reduced by half by boiling off solvent at atmospheric pressure. The remainder of the solvent was removed by distillation through a one foot long Vigreux column at 100 mm. pressure and then the product was distilled at 20 mm. pressure to give 14.0 g., b.p. 50–60°. The product was distilled again at 20 mm. to give 13 g. (66% yield) of dimethylnitrosamine, b.p. 52–57°. An infrared spectrum of the material was practically identical with that of an authentic sample of dimethylnitrosamine except for a small absorption band at 6.04 μ. The contaminant was not identified but was shown not to be dimethylnitramine on the basis of infrared data.

Diisopropylcarbamyl Chloride and Silver Nitrate with Nitrogen Dioxide in Carbon Tetrachloride.—Five and one-tenth grams (0.030 mole) of powdered silver nitrate was added to 3.3 g. (0.020 mole) of diisopropylcarbamyl chloride dissolved in 50 ml. of carbon tetrachloride. Nitrogen dioxide was bubbled through the stirred reaction mixture. The reaction mixture was heated to 50° and held there for 20 minutes. The silver salts were filtered off, and the carbon tetrachloride evaporated. The residue was distilled at 2 mm. pressure to give 1.0 g. of liquid material, b.p. 82–85°. The elemental analyses were as follows: C, 42.47; H, 9.30; N, 20.52. These analyses do not correspond to those for either diisopropylnitramine or nitrosamine; furthermore, both of the latter compounds are solids.

Dimethylcarbamyl Chloride and Silver Nitrate in Acetonitrile in the Presence of Nitric Oxide.—Dry helium was passed through a 1000-ml. reaction vessel containing 32.3 g. (0.300 mole) of dimethylcarbamyl chloride in 200 ml. of dry acetonitrile to remove oxygen. Nitric oxide was then passed into the vigorously stirred solution for 5 minutes. While maintaining the nitric oxide atmosphere and the stirring, 51.0 g. (0.300 mole) of silver nitrate in 100 ml. of acetonitrile was added from an addition funnel. Silver chloride precipitated immediately and the temperature soon rose to 40°. Nitrogen dioxide then appeared in the gas and liquid phases and the temperature climbed rapidly to 70° even though a Dry Ice–acetone-bath was placed around the flask when the temperature reached 50°. The evolution of gas was so vigorous that a considerable amount of the reaction mixture was carried out of the flask. The temperature soon dropped to 50° where it was maintained for 5 minutes. The reaction was then worked up in exactly the same manner as in the experiment where no nitric oxide was used to give 8.7 g. (40% yield) of dimethylnitrosamine[11] and 10.6 g. (40% yield) of dimethylnitramine, m.p. 50–54°. Recrystallization from ether gave dimethylnitramine, m.p. 55–57°.

Analysis of Gases Evolved from the Reactions of Dialkylcarbamyl Chloride with Silver Nitrate.—Small samples (0.01 mole) of the appropriate carbamyl chloride was added to 0.01 mole of silver nitrate in 10 ml. of solvent in a closed system fitted with a gas buret for measuring the amount of gas evolved. The system was swept out with dry helium before the reactants were mixed. The gas samples were analyzed on a mass spectrometer by Dr. S. Ruven Smith of this Laboratory. The results are given in Table II in the text.

Measurements of Rates of Gas Evolution.—The standard silver salt solutions were made up by weighing reagent grade silver nitrate or dry freshly prepared silver nitrite into volumetric flasks and making up to volume with acetonitrile which had been distilled from calcium hydride. The carbamyl chlorides were distilled under reduced pressure and center cuts were used for making up standard solutions with dry acetonitrile. Five milliliter samples each of a silver salt solution and a carbamyl chloride solution were placed in separate legs of an inverted Y-tube arrangement which permitted mixing by tilting after the reactants had been thermally equilibrated with the constant temperature bath.[15] The reaction vessel was attached to a gas buret for measuring the volume of the evolved gas. The reaction mixture was constantly agitated to facilitate liberation of the gases. The gas volume due to solvent vapor was subtracted from the measured gas volume. The vapor pressure of acetonitrile at 38.90° was interpolated from a plot of the logarithm of the vapor pressure at various temperatures *versus* the reciprocal of the absolute temperature.[16]

TABLE IV

GAS VOLUME *versus* TIME DATA ON THE REACTION OF 5.0 ML. OF 2.0 N $(CH_3)_2NCOCl$ AND 5.0 ML. OF 0.20 N $AgNO_3$ ACETONITRILE SOLUTIONS AT 38.90 ± 0.03°[a]

Time, min.	V_t, ml. CO_2	$V_\infty - V_t$, ml.	Time, min.	V_t, ml. CO_2	$V_\infty - V_t$, ml.
0	0.0	12.2	7	8.6	3.6
1	1.6	10.6	8	9.1	3.1
2	3.5	8.7	9	9.5	2.7
3	5.2	7.0	10	10.0	2.2
4	6.3	5.9	12	10.7	1.5
5	7.2	5.0	14	11.3	0.9
6	7.9	4.3	40	12.2	0.0

[a] The acetonitrile vapor has been subtracted from these volumes. The barometric pressure was 705 mm.

Measurement of the Rate of Silver Chloride Deposition.—The 0.200 N solutions of silver nitrate and dimethylcarbamyl chloride in dry acetonitrile were thermostated at 38.90° and then a 5-ml. sample of each solution was pipetted into a flask immersed in the bath. After the proper time interval the flask was removed and the precipitated silver chloride filtered off, washed, dried and weighed. This procedure was followed for each point. The rates were then determined by the usual graphical treatment of the data.

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[15] The inverted Y-tube apparatus was designed by R. H. Boschan of this Laboratory.

[16] C. D. Hodgman, "Handbook of Chemistry and Physics," thirty-third Edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1951, p. 1967.

CHINA LAKE, CALIF.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, UNION CARBIDE CHEMICALS CO.]

Synthesis of Some Epoxy Vinyl Monomers by Epoxidation with Peracetic Acid[1]

BY FREDERICK C. FROSTICK, JR., BENJAMIN PHILLIPS AND PAUL S. STARCHER

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A number of epoxy vinyl monomers—compounds which contain both a polymerizable double bond and an oxirane ring and which can be used in making cross-linked resins—were prepared by the peracetic acid epoxidation method. Studies of rates of epoxidation of several different types of double bonds with peracetic acid in various solvents were made to show the applicability of selective epoxidation.

The recent development of a process for the manufacture of peracetic acid in an inert solvent,[2] such as acetone or ethyl acetate, has allowed the preparation of many new types of epoxides. A particularly interesting class comprises those which contain both a reactive oxirane ring and a reactive double bond in the same molecule. These compounds, which we call epoxy vinyl monomers, are

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[1] Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Durham, N. C., November 17, 1957.

[2] B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, THIS JOURNAL, **79**, 5982 (1957); see also B. Phillips, P. S. Starcher, and B. D. Ash, *J. Org. Chem.*, **23**, 1823 (1958).

especially useful in that they can be converted to polymers through either the oxirane rings or the polymerizable double bonds and can subsequently be cross-linked through whichever of these two groups was not used in the initial polymerization. Examples of epoxy vinyl monomers, mostly new compounds, which we have prepared are shown with their physical properties in Table I. The compounds in the table are largely vinyl and allyl esters; acrylic, methacrylic, and crotonic esters; and allyl ethers—all being known types of vinyl monomers. Each of the products has been tested as a monomer in vinyl-type polymerization and has been found to homopolymerize and copolymerize at a rate considered normal for its class.

Each of the compounds listed in Table I was prepared by selective epoxidation of the corresponding diolefin with peracetic acid in an inert solvent. The epoxidations were carried out batchwise by dropwise addition of a 20–30% solution of peracetic acid to a reaction flask containing the stirred diolefin. The reaction temperature was dependent upon the reactivity of the double bonds toward peracetic acid. The rate of addition of peracetic acid was slow enough so that the reaction was under control with only moderate external cooling or heating necessary at any time. After addition of peracetic acid, the reaction was allowed to continue until essentially complete. Reaction times shown in the table include both addition of peracetic acid and further reaction. For most of the epoxy vinyl monomers prepared, the yields were very good.

The reaction of peracetic acid with a double bond to produce an epoxide group is generally considered to be an electrophilic attack of the peracid on the double bond.[3–5] Thus, double bonds with relatively high electron densities are easy to epoxidize, whereas double bonds with low electron densities are hard to epoxidize.[4,5] Rates of epoxidation of many olefinic compounds by peracetic acid in acetic acid solution have been determined by several workers and tabulated by Swern.[6] However, acetic acid is not a satisfactory medium for many epoxidations, particularly where reactive epoxide rings are formed, since further reaction frequently occurs between the epoxide rings and acetic acid.[2,6] Apparently, very little work has been reported on rates of epoxidation of olefins by peracetic acid in other solvents. Also, there appears to be very little published information on rates of epoxidation of double bonds with relatively low electron densities.[6] In the course of our synthetic work we have had occasion to determine rates of epoxidation of certain types of double bonds with peracetic acid in several solvents. Tables II and III present some of the results we have obtained which are pertinent to the selective epoxidations reported in this paper. In Table II are listed for comparison the absolute second-order rates of reaction of several olefins with peracetic acid in ethyl acetate solution at 25°. From this table, it can be seen that the rates vary from essentially no reaction at all (for vinyl esters) to very fast reactions for certain other double bonds. Thus, appropriate combinations of different olefinic groups will allow essentially complete selectivity in many preparations of epoxy vinyl monomers. One may note, for example, that treatment of vinyl 3-cyclohexenecarboxylate with peracetic acid should afford vinyl 3,4-epoxycyclohexanecarboxylate and that this indeed is the case (84% yield). It is also interesting to note that epoxidation may occur selectively on a given type of double bond in one combination and, on the other hand, be essentially untouched in another combination. For example, the rate of epoxidation of allyl acetate is greater than ethyl crotonate, but less than ethyl 3-cyclohexenecarboxylate, so selective epoxidation of allyl crotonate produces mainly glycidyl crotonate while selective epoxidation of allyl 3-cyclohexenecarboxylate produces allyl 3,4-epoxycyclohexanecarboxylate. Furthermore, it can be seen that differences in groups somewhat removed from the carbons attached to the double bond can influence the rate of epoxidation; in this connection, the difference in rate of epoxidation of allyl esters and allyl ethers is illustrative.

In Table III, results are shown of a study of the reaction of peracetic acid in various solvents with several compounds containing double bonds with widely different reactivities toward peracetic acid. Second-order rate constants were calculated from the data obtained from periodic analyses for unreacted peroxide.[6,7] Previous studies of epoxidation rates of olefins with peracids have established that the reaction in general is first order with respect to both olefin and peracid,[4,6–8] and that it is not acid catalyzed.[4,7,9] Our studies in these two respects were somewhat limited, but appear to confirm these conclusions. The data reported in Table III were obtained from reactions of equimolar amounts of peracetic acid and olefin during the initial stages of the reactions, that is, before 20% of the peracid had disappeared.[10] However, we obtained essentially the same rate values in experiments where we employed up to a maximum of 25% molar excess of either olefin or peracetic acid. In our study of acid catalysis, 0.5 weight per cent. sulfuric acid was added to peracetic acid in ethyl acetate prior to mixing the reactants. Some loss of peroxide stability was observed, especially initially, compared to solutions with no H_2SO_4 (see Experimental). We found essentially the same epoxidation rates in either the presence or absence of the sulfuric acid after allowance was made for the extra peroxide loss.

It is interesting to note from Table III that while there are small variations in epoxidation rates of a particular olefin group in different solvents,[11] these variations are of a rather minor nature. On the other hand, variations in the heat of activation,

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(3) P. D. Bartlett, *Record Chem. Progr.*, **11**, 51 (1950).

(4) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(5) D. Swern, THIS JOURNAL, **69**, 1692 (1947).

(6) D. Swern, *Chem. Revs.*, **45**, 1 (1949).

(7) J. Böeseken and J. Sturrman, *Rec. trav. chim.*, **56**, 1034 (1937).

(8) J. Böeseken and J. S. P. Blumberger, *ibid.*, **44**, 90 (1925).

(9) S. Medvedev and O. Blokh, *J. Phys. Chem., U.S.S.R.*, **4**, 721 (1933).

(10) It was demonstrated (see Experimental) that, in each case, a good yield of isolable epoxide was obtained from peracetic acid in ethyl acetate solution.

(11) It has previously been observed that rates of epoxidation with perbenzoic acid vary with solvent; see ref. 4; also see A. J. Tomisek and H. R. Mahler, THIS JOURNAL, **73**, 4685 (1951).

TABLE I

PREPARATION OF EPOXY VINYL MONOMERS FROM DIOLEFINS AND PERACETIC ACID BY SELECTIVE EPOXIDATION

Reaction		Moles		B.p.			Yield,
Temp., °C.	Time, hours	AcOOH/olefin		°C.	Mm.	$n^{30}D$	%
40–45	6	0.64/0.42	Vinyl 4,5-epoxypentanoate[a]	72–73[b]	7	1.4424	47
40–60	8	3.74/2.99	Vinyl 10,11-epoxyundecanoate[c]	101[d]	0.2	1.4509	38
35	6.25	0.78/0.71	Vinyl 9,10-epoxystearate[e]	163–167	0.07	1.4539	57[f]
30–35	13	2.2/2.57	Vinyl 3,4-epoxycyclohexanecarboxylate[g]	75–76[h]	1	1.4741	84
25–30	8.5	2.75/2.20	Vinyl 3,4-epoxy-6-methylcyclohexanecarboxylate[i]	99–102[h]	5	1.4691	71
40–55	6	0.64/0.42	Allyl 4,5-epoxypentanoate[j]	68–69	1.5	1.4430	65
40–55	9	1.96/1.57	Allyl 5,6-epoxyhexanoate[k]	66–68	0.3	1.4450	56
40–55	7.5	3.18/2.54	Allyl 10,11-epoxyundecanoate[l]	125–130	0.5–1.0	1.4492–1.4507	72
35–40	7.67	1.10/1.00	Allyl 9,10-epoxystearate[m]	180–195	0.5–1.0	1.4547	91
35–40	8.25	3.43/1.37	Allyl 9,10,12,13-diepoxystearate[n]	210	1	1.4614	87
40–50	9	1.74/5.23	Allyl 2,3-epoxy-2-ethylhexanoate[o]	91	3	1.4415	33[p]
40	17.25	1.76/1.55	Allyl 3,4-epoxy-2-hydroxybutanoate[q]	82–90	1	1.4590–1.4601	27
45–50	7	5.05/4.05	Allyl 3,4-epoxy-2-hydroxypentanoate[r]	108–110	5	1.4526	59
40–45	5	6.11/4.89	Allyl 3,4-epoxycyclohexanecarboxylate[s]	91–95	2	1.4709	78
40	2.5	0.799/0.639	Allyl 3,4-epoxy-6-methylcyclohexanecarboxylate[t]	122	6	1.4671	86
30–55	21.5	2.93/2.38	2,3-Epoxybutyl acrylate[u]	46.5[v]	2	1.4381	33
40–50	9	2.44/2.32	2,3-Epoxy-2-methylpropyl acrylate[w]	45	1.5	1.4380	62
40	5	1.61/1.46	2,3-Epoxy-2-ethylhexyl acrylate[x]	80[d]	1.5	1.4431	38
30–50	9.5	2.90/2.30	2,3-Epoxycyclopentyl acrylate[y]	75–77[z]	2.5	1.4659–1.4674[aa]	44
0–3	14	1.15/1.00	3,4-Epoxycyclohexylmethyl acrylate[bb]	105[cc]	2.4	1.4770	40
30–35	8	2.78/2.22	3,4-Epoxy-6-methylcyclohexylmethyl acrylate[dd]	106–108[z]	1	1.4760	76[ee]
70–75	6.75	4.0/20.0	2,3-Epoxypropyl crotonate[ff]	71	3	1.4550	81
40–45	11	1.80/1.20	2,3-Epoxy-2-methylpropyl crotonate[gg]	66–68	2	1.4490	72
50–55	12.5	4.74/3.00	2,3-Epoxybutyl crotonate[hh]	67–78	1–2	1.4492	71
40	14	0.55/0.46	2,3-Epoxycyclopentyl crotonate[ii]	69	1.5	1.4738	30
30–35	10	6.25/5.00	3,4-Epoxy-6-methylcyclohexylmethyl crotonate[jj]	116	1	1.4804	84
70	..[kk]	5.0/20	3,4-Epoxy-1-vinylcyclohexane[ll]	61–63	15	1.4660–1.4670[mm]	82
40–45	7	2.00/8.03	Allyl 2,3-epoxy-2-methylpropyl ether[nn]	45–47	9	1.4252	75
35	4	0.615/0.585	Allyl 3,4-epoxycyclohexylmethyl ether[oo]	90–92	3	1.4670	66
25–30	6	2.0/4.0	Allyl 2,3-epoxybutyl ether[pp]	112	150	1.4273	66
25–28	24	0.83/2.38	Allyl 2,3-epoxycyclopentyl ether[qq]	78	10	1.4624	73

[a] *Anal.* Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09; oxirane oxygen, 11.26. Found: C, 59.40, 59.26; H, 7.27, 7.34; oxirane oxygen, 11.01. [b] Distilled in the presence of Agerite white. [c] *Anal.* Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80; oxirane oxygen, 7.08. Found: C, 68.83, 68.73; H, 9.77, 9.75; oxirane oxygen, 6.37. [d] Distilled in the presence of dinitrochlorophenol. [e] *Anal.* Calcd. for $C_{20}H_{36}O_3$: oxirane oxygen, 4.94. Found: oxirane oxygen, 4.75. Product found 96.2% pure by analytical bromination. [f] 83% yield obtained on residue product of approximately same purity. [g] *Anal.* Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19; oxirane oxygen, 9.47. Found: C, 64.26; H, 7.10; oxirane oxygen, 9.14. Product found 101.4% pure by analytical bromination. [h] Distilled in the presence of pyrogallol. [i] *Anal.* Calcd. for $C_{10}H_{14}O_3$: sapon. equiv., 182; oxirane oxygen, 8.79. Found: sapon. equiv., 175.5; oxirane oxygen, 8.62. Product found 101% pure by analytical bromination. [j] *Anal.* Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.69; sapon. equiv., 156; oxirane oxygen, 10.24. Found: C, 61.10; H, 7.67; sapon. equiv., 153; oxirane oxygen, 10.24. [k] *Anal.* Calcd. for $C_9H_{14}O_3$: C, 63.54; H, 8.24 Found: C, 63.19, 63.21; H, 8.18, 8.36. [l] *Anal.* Calcd. for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06; oxirane oxygen, 6.67. Found. C, 69.81; H, 10.18; oxirane oxygen, 6.57. [m] *Anal.* Calcd. for $C_{21}H_{38}O_3$: C, 74.51; H, 11.31; sapon. equiv., 338; oxirane oxygen, 4.73. Found: C, 73.75; H, 11.12; sapon. equiv., 330; oxirane oxygen, 4.72. [n] *Anal.* Calcd. for $C_{21}H_{36}O_4$: C, 71.54; H, 10.29; sapon. equiv., 352; oxirane oxygen, 9.09. Found: C, 71.56; H, 10.35; sapon. equiv., 338; oxirane oxygen, 7.65. [o] *Anal.* Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15; sapon. equiv., 198.2. Found: C, 66.81; H, 9.31; sapon. equiv., 195. [p] Some diepoxide was produced. [q] *Anal.* Calcd. for $C_7H_{10}O_4$: C, 53.18; H, 6.33; sapon. equiv., 158; oxirane oxygen, 10.1. Found: C, 52.49; H, 6.39; sapon. equiv., 158; oxirane oxygen, 9.56. [r] *Anal.* Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03; sapon. equiv., 172.2; oxirane oxygen, 9.30. Found: C, 55.52; H, 7.13; sapon. equiv., 173.1; oxirane oxygen, 8.19. Product found 100% pure by analytical bromination. [s] *Anal.* Calcd. for $C_{10}H_{14}O_3$: sapon. equiv., 182; oxirane oxygen, 8.79. Found: sapon. equiv., 183.5; oxirane oxygen, 8.61. Product found 102.5% pure by analytical bromination. [t] *Anal.* Calcd. for $C_{11}H_{16}O_3$: sapon. equiv., 196; oxirane oxygen, 8.17. Found: sapon. equiv., 204; oxirane oxygen, 8.05. Product found 96% pure by analytical bromination. [u] *Anal.* Calcd. for $C_7H_{10}O_3$: oxirane oxygen, 11.26. Found: oxirane oxygen, 11.21. Product found 97.9% pure by analytical bromination. [v] Distilled in the presence of trinitrobenzene. [w] *Anal.* Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09; sapon. equiv., 142; oxirane oxygen, 11.26. Found: C, 59.17, 59.14; H, 7.13, 6.93; sapon. equiv., 135; oxirane oxygen, 10.81. [x] *Anal.* Calcd. for $C_{11}H_{18}O_3$: sapon. equiv., 198. Found: sapon. equiv., 196.7, 199. [y] *Anal.* Calcd. for $C_8H_{10}O_3$: C, 62.32; H, 6.53; oxirane oxygen, 10.4. Found: C, 62.59; H, 6.59; oxirane oxygen, 9.88. [z] Distilled in the presence of the monomethyl ether of hydroquinone. [aa] Mixture of *cis* and *trans* isomers. The infrared absorption spectrum was consistent with the proposed structures. [bb] *Anal.* Calcd. for $C_{10}H_{14}O_3$: oxirane oxygen, 8.79. Found: oxirane oxygen, 8.67. [cc] Distilled in the presence of Agerite powder. [dd] *Anal.*

Calcd. for $C_{11}H_{16}O_3$: oxirane oxygen, 8.17. Found: oxirane oxygen, 8.03. [ee] 94% yield obtained on residue product analyzing 95.3% pure by analysis for oxirane oxygen. [ff] *Anal.* Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09; oxirane oxygen, 11.26. Found: C, 58.96, 59.08; H, 7.18, 7.40; oxirane oxygen, 11.12. [gg] *Anal.* Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75; oxirane oxygen, 10.26. Found: C, 61.11; H, 7.67; oxirane oxygen, 9.99. [hh] *Anal.* Calcd. for $C_8H_{12}O_3$: oxirane oxygen, 10.26. Found: oxirane oxygen, 10.14. [ii] This preparation by D. L. Heywood. *Anal.* Calcd. for $C_9H_{12}O_3$: sapon. equiv., 168. Found: sapon. equiv., 158. [jj] *Anal.* Calcd. for $C_{12}H_{18}O_3$: C, 68.60; H, 8.62; sapon. equiv., 210; oxirane oxygen, 7.62. Found: C, 68.86; H, 8.71; sapon. equiv., 208.4; oxirane oxygen, 7.52. [kk] Contact time was less than one minute. Epoxidation carried out in a continuous operation. [ll] F. Strain, U. S. Patent 2,765,296 (1956), Distillers Co., Ltd.; L. S. Abbott, British Patent 692,417 (1953); and R. E. Foster, U. S. Patent 2,687,406 (1954). *Anal.* Calcd. for $C_8H_{12}O$: oxirane oxygen, 12.9. Found: oxirane oxygen, 12.8, 12.7. [mm] Mixture of *cis* and *trans* isomers. [nn] *Anal.* Calcd. for $C_7H_{12}O_2$. oxirane oxygen, 12.5. Found: oxirane oxygen, 12.5. [oo] *Anal.* Calcd. for $C_{10}H_{16}O_2$: oxirane oxygen, 9.53. Found: oxirane oxygen, 9.36. [pp] *Anal.* Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.38; oxirane oxygen, 12.5. Found: C, 65.28; H, 9.44; oxirane oxygen, 12.0. [qq] *Anal.* Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63; oxirane oxygen, 11.4. Found: C, 67.43; H, 9.08; oxirane oxygen, 11.2.

TABLE II

REACTION OF OLEFINS WITH PERACETIC ACID IN ETHYL ACETATE AT 25°

Olefin	10^6k[a]
Vinyl acetate	<0.1[b]
Ethyl acrylate	< .1[b]
Ethyl crotonate	.150
Allyl acetate	.669
Ethyl 2-ethyl-2-hexenoate	4.18
Allyl ether	5.29
Styrene	34.3
Ethyl 3-cyclohexenecarboxylate	123
Cyclohexene	283

[a] k is the specific reaction rate in liters per mole per second. [b] Exact rate could not be measured since decomposition rate of peracetic acid is apparently greater than epoxidation rate.

$\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$, with solvent are often more marked. When comparisons are made in the variation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ in the epoxidation of widely different types of olefins, it will be noted that these are much greater than those shown in previously published epoxidation rate studies where electron densities at the double bonds to be epoxidized were more nearly the same.[4,7] With the possible exception of the reaction of peracetic acid and allyl acetate in ethyl acetate solution, however, it appears that no change in mechanism of epoxidation is indicated.

Diolefins which contain double bonds of approximately the same reactivity toward peracetic acid cannot be selectively epoxidized. However, they may be converted to epoxy vinyl monomers by effecting a partial epoxidation. In this method, peracetic acid is allowed to react with a large excess of diolefin so that essentially only one epoxide group in each molecule of product is produced. The epoxy vinyl monomer is isolated and excess diolefin is then recycled. In Table IV are listed some representative preparations of this type.

Experimental

Preparation of Starting Materials.—Vinyl esters were prepared by the exchange reaction from the appropriate acid and excess vinyl acetate.[12]

Allyl esters were prepared by esterification of the appropriate acid with allyl alcohol using either 0.5% sulfuric acid or 0.5% *p*-toluenesulfonic acid catalyst. **Allyl 2-hydroxy-3-butenoate** was prepared from acrolein, HCN, aq. HCl and allyl alcohol, and **allyl 2-hydroxy-3-pentenoate** from crotonaldehyde instead of acrolein, as described previously.[13]

Acrylic and crotonic esters were prepared by direct esterification using an acidic catalyst, with the exception of those

TABLE III

EPOXIDATION OF OLEFINS WITH PERACETIC ACID

Olefin	Solvent	Temp., °C.	10^6k[a]	$\Delta H^{\ddagger}$, kcal.	$-\Delta S^{\ddagger}$, e.u.
Allyl ether[b]	Ethyl acetate	20	3.14		
		30	8.56	18.0	22.2
		35	13.9		
		50	55.3		
	Benzene	25	38.3	15.2	28.1
		35	88.6		
Allyl acetate	Ethyl acetate	24	0.585		
		30	1.35	24.0	6.2
		45	9.10		
	Acetic acid	23	2.65		
		30	5.70	19.5	18.0
		45	24.3		
	Benzene	23	3.38	18.8	19.9
		45	31.0		
Cyclohexene	Ethyl acetate	0	20.2		
		15	104	16.9	16.2
		20	172		
		25	283		
	Acetic acid	15	82.2[c]		
		25.8	2150[d]	15.6	18.6
		39.6	6740[d]		
Ethyl crotonate	Ethyl acetate	30	0.262		
		40	0.793	20.1	22.0
		60	5.27		
Ethyl 3-cyclohexenecarboxylate	Ethyl acetate	25	123	16.9	19.7
		35	313		
	Acetic acid	15	345[e]		
	Benzene	0	115	14.2	20.0
		15	452		
Ethyl 2-ethyl-2-hexenoate	Ethyl acetate	40	19.2	18.8	18.5
		60	117.5		
Styrene	Ethyl acetate	20	22.0		
		25	34.3	16.2	22.6
		30	55.3		
		40	127		
	Acetic acid	20.5	124		
		25	186	13.9	29.3
		25.8	188[d]		
		40.8	574[d]		
	Benzene	0	26.8	14.3	27.0
		20	162		

[a] The specific reaction rate constant, k, is in liters per mole per second. [b] See footnote 19. [c] This value obtained by us agrees with literature value (see ref. 7). [d] Taken from literature (ref. 7). [e] At 0°, the reaction solution froze; at 25°, the reaction was too fast (k was greater than 7×10^{-4}) to measure accurately.

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(12) W. J. Toussaint and L. G. MacDowell, Jr., U. S. Patent 2,299,862 (1942).

(13) H. A. Stansbury, Jr., and H. R. Guest, U. S. Patent 2,786,073 (1957).

TABLE IV

PREPARATION OF EPOXY VINYL MONOMERS FROM OLEFINS AND PERACETIC ACID BY PARTIAL EPOXIDATION

Olefin	Reaction		Moles AcOOH/ olefin	Epoxide	B.p.		$n^{30}\text{D}$	Yield, %
	Temp., °C.	Time, hours			°C.	Mm.		
Diallyl ether	50–55	6	2.42/7.26	Allyl glycidyl ether	74–76	50[a]	1.4310[a]	66
Diallyl maleate	50	11.5	1.0/4.0	Allyl glycidyl maleate[b]	138–141	2.5[c]	1.4736	71
Butadiene	30	4.5	1.0/1.4	1,2-Epoxy-3-butene[d]	68	Atm.	1.4124	56[e]
2,5-Dimethyl-1,5-hexadiene	30–35	2.33	1.0/3.0	1,2-Epoxy-2,5-dimethyl-5-hexene[f]	62–63	30	1.4302	61
Dicyclopentadiene	40	3.0	1.0/3.0	Dicyclopentadiene monoxide[g]	92–94	5[h]	....	75
Ethylene glycol dicrotonate	75	13	1.1/1.0	Ethylene glycol crotonate 2,3-epoxybutyrate[i]	133–137	2	1.4595	47

[a] Lit. values: b.p. 87.5–88° at 80 mm., $n^{20}\text{D}$ 1.4345 (T. W. Evans and K. E. Marple, U. S. Patent 2,314,039 (1943)). [b] Oxirane oxygen: calcd. 7.55, found 7.58. [c] Distilled in presence of Agerite white polymerization inhibitor. [d] Oxirane oxygen: calcd. 22.8, found 22.6. [e] This experiment by D. L. MacPeek. [f] *Anal.* Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.55; H, 10.92. [g] Mixture of isomers. [h] Solid, m.p. 71–76°; K. Alder and G. Stein, *Ann.*, **485**, 223 (1930). [i] *Anal.* Calcd. for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59; sapon. equiv., 107.1. Found: C, 55.75; H, 6.48; sapon. equiv., 104.5.

examples noted where an ester exchange or other procedure was employed.

Table V presents physical properties and yields of the various esters prepared.

TABLE V

PREPARATION OF UNSATURATED ALCOHOL ESTERS OF UNSATURATED ACIDS

Ester	B.p.		$n^{30}\text{D}$	Yield, %
	°C.	Mm.		
Vinyl 4-pentenoate[a]	42	16	1.4280	50
Vinyl undecylenate[b]	75–83	0.08	1.4450	60
Vinyl oleate[c]	148–160	1	1.4540	45
Vinyl 3-cyclohexenecarboxylate	74	10	1.4678	63
Vinyl 6-methyl-3-cyclohexenecarboxylate[d]	54	2.5	1.4627	69
Allyl crotonate[e]	83	5	1.4416	88
Allyl 4-pentenoate[f]	41–44	11	1.4278	61
Allyl 5-hexenoate[g]	47	3	1.4346	56
Allyl undecylenate[h]	108–112	2	1.4449	91
Allyl oleate[c]	170	1	1.4540	77
Allyl linoleate[i]	160–162	0.5	1.4622	88
Allyl 2-ethyl-2-hexenoate[j]	86–87	5	1.4523	89
Allyl 2-hydroxy-3-butenoate[k]	47–49	2	1.4490	80
Allyl 2-hydroxy-3-pentenoate[k]	77	4	1.4562	55
Allyl 3-cyclohexenecarboxylate[l]	91	10	1.4670	83
Allyl 6-methyl-3-cyclohexenecarboxylate[m]	85	6	1.4632	81
Crotyl acrylate	55[n]	15	1.4363	74
2-Methyl-2-propenyl acrylate[o]	68	50	1.4310	82
2-Ethyl-2-hexenyl acrylate[p]	57	0.8	1.4475	37
2-Cyclopentenyl acrylate[q]	35–37	3.5	1.4651	63
3-Cyclohexenemethyl acrylate[r]	63	2	1.4718	81
6-Methyl-3-cyclohexenemethyl acrylate[s]	72	2	1.4705	87
2-Methyl-2-propenyl crotonate[t]	89–90	40	1.4451	65
Crotyl crotonate[u]	85–87	25	1.4495	47
2-Cyclopentenyl crotonate[v]	73	7	1.4739	31
6-Methyl-3-cyclohexenemethyl crotonate[w]	112	4	1.4777	90

[a] *Anal.* Calcd. for $C_7H_{10}O_2$: C, 66.57; H, 7.99; sapon. equiv., 126.2. Found: C, 66.82; H, 8.14; sapon. equiv., 129.1. Product found 96.6% pure by analytical bromination. [b] Prepared from Baker Castor Oil Co. undecylenic acid. [c] Prepared from Emery Industries Grade 233LL Elaine oleic acid. [d] Sapon. equiv. (in presence of phenylhydrazine) found 166 (theory 166). Analyzed 97.0% pure by analytical bromination. [e] Analyzed 99.2% pure by saponification; V. P. Golendew, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 1408 (1940), reports b.p. 88–89° at 70 mm., $n^{20}\text{D}$ 1.4465. [f] Sapon. equiv. found 124 (theory 126). Analyzed 98.9% pure by analytical bromination. [g] *Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.14; H, 9.09; sapon. equiv., 154. Found: C, 70.38; H, 9.13; sapon. equiv., 155. Product analyzed 98.0% pure by analytical bromination. [h] *Anal.* Calcd. for $C_{14}H_{24}O_2$: C, 74.91; H, 10.78; sapon. equiv., 224. Found: C, 74.87; H, 10.82; sapon. equiv., 224. [i] Linoleic acid prepared by method of *Org. Syntheses*, **22**, 79 (1942); ester sapon. equiv. found 332 (theory 330); iodine number, 220. [j] Sapon. equiv. found 182.2 (theory 182.5). [k] Ref. 13. [l] Sapon. equiv. found 162.5 (theory 166). Product found 98.2% pure by analytical bromination. [m] Sapon. equiv. found 176 (theory 180). Product found 98.5% pure by analytical bromination. [n] In presence of 0.5% trinitrobenzene. [o] Prepared by J. W. Lynn from ethyl acrylate and excess methallyl alcohol with titanium tetrabutylate catalyst; sapon. equiv. found 129 (theory 126). [p] Prepared by T. F. Carruthers from 2-ethyl-2-hexenol and excess ethyl acrylate with magnesium methylate catalyst and phenothiazine inhibitor; sapon. equiv. found 184.5 (theory 182). [q] Prepared by T. F. Carruthers from 2-cyclopentenol and excess ethyl acrylate with magnesium methylate catalyst and phenothiazine inhibitor. *Anal.* Calcd. for $C_8H_{10}O_2$: C, 69.54; H, 7.28. Found: C, 69.23; H, 7.32. [r] Prepared from 3-cyclohexenemethanol and excess methyl acrylate with *p*-toluenesulfonic acid and pyrogallol inhibitor; sapon. equiv. found 171 (theory 166). [s] *Anal.* Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 8.88; sapon. equiv., 180. Found: C, 73.26; H, 8.70; sapon. equiv., 175. Distilled in presence of monomethyl ether of hydroquinone. [t] Prepared from crotonic anhydride and methallyl alcohol; sapon. equiv. found 140.5 (theory 140.2). Analyzed 99.4% pure by analytical bromination. [u] *Anal.* Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.62; sapon equiv., 140. Found: C, 68.34; H, 8.70; sapon. equiv., 140. [v] Sapon. equiv. found 155 (theory 152). [w] Sapon. equiv. found 194 (theory 194).

Allyl β-methylallyl ether[14] (b.p. 77–78° at 255 mm., $n^{30}\text{D}$ 1.4181) was prepared in 58% yield by adding 20 moles of methallyl chloride dropwise over five hours to a stirred slurry of 15 moles of allyl alcohol and 17 moles of powdered KOH at 50–60°, and then allowing the reaction mixture to stand at room temperature for 60 hours. After being diluted with diethyl ether and washed with water, the mixture was fractionally distilled for isolation of the product. **Allyl crotyl ether** (b.p. 92–95° at 300 mm., $n^{30}\text{D}$ 1.4248, yield 79%) was prepared in the same manner from excess

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(14) M. Tamele, C. J. Ott, K. E. Marple and G. Hearne, *Ind. and Eng. Chem.*, **33**, 115 (1941).

crotyl chloride, allyl alcohol and KOH at 30–40° reaction temperature.

Allyl 3-cyclohexenemethyl ether (b.p. 61° at 4 mm., $n^{30}D$ 1.4621) was prepared from excess allyl alcohol and 3-cyclohexenemethanol with BF_3–HgO catalyst.[15] **Allyl 2-cyclopentenyl ether** (b.p. 74° at 53 mm., $n^{30}D$ 1.4550, yield 74%) was prepared by the same procedure.

4-Vinyl-1-cyclohexene, purchased from Distillation Products, Inc., was redistilled (b.p. 96° at 305 mm., $n^{30}D$ 1.4606–1.4610).

Preparation of Epoxy Vinyl Monomers.—The compound to be epoxidized was placed in a flask equipped with a stirrer, thermometer, reflux condenser and dropping funnel and heated to the appropriate reaction temperature. Peracetic acid (as a 23–28% solution in either ethyl acetate or acetone solvent[2]) was added dropwise over a period of approximately one to three hours to the reaction flask. The time of addition depended on the amount of the peracetic acid to be added and on the ease of the epoxidation reaction. Large amounts of peracetic acid in contact with active double bonds were especially avoided. The reaction solution was stirred and cooled or heated as required to maintain the reaction temperature. After addition of the peracetic acid, the reaction was continued until iodimetric analysis for peracetic acid content[2] indicated that the reaction was essentially complete. The reaction mixture was then added dropwise to a still kettle containing ethylbenzene under reflux at 30–50 mm. pressure. During the addition, solvent, acetic acid, unreacted peracetic acid and ethylbenzene were continuously removed at the still-head. Under these conditions the concentration of acetic acid in the still-kettle was always kept at a minimum. When the reaction mixture had all been added, the excess ethylbenzene was distilled off, and the products were isolated by fractional distillation. Tables I and IV contain details for the individual preparations. The reaction times listed include both addition time for peracetic acid and further reaction. Yields reported are those for purified products. The reported oxirane oxygen values were determined by the pyridinium chloride–pyridine or pyridinium chloride–chloroform methods.[16] For some of the less reactive epoxides, longer reaction times were necessary to obtain quantitative results. These methods of epoxide analysis were not found quantitatively applicable to certain types of epoxy compounds, particularly glycidic esters, polycyclic systems and those with highly substituted oxirane rings.

Each of the unsaturated epoxides in Table I was tested as a monomer in vinyl-type polymerizations and was found to homopolymerize and copolymerize at a rate considered normal for its class. The presence of unreacted allyl ester double bonds in the allyl esters of 5,6-epoxyhexanoic acid, 10,11-epoxyundecanoic acid and 2,3-epoxy-2-ethylhexanoic acid was shown by treatment of each of these esters with excess 3-cyclohexenemethanol or 2-ethylhexanol and sodium alcoholate catalyst under reflux at reduced pressure. There were obtained yields of 80, 87 and 88%, respectively, of the theoretical amount of allyl alcohol, which was identified by characteristic odor, characteristic resorcinol test[17] and preparation of the α-naphthylurethan, m.p. 103–105° and mixed m.p. 104.5–105.5°.[17]

Epoxidation Rate Studies.—The procedure was essentially the same as that used in previous studies.[4,7,8] To a weighed quantity of olefin (0.10–0.15 mole) was added an equivalent amount of a solution of peracetic acid (0.09–0.12 *M*) in the selected solvent.[18] The reaction solution was constantly agitated and cooled or heated as necessary during the reaction, and the recorded temperature was maintained within ±0.3°. Progress of the reaction was determined by analysis for peracetic acid.[7] Aliquot portions (1–2 ml.) of the solution were withdrawn at time intervals and analyzed for unreacted peracetic acid iodimetrically.[2] Molar concentrations of unreacted peracetic acid were plotted against time and straight lines were obtained for every epoxidation.

The rate measurements were obtained in the early stages of the epoxidation reaction (before 20% conversion) so that it could be assumed that the change in reaction medium due to product formation exerted a negligible effect on the rates. Second-order rate constants (first order with respect to molar concentration of both olefin[19] and peracetic acid[7–9]) were calculated for each set of conditions. The heat of activation, $\Delta H^\ddagger$, and entropy of activation, $\Delta S^\ddagger$ (from rates at 25°), were obtained from the rate constants by standard methods.[4,20,21]

$$\log \frac{k_2}{k_1} = \frac{\Delta H^\ddagger (T_2 - T_1)}{2.303\ RT_2T_1}$$

$$k = \frac{RT}{Nh}e^{\Delta S^\ddagger/R}\ e^{-\Delta H^\ddagger/RT}$$

The data on epoxidation of ethyl 3-cyclohexenecarboxylate at 25° in ethyl acetate solution are shown as an example. To ethyl 3-cyclohexenecarboxylate (16.95 g., 0.110 mole) was added 98.8 g. of an 8.46% solution of peracetic acid (8.36 g., 0.110 mole) in ethyl acetate at 25°. Analyses for peracetic acid were obtained as tabulated below. The observed density of the peracetic acid solution at 25° was 0.9187.

Time, min.	% AcOOH	Concn. AcOOH molar
0 (theory)	7.23	0.875
2.0	7.15	.864
6.0	6.98	.844
10.0	6.84	.826
15.0	6.64	.803
22.0	6.34	.766
25.0	6.17	.746

The concentration of ethyl 3-cyclohexenecarboxylate was assumed to be exactly equal to the concentration of peracetic acid throughout the run.

Allyl glycidyl ether was readily prepared in 66% yield (see Table IV). Allyl acetate was converted to **glycidyl acetate** (b.p. 20–60.5° at 10 mm., $n^{30}D$ 1.4192[22]) obtained in 61% yield from peracetic acid and allyl acetate in ethyl acetate at 65–70° for 5.3 hours. **Cyclohexene oxide** (b.p. 54–55° at 50 mm., $n^{30}D$ 1.4462; 98.4% pure by epoxide analysis) was prepared in 75% yield from 3.0 moles of peracetic acid and 24.0 moles of cyclohexene at 25–30° for 3.5 hours, followed by extraction with water to remove acetic acid, and isolation of the epoxide by fractional distillation.

The conversions of ethyl crotonate to **ethyl 2,3-epoxybutyrate** in 75% yield, and ethyl 2-ethyl-2-hexenoate to

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(15) P. S. Starcher, U. S. Patent 2,863,925 (1958).

(16) J. J. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss in "Organic Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 136.

(17) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Order I, John Wiley and Sons, Inc., New York, N. Y., 1941, No. 1:6145.

(18) Peracetic acid in ethyl acetate was prepared as described in ref. 2 and contained 1.5–2.3% acetic acid. Peracetic acid in benzene was a distilled product prepared by the method of B. Phillips, P. S. Starcher and B. D. Ash, U. S. Patent 2,814,641 (1957), and contained less than 0.1% acetic acid. Peracetic acid in acetic acid was flash distilled after preparation according to F. P. Greenspan, U. S. Patent 2,490,800 (1949).

(19) Attention is called to the fact that *molar* concentrations were used in the calculation of rates of reaction of diallyl ether since these values gave a constant $\Delta H^\ddagger$ in the range 20–50°. Second-order rates calculated from concentration of *equivalents* of double bonds from the same reactions failed to give a constant $\Delta H^\ddagger$. The results in Table III for diallyl ether may be compared with the following (unduplicated) second-order rates obtained from the reaction of allyl propyl ether (purity above 90%) and peracetic acid in ethyl acetate solution: $k_{30°} = 4.53 \times 10^{-6}$ liters per mole per second; $k_{50°} = 26.8 \times 10^{-6}$ liters per mole per second.

(20) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941.

(21) Values for $\Delta H^\ddagger$ shown in Table III may be considered accurate within ±0.5 kcal. Inherent errors in determining $\Delta S^\ddagger$ may be somewhat greater since errors in *k* and $\Delta H^\ddagger$ may be compounded. A temperature variation of ±0.3° (our experimental) may account for errors of ±0.2 kcal. in $\Delta H^\ddagger$. Changes in concentrations of reactants for reactions at temperatures other than 25° due to thermal expansions of the solvents were ignored in our calculations.

(22) Lit. values: b.p. 74–76° at 25 mm. [P. A. Levene and A. Walti, *J. Biol. Chem.*, **77**, 685 (1928)]; b.p. 82–84° at 40 mm.; $n^{20}D$ 1.4201 [D. I. Weisblat, B. J. Magerlein and A. R. Hanze, U. S. Patent 2,578,767 (1951)].

ethyl-2,3-epoxy-2-ethylhexanoate in 79% yield were previously reported.[23]

Ethyl 7-oxabicyclo[4.1.0]heptane-3-carboxylate (b.p. 85° at 3.0 mm., $n^{30}\text{D}$ 1.4568) was prepared in 84% yield from 25% excess peracetic acid and ethyl 3-cyclohexenecarboxylate at 40° for six hours.[24]

Styrene oxide (b.p. 194° at atm. pressure[25] or 75° at 10 mm., $n^{30}\text{D}$ 1.5300) was prepared in 60–75% yield from peracetic acid in ethyl acetate and excess styrene in various procedures similar to those using perbenzoic acid.[25]

Stability Studies on Peracetic Acid in Ethyl Acetate Solution at 45°.—Samples of peracetic acid solutions were maintained in a constant temperature bath at 45 ± 0.5° and analyzed periodically. Bottle I contained peracetic acid in ethyl acetate stabilized with 0.1% by weight Victawet 35B.[26] Bottle II was the same except that 0.5% by weight concentrated sulfuric acid was added at the start. The results tabulated below are typical for concentrated solutions at a higher temperature.

Time, hours	Bottle I, % AcOOH	Bottle II, % AcOOH
0	23.97	23.9
2	23.95	23.7
4.5	23.93	23.1
6.5	23.91	22.6
10	23.88	22.0
15	23.84	21.5
18	23.81	21.3
21	23.78	21.1
24	23.75	19.8

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[23] D. L. MacPeek, P. S. Starcher and B. Phillips, THIS JOURNAL, **81**, 680 (1959).

[24] B. Phillips and P. S. Starcher, U. S. Patent 2,794,812 (1957).

[25] H. Hibbert and P. Burt, *Organic Syntheses*, Vol. I, Sec. Ed., John Wiley and Sons, New York, N. Y., 1951, p. 494.

[26] According to the manufacturer, Victor Chemical Works, "Victawet 35B" has the formula $Na_5R_5(P_3O_{10})_2$, where R = 2-ethylhexyl. See Chemical Materials Catalog, **9**, 512 (1958), Reinhold Publishing Corp., New York, N. Y.

[CONTRIBUTION FROM THE BIOCHEMISTRY DEPARTMENT, UNIVERSITY OF PITTSBURGH SCHOOL OF MEDICINE]

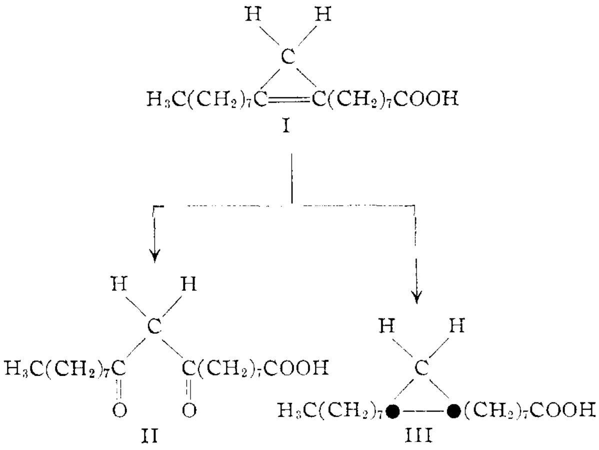
An Unequivocal Synthesis of Dihydrosterculic Acid[1,2]

BY KLAUS HOFMANN AND CLAYTON W. YOHO

RECEIVED DECEMBER 1, 1958

A synthesis of DL-*cis*-9,10-methyleneoctadecanoic acid is described, and the synthetic acid was found to be identical with dihydrosterculic acid.

In 1952, Nunn described the isolation of a novel type of fatty acid (sterculic acid) from the seedfat of the tropical tree *Sterculia foetida*, and from the results of degradative studies assigned structure I to this compound.[3] Essentially two compounds, namely, the diketo acid II[3,4] and the hydrogenation product (dihydrosterculic acid) III provided the basis for this assignment of structure. The acid II established the location of the double bond, whereas III pointed to the cyclopropane nature of sterculic acid. Three independent groups of workers[5–7] have described syntheses of II and its identity with the degradation product from sterculic acid has been established beyond any reasonable doubt. The structure of dihydrosterculic acid remained to be verified.



We have postulated[8] a *cis* configuration for dihydrosterculic acid, since it seemed highly plausible that catalytic reduction of a compound possessing the structure I suggested for sterculic acid would result in a predominant *cis*-addition of hydrogen. Thus, DL-*cis*-9,10-methyleneoctadecanoic acid became the most logical structure for dihydrosterculic acid.

In a preliminary communication[2] we have described a synthesis of DL-*cis*-9,10-methyleneoctadecanoic acid and have found this acid to be identical with dihydrosterculic acid. Identification was based on melting and mixed-melting point determinations of the acids and their amides, matching infrared absorption spectra and, most significantly, on detailed X-ray diffraction studies. A full account of these latter investigations has appeared[9]; experimental details pertaining to the synthetic aspects of the problem are presented in this study.

Cyclopropane-*cis*-1,2-diacetic acid (IV),[10] the starting material for the present investigation, was converted into its monomethyl ester and the latter was transformed into the acid chloride. Re-

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[1] Supported by grants from the American Cancer Society, upon recommendation of the Committee on Growth of the National Research Council, and by the U. S. Public Health Service.

[2] A preliminary communication describing some of the results of this investigation has appeared in THIS JOURNAL, **79**, 3608 (1957).

[3] J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

[4] P. K. Faure and J. C. Smith, *ibid.*, 1818 (1956).

[5] D. G. Brooke and J. C. Smith, *ibid.*, 2732 (1957).

[6] B. A. Lewis and R. A. Raphael, *Chemistry & Industry*, 50 (1957).

[7] V. V. Narayanan and B. C. L. Weedon, *ibid.*, 394 (1957).

[8] K. Hofmann, O. J. Jucker, W. R. Miller, A. C. Young, Jr., and F. Taussig, THIS JOURNAL, **76**, 1799 (1954).

[9] T. Brotherton and G. A. Jeffrey, *ibid.*, **79**, 5132 (1957).

[10] K. Hofmann, S. Orochena, S. M. Sax and G. A. Jeffrey, *ibid.*, **81**, 992 (1959).