, the resulting solution was adjusted to pH 5 by the addition of acetic acid and 48 mg of hydrated ruthenium dioxide (55% RuO_2) was added.[31] A solution of 2.59 g (12.1 mmoles) of $NaIO_4$ in 15 ml of water was added, dropwise with stirring over a 15-min period. After the addition was complete, the mixture was stirred for an additional 10 min and then the excess oxidant was consumed with added isopropyl alcohol. The resulting solution was made basic, filtered through Celite, acidified, and extracted repeatedly with ethyl acetate. The organic extract was washed with aqueous $NaHSO_3$, dried, and concentrated to leave 300 mg of crude acid **27a** which crystallized from a benzene–ethyl acetate–petroleum ether (bp 30–60°) mixture as 216 mg of white plates, mp 134–136°. The various aqueous layers were treated with excess $NaHSO_3$, then saturated with NaCl, and continuously extracted with ether to separate an additional 121 mg (total 337 mg or 40%) of the acid **27a**. Recrystallization separated 275 mg of the acid **27a**, mp 136–137°, which melted at 136–137.5° (lit.[17] mp 140°) after sublimation (0.1 mm and 115° bath). A 100-mg sample of the diacid **27a** was esterified with excess ethereal diazomethane to yield 90 mg (75%) of the diester **27b** as white needles: mp 41–43° from an ether–petroleum ether (bp 30–60°) mixture (recrystallization raised the melting point of the diester **27b** to 42–43.5° (lit.[17a] mp 46°)); infrared (CCl_4), 1740 cm^{-1} (ester C=O); nmr (CCl_4), δ 3.61 (6 H singlet, OCH_3), 1.5–2.2 (3 H multiplet, cyclopropane CH), and 1.19 (3 H doublet, J = 5.5 cps, CH_3C); mass spectrum, no molecular ion, abundant fragment peaks at *m/e* 141, 113, 81, 59, 53, 41, and 39.

Preparation of the Crotyl Esters 23–25.—After a mixture of 5.02 g (43 mmoles) of fumaric acid, 30 ml of thionyl chloride, and 30 ml of benzene had been refluxed with stirring for 17 hr, the mixture was filtered to remove a small amount of unchanged diacid and then concentrated under reduced pressure. A solution of the residue in 50 ml of benzene was cooled in an ice bath and then a mixture of 6.5 g (90 mmoles) of crotyl alcohol and 9.0 g (89 mmoles) of triethylamine was added with stirring. After the resulting dark reaction mixture had been stirred for 30 min, it was filtered and the filtrate was concentrated and distilled to separate 6.59 g (68%) of the crude diester **23** as a yellow liquid, bp 100–111° (0.09 mm). An ether solution of 5.64 g of this crude product was washed successively with aqueous $NaHCO_3$ and with aqueous NaCl and then dried, concentrated, and distilled to separate 4.44 g of the diester **23** as a colorless liquid, bp 97–101° (0.27 mm). A center fraction of the pure[21] diester **23**, bp 98–100° (0.27 mm), $n^{24.5}D$ 1.4750, was used for characterization: infrared (CCl_4) 1730 (conjugated ester C=O), 1675 (C=C), 1645 (conjugated C=C), and 965 and 975 cm^{-1} (*trans*-CH=CH); ultraviolet maximum, 208 mμ (ε 20,400); nmr (CCl_4), δ 6.74 (2 H singlet, -COCH=CHCO-), 5.2–6.2 (4 H multiplet, vinyl CH), 4.55 (4 H, doublet of partially resolved multiplets, J = 5 cps, $-CH_2O$), and 1.74 (6 H doublet of partially resolved multiplets, J = 5.5 cps, CH_3C).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19; mol wt, 224. Found: C, 64.34; H, 7.28; mol wt, 224 (mass spectrum).

A mixture of 5.0 g (51 mmoles) of maleic anhydride, 17 ml of crotyl alcohol, 50 ml of benzene, and 2.5 g of Dowex 50W-X10 resin (H^+ form) was refluxed with stirring and continuous separation of water for 20.5 hr. After the mixture had been cooled and filtered, the filtrate was washed successively with aqueous $NaHCO_3$ and with aqueous NaCl and then dried, concentrated, and distilled. The diester was collected as 2.20 g (19%) of colorless liquid, bp 82–90° (0.07 mm). A center fraction from the distillation, bp 88–90° (0.07 mm), $n^{24.5}D$ 1.4705, contained[21] the maleate **24** accompanied by *ca.* 5% of a more rapidly eluted impurity with the retention time of the fumarate ester **23**. A collected[21] sample of the diester **24** was used for characterization: infrared (CCl_4), 1735 (conjugated ester C=O), 1675 (C=C), 1645 (conjugated C=C), and 970 cm^{-1} (*trans*-CH=CH); ultraviolet, only end absorption, ε 8100 at 210 mμ; nmr (CCl_4), δ 6.11 (2 H singlet, COCH=CHCO), 5.2–6.0 (4 H multiplet, vinyl CH), 4.52 (4 H doublet of partially resolved multiplets, J = 5 cps, $-CH_2O$), and 1.72 (6 H doublet of partially resolved multiplets, J = 5 cps, CH_3C).

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19; mol wt, 224. Found: C, 64.06; H, 7.20; mol wt, 224 (mass spectrum).

The aqueous alkaline washings from the preparation of the maleic ester **24** were acidified followed by the usual manipulations to separate 8.10 g of a colorless liquid which we presume to be the monocrotyl ester of maleic acid: infrared (CCl_4), 2300–3600 (broad, carboxyl O–H), 1740 (ester C=O), 1715 (carboxyl C=O), 1635 (conjugated C=C), and 965 cm^{-1} (*trans*-CH=CH).

A solution of 5.0 g (35 mmoles) of cyclohexylacetic acid[32] and 16.5 g (139 mmoles) of thionyl chloride in 25 ml of benzene was refluxed for 3 hr and then cooled and concentrated under reduced

(30) A. H. Lewin, M. J. Zovko, W. H. Rosewater, and T. Cohen, *Chem. Commun.*, No. 2, 80 (1967).

(31) The oxidation procedure using catalytic amounts of RuO_2 which is oxidized by $NaIO_4$ was described by H. Nakata, *Tetrahedron*, **19**, 1959 (1963).

(32) Cyclohexylacetic acid, mp 26–28°, was prepared in 85% yield by the hydrogenation of phenylacetic acid as previously described: R. Adams and J. R. Marshall, *J. Am. Chem. Soc.*, **50**, 1970 (1928).

pressure. A solution of the residual crude acid chloride (a yellow liquid) in 15 ml of methylene chloride was cooled in an ice bath and then a solution of 2.6 g (36 mmoles) of crotyl alcohol and 3.6 g (36 mmoles) of triethylamine in 10 ml of methylene chloride was added dropwise and with stirring over a 15-min period. The resulting mixture was stirred at 0° for 0.5 hr and at room temperature for 0.5 hr and then filtered. After the filtrate had been washed successively with dilute, aqueous HCl, with aqueous $NaHCO_3$, and with aqueous NaCl, it was dried, concentrated, and distilled to separate 5.43 g (78%) of the ester **25**, bp 70–75° (0.1 mm). A center fraction contained the pure[21] ester **25**: bp 75° (10 mm); $n^{25.5}D$ 1.4605; infrared (CCl_4), 1740 (ester C=O), 1675 (C=C), and 970 cm^{-1} (*trans*-CH=CH); nmr (CCl_4), δ 5.2–6.0 (2 H multiplet, vinyl CH), 4.38 (2 H doublet of partially resolved multiplets, J = 5 cps, $-CH_2O$), and 0.9–2.5 (16 H multiplet, aliphatic CH).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27; mol wt, 196. Found: C, 73.28; H, 10.27; mol wt, 196 (mass spectrum).

The Copper-Catalyzed Decomposition of the Diazo Ester 19.—A solution of 2.12 g (10.3 mmoles) of the diazo ester **19** in 150 ml of cyclohexane was added, dropwise and with stirring over an 8-hr period, to a suspension of 3.30 g of Cu_2O in 150 ml of refluxing cyclohexane. The resulting mixture was refluxed for an additional 30 min and then filtered and the filtrate was concentrated. Chromatography of the residual oil (1.91 g) on Florisil separated 716 mg of colorless oil containing the esters **28** and **29** (and other components) in the early fractions eluted with 5–10% ether in benzene and 383 mg (21%) of the crude lactone **30** in later fractions eluted with 10–50% ether in benzene. The crude lactone was distilled in a short-path still (0.1 mm and 125–148° bath) and the distillate was crystallized from an ether–hexane mixture to separate the pure lactone **30** as white needles: mp 49–51°; infrared (CCl_4), 1735 and 1725 (shoulder) (δ-lactone C=O); ultraviolet, only end absorption, ϵ 906 at 210 mμ; nmr (CCl_4), δ 4.3–4.7 (1 H multiplet, >CHO) and 1.0–2.5 (13 H multiplet, aliphatic CH); mass spectrum, molecular ion at m/e 178, abundant fragment peaks at m/e 136, 134, 121, 91, 79, 77, and 39.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.95; H, 7.82.

The early ester containing chromatographic fractions from several runs were combined (total 1.10 g) and chromatographed on silicic acid. The early fractions (394 mg, 7% yield based on the diazo ester **19**) were distilled in a short-path still (0.1 mm and 140–160° bath) to separate 320 mg of the cyclohexylacetic ester **29** as a colorless liquid: infrared (CCl_4), 1735 (ester C=O), ultraviolet, only end absorption, ϵ 2345 at 210 mμ; nmr (CCl_4), δ 4.7–5.3 (1 H multiplet, >CHO) and 0.9–2.6 (*ca.* 25 H multiplet, aliphatic CH); mass spectrum, no molecular ion, abundant fragment peaks at m/e 121, 120, 92, 91, 79, 55, and 41.

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.82; H, 9.99. Found: C, 77.93; H, 10.46.

Following the procedures described previously, cyclohexylacetyl chloride, prepared from 1.05 g (7.4 mmoles) of cyclohexylacetic acid and 1.6 g of thionyl chloride, was treated with solution of 862 mg (6.2 mmoles) of the alcohol **2** and 743 mg (7.4 mmoles) of triethylamine in 10 ml of methylene chloride. The crude neutral product (1.63 g) was distilled in a short-path still (0.08 mm and 110–150° bath) to separate 1.48 g (91%) of the crude ester **29** which contained[21] two minor, more rapidly eluted impurities A collected[21] sample of the ester **29** was identified with the previously described sample by comparison of gas chromatographic retention times, infrared spectra, and mass spectra.

After a number of intermediate fractions, the later fractions from the above silicic acid chromatography, 163 mg (4%) of the crude maleic ester **28** eluted with 8% ether in hexane, were distilled in a short-path still (0.1 mm and 190–215° bath) to separate 113 mg of the maleic ester **28** (probably a mixture of stereoisomers) as a colorless, viscous liquid: infrared (CCl_4), 1735 (ester C=O) and 1645 cm^{-1} (conjugated C=C); ultraviolet, only end absorption, ϵ 12,400 at 210 mμ; nmr (CCl_4), δ 6.08 (2 H singlet, COCH=CHCO), 4.7–5.3 (2 H multiplet, >CHO), and 1.4–2.7 (*ca.* 24 H multiplet, aliphatic CH).

Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.12; H, 8.05.

The Copper-Catalyzed Decomposition of the Diazo Ester 20.—Following the procedures described above, a solution of 2.20 g (10 mmoles) of the diazo ester **20** in 125 ml of cyclohexane was added to a suspension of 3.1 g of Cu_2O in 125 ml of cyclohexane over a 12.5 hr period. The crude product (2.58 g), isolated as previously described, was chromatographed on Florisil. The early fractions, 758 mg (*ca.* 40%) believed to contain a mixture of dimeric esters **31** and **32** and other products, eluted with 5% ether in hexane were followed by 434 mg (23%) of fractions, eluted with 50% ether in hexane, which contained the lactone **33** as an oil. The lactone fraction was rechromatographed and then crystallized from an ether–hexane mixture to separate the pure lactone **33** as white needles: mp 54–55.5°; infrared (CCl_4), 1735 and 1715 cm^{-1} (shoulder) (δ-lactone C=O); nmr (CCl_4), δ 4.2–4.7 (1 H multiplet >CHO) and 1.1–2.5 (15 H multiplet, aliphatic CH); mass spectrum, molecular ion at m/e 192, abundant fragment peaks at m/e 109, 91, 79, 77, 43, 41, and 39.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.03; H, 8.42.

A comparable decomposition of 2.16 g of the diazo ester **20** conducted in *n*-hexane in the presence of $CuSO_4$ yielded only 120 mg (6%) of the crude lactone **33** accompanied by 1.06 g of a rapidly eluted fraction containing the ester by-products. This material was rechromatographed on silicic acid to separate 190 mg of an early liquid fraction eluted with 3% ether in hexane containing[21] two or three unknown components, 214 mg (11%) of material believed to be the crude fumarate ester **31**, and 412 mg (22%) of material believed to be the crude maleate ester **32**. The crude fumarate **31** was crystallized from hexane to separate 110 mg of the partially purified ester **31** as white prisms, mp 73–83°; additional recrystallization raised the melting point to 76–84°. The spectral properties of the partially purified material are consistent with the assumption that this material is the fumarate ester **31**: infrared (CCl_4), 1725 (conjugated ester C=O) and 1640 cm^{-1} (conjugated C=C); nmr (CCl_4), δ 6.72 (2 H singlet, COCH=CHCO), 4.6–5.3 (2 H multiplet, >CHO), and 1.1–2.5 (*ca.* 28 H multiplet, aliphatic CH).

The crude maleate **32** was distilled in a short-path still (0.12 mm and 220–245° bath) to separate 181 mg of material believed to be the maleate ester **32** accompanied by other impurities: infrared (CCl_4), 1730 (conjugated ester C=O) and 1645 cm^{-1} (conjugated C=C); nmr (CCl_4), δ 6.07 (*ca.* 2 H singlet, COCH=CHCO), 4.7–5.3 (*ca.* 2 H multiplet, >CHO), 1.2–2.5 (*ca.* 28 H multiplet, aliphatic CH), and a number of small peaks in various regions of the spectrum.

Registry No.—**2**, 14661-60-0; 3,5-dinitrobenzoate of **3**, 14661-61-1; **4**, 5689-10-1; **6**, 14661-63-3; **8**, 13837-12-2; **9**, 5111-69-3; **10**, 13846-74-7; **11**, 1730-48-9; **13**, 14661-68-8; **14**, 14661-69-9; **15**, 14746-03-3; **16**, 14661-70-2; **17a**, 14661-71-3; **17b**, 14723-36-5; **18**, 14661-73-5; **19**, 14661-74-6; **20**, 14661-75-7; **23**, 14661-76-8; **24**, 14661-77-9; **25**, 14661-78-0; **26**, 14728-14-4; **27b**, 14661-79-1; **28**, 14661-80-4; **29**, 14661-81-5; **30**, 14661-82-6; **33**, 14754-79-1.