tion directly as solids. All four were recrystallized from hexane. Yields were about 0.5 g. of each. Physical constants, analytical data and infrared bands are given in Table III.

TABLE III

FOUR ISOMERIC 4-*t*-BUTYLCYCLOHEXYL 4-*t*-BUTYLCYCLOHEXANECARBOXYLATES[b]

Isomer	M.p., °C.	Carbon, %[a]	Hydrogen, %[a]
cis–cis	96–96.5	78.20	11.85
trans–cis	68–69	78.34	11.92
cis–trans	54.5–55.5	78.52	11.97
trans–trans	153–154	78.23	11.65

[a] Calcd. for $C_{21}H_{38}O_2$: C, 78.21; H, 11.88. [b] Infrared bands, carbon tetrachloride solution (s = strong, m = medium, w = weak, br = broad, sh = shoulder): *cis–cis* 6.75s, 6.89s, 7.16m, 7.32s, 7.47m, 7.67m-s, 8.1sh, 8.37s, 8.54s, 8.73s, 9.01m-s, 9.12m, 9.68s, 9.98m, 10.57m, 10.74m, 11.0w, 11.15m; *trans–cis*, 6.79s, 6.87s, 7.16m, 7.32s, 7.44m, 7.67m-s, 8.4–8.55s, br, 8.73s, 8.94m, 9.13m, 9.6–9.65sh, br, 9.8–9.95s, br, 10.33m, 10.85w, 11.07m; *cis–trans*, 6.79s, 6.87s, 7.16m, sh, 7.32s, 7.56m-s, 7.90m, sh, 8.05–8.15m-s, br, 8.37s, 8.6–8.65s, 8.80m, sh, 9.02m-s, 9.65–9.70s, 9.98m, 10.31–10.41w-m, 10.78w, 11.12m; *trans–trans*, 6.73, 6.78s, twin, 6.86s, 7.16m-s, 7.30s, 7.51m-s, 7.63m, 7.86m, 8.02s, 8.12m-s, sh, 8.36s, 8.53–8.62s, 8.79m-s, 8.93m, 9.01m, 9.13m-w, 9.56s, br, 9.73–9.77s, 10.32w, 10.92m, 11.06m, 11.57w.

Kinetic Procedure.—The apparatus and procedure was similar to that previously described.[6] Nitrogen, after purification through Fieser solution, saturated lead acetate, concentrated sulfuric acid and a calcium chloride drying tower, was saturated with the organic solvent at condenser-water temperature to eliminate evaporation losses during a run. Samples were taken with a hypodermic needle, with nitrogen flow stopped momentarily, transferred to a special tube[32] fitted with a standard Luer joint which matched the infrared cells, and cooled. The concentration of peroxide at different times was determined by infrared analysis and in some instances checked by iodometric titration. The 5.65 μ band of both II and III obeyed the Beer–Lambert law over the concentration range used, with ϵ 0.501 and 0.538 l. cm.$^{-1}$ mmole^{-1}, respectively. The first-order rate constants (Table I) were calculated in the usual way.

Product Studies.—The apparatus was the same as used in the kinetic studies except that the exit gases were passed through a cold trap (Dry Ice–dichloromethane), a tared Ascarite tube, a protective Ascarite tube and two drying tubes (magnesium perchlorate and Drierite). A weighed amount (1.5–2.5 mmoles) of peroxide was dissolved in about 45 ml. of 1,1,2,2-tetrabromoethane (purified by crystallization), cooled in an ice-bath, swept with dry nitrogen for 20 minutes, then decomposed in a nitrogen atmosphere at 50.7° for 8 hours (*cis*-peroxide) or 12 hours (*trans*-peroxide). Carbon dioxide was determined by weighing the Ascarite tube. The reaction mixture was combined with the cold trap contents, diluted to 50 ml. with solvent, and the amount of ester determined using infrared analysis (ϵ 0.373 l. cm.$^{-1}$ mmoles^{-1} at 5.78 μ). The solution then was carefully distilled at 0.5 mm. and the first fraction (56°) was analyzed for *cis*- and *trans*-4-*t*-butylcyclohexyl bromides using infrared (ϵ 0.0432 and 0.0321 l. cm.$^{-1}$ mmoles^{-1} at 11.68 and 12.28 μ for the *cis*- and *trans*-bromides, respectively). The second fraction contained no measurable quantity of bromides. After all the solvent was removed, the residue was dried *in vacuo* and a spectrum taken to determine the isomeric composition of the esters. Results are summarized in Table II.

(32) This tube design was similar to one of D. F. DeTar and V. Gold described by D. F. DeTar and A. A. Kazimi, THIS JOURNAL, **77**, 3842 (1955).

EAST LANSING, MICH.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Reactions of Hydrogen Peroxide. V.[1] Alkaline Epoxidation of Acrolein and Methacrolein

BY GEORGE B. PAYNE

RECEIVED MARCH 6, 1959

Acrolein and methacrolein have been converted to their respective epoxides, glycidaldehyde and α-methylglycidaldehyde, by the action of hydrogen peroxide at *p*H 8–8.5. These new epoxy aldehydes were obtained as distilled aqueous solutions free of acidic by-products in 68 and 79% yields, respectively. Corresponding yields of anhydrous products were 40 and 64%. Glyceraldehyde has been secured by an acid-catalyzed hydration of glycidaldehyde. Glycidonitrile, a new epoxy nitrile, was prepared from the acetate of glycidaldoxime by thermal deacetylation.

An early attempt to epoxidize simple α,β-unsaturated aldehydes by means of hydrogen peroxide under alkaline conditions was reported by Weitz and Scheffer[2] in their original study of the epoxidation of α,β-unsaturated ketones. They used a relatively large amount of caustic (as high as 40 mole % based on hydrogen peroxide) in attempts to epoxidize both cinnamaldehyde and crotonaldehyde, but observed only acidic products from both reactions.

Owing, perhaps, to Weitz and Scheffer's failure to obtain simple epoxidation, little other work appears to have been done in the past on the epoxidation of α,β-unsaturated aldehydes in general or on the simpler analogs in particular. Recently, however, there have been reports of the successful alkaline epoxidations of such materials as 1-benzoyl-5-formyl-1,2,2a,3-tetrahydrobenz(cd)indole[3] and 2,3-diphenylacrolein.[4] As an alternative method of preparing epoxy aldehydes, Schaer[5] has allowed some simple α,β-unsaturated aldehydes to react with sodium hypochlorite.

Glycidaldehyde.—In the present study it has been found possible to effect the epoxidation of even the most sensitive aldehyde such as acrolein[6] by carrying out the reaction under controlled *p*H conditions. For example, when acrolein was added dropwise at 25–30° to a dilute hydrogen peroxide solution maintained at *p*H 8–8.5 by the continuous addition of dilute sodium hydroxide solution, the acrolein was converted to glycidaldehyde (I) in yields of 75–85% as determined by titration for oxirane oxygen. Although the epoxidation could be carried out in the general *p*H range of 7–9.5, optimum yields were secured at 8–8.5. Acidic by-prod-

(1) See G. B. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 54 (1959), for paper IV of this series.

(2) E. Weitz and A. Scheffer, *Ber.*, **54B**, 2327 (1921).

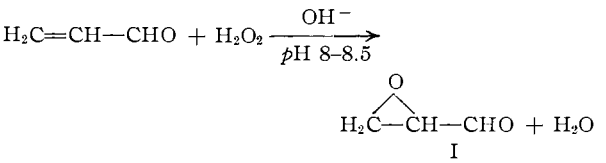
(3) E. C. Kornfeld, *et al.*, THIS JOURNAL, **78**, 3087 (1956).

(4) H. E. Zimmerman, L. Singer and B. S. Thyagarajan, *ibid.*, **81**, 108 (1959).

(5) C. Schaer, *Helv. Chim. Acta*, **41**, 614 (1958).

(6) G. B. Payne, THIS JOURNAL, **80**, 6461 (1958).

ucts from the reaction were determined quantitatively by observing the amount of alkali consumed in maintaining the desired *p*H. In general, this mixture of acids amounted to 5–15 mole %, with less being formed under the more dilute conditions; conversely, yields of epoxy aldehyde were highest when dilution was greatest.

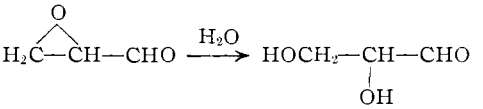


Kreis Test.—Glycidaldehyde has been mentioned many times in the chemical literature (the earlier name given to it was "epihydrinaldehyde"), usually in conjunction with the so-called "Kreis test."[7] The latter is a color test with phloroglucinol used to measure the degree of oxidative changes in fats. Glycidaldehyde has been postulated as one of the substances formed when rancid fat is brought into contact with the hydrochloric acid used in the Kreis test.[8] Attempts[9] have been made to synthesize glycidaldehyde in order to prove that it did, indeed, give a positive test; no earlier syntheses were successful, however.[10]

As recently as 1954 glycidaldehyde was still thought to be the substance responsible for a positive Kreis test with rancid fats.[11] In 1951, however, Patton and co-workers[12] had concluded that glycidaldehyde was *not necessarily* responsible, since malondialdehyde also gave a color spectrally similar to the Kreis colors obtained with rancid lard and oxidized milk fat.

Needless to say, one of the first experiments carried out with glycidaldehyde, after its isolation and characterization, was a Kreis test. This test was *negative;* the color that did develop *very slowly* was observed not to be the same as the typical Kreis color.

Glyceraldehyde.—Crude reaction mixtures containing glycidaldehyde were observed to undergo a slow but steady hydration reaction to give glyceraldehyde (II) on storage at room temperature.



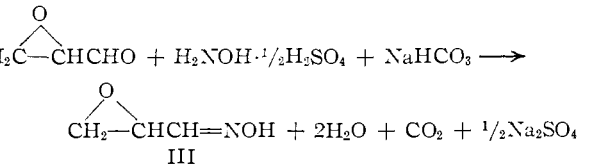
Because of the presence of sodium salts of acidic by-products, however, the glyceraldehyde thus formed was difficult to purify. A better procedure involved flash distillation to give an aqueous glycidaldehyde solution free of salts, followed by acid-catalyzed hydration. In this manner, crystalline glyceraldehyde dimer was secured in an over-all yield of 57% based on acrolein originally charged. This synthesis of glyceraldehyde from acrolein *via* glycidaldehyde represents a considerable advance in ease of operation and yield over procedures recently employed.[13,14]

Anhydrous Glycidaldehyde.—Attempts to isolate the anhydrous epoxy aldehyde by saturating an aqueous solution with ammonium sulfate and extracting with ether were not fruitful due to the high water solubility of this material (it undoubtedly exists in solution as the carbonyl hydrate). Surprisingly, however, warm cyclohexanone was a moderately efficient extractant and through its use the pure anhydrous product was isolated by distillation in 40% yield based on acrolein.

Glycidaldehyde free of water is a surprisingly stable material. On refluxing at atmospheric pressure (b.p. 112–113°) for limited periods it slowly turned pale yellow (probably due to the formation of traces of pyruvaldehyde), but could be recovered by distillation with almost no loss to higher boiling products.

Simple Derivatives of Glycidaldehyde.—For further characterization of this new epoxy aldehyde, the 2,4-dinitrophenylhydrazone derivative was prepared in ethanol solution using a small amount of acetic acid as catalyst. With mineral acid catalyst, of course, the epoxide linkage underwent solvolysis; acetic acid as solvent was also unsatisfactory.

An oxime was secured, again by a special procedure: a suspension of hydroxylamine sulfate and sodium bicarbonate in ether containing anhydrous glycidaldehyde was stirred vigorously at 15° and the reaction initiated by adding a small amount of water. When carbon dioxide evolution was slow,



the ethereal solution containing glycidaldoxime (III) was decanted, dried and distilled. The oxime was found to be quite unstable and underwent slow polymerization even when stored in the cold. When stored at room temperature, it slowly warmed over a period of about 2 hours to the point where it polymerized *explosively*.

The oxime was converted to its more stable acetate (IV) by treatment with acetic anhydride. The acetate, in turn, could be deacetylated at 50 mm. and 140–145° to give glycidonitrile (V), an apparently new epoxy nitrile.

α-Methylglycidaldehyde.—Methacrolein (α-methylacrolein) was epoxidized by the same procedure employed with acrolein to give α-methylglycidaldehyde in a crude titrated yield of 82%. Flash distillation afforded the epoxy aldehyde as an aqueous salt-free solution in 79% yield based on methacrolein. The isolation of anhydrous product

(7) H. Kreis, *Chem.-Ztg.*, **23**, 802 (1899).

(8) W. C. Powick, *J. Agr. Research*, **26**, 323 (1923).

(9) E. Mundinger, *Milch. Forsch.*, **7**, 292 (1929); K. Täufel and F. K. Russow, *Z. Unters. Lebens.*, **65**, 540 (1933).

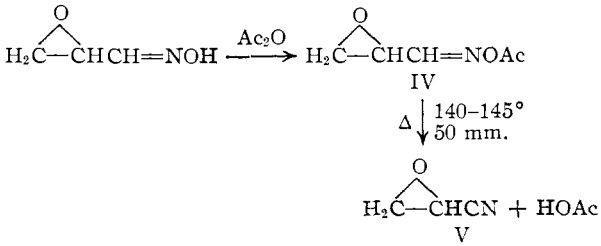
(10) Glycidaldehyde diethyl acetal has recently been studied by J. B. Wright and co-workers; see THIS JOURNAL, **79**, 1690, 1694 (1957).

(11) N. P. Materanskay and M. Nechaev, *Union Sci. Research Inst. Molochnaya Prom.*, **15**, No. 6, 28 (1954); *C. A.*, **49**, 1983 (1955).

(12) S. Patton, M. Keeney and G. W. Kurtz, *J. Am. Oil Chemists' Soc.*, **28**, 391 (1951).

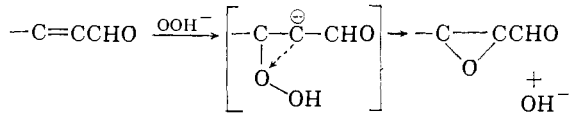
(13) E. J. Witzmann, W. L. Evans, H. Hass and E. F. Schroeder, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 305.

(14) W. F. Gresham and W. E. Grigsby, *J. Org. Chem.*, **14**, 1103 (1949).



proved to be less troublesome than with glycidaldehyde, and a 64% over-all yield resulted from ether extraction followed by distillation.

Mechanism of Reaction.—The epoxidation of an α,β-unsaturated aldehyde by alkaline hydrogen peroxide probably proceeds by an initial attack of perhydroxyl ion on the β-carbon atom followed by ring enclosure and elimination of hydroxyl.



This mechanism is, of course, the same as that postulated by Bunton and Minkoff[15] for the analogous reaction with α,β-unsaturated ketones.

Experimental

Glycidaldehyde from Acrolein. Procedure A.—To a 1-liter, 5-neck, round-bottom flask equipped with mechanical stirrer, dropping funnels, thermometer and standard electrodes connected to a Beckman *p*H meter, were charged 59.2 g. (0.53 mole) of 30.8% hydrogen peroxide and 390 ml. of distilled water. The *p*H was adjusted to 8.0 by the addition of several drops of 1 *N* sodium hydroxide and then 28 g. (0.50 mole) of acrolein was added dropwise with stirring over 1 hr. at 25–30°. The *p*H was maintained at 8.0–8.5 by the addition of 1 *N* caustic. After an additional hour at the same temperature and *p*H, an iodometric titration indicated the consumption of 0.48 mole of hydrogen peroxide; one hour later the consumption was 0.49 mole. Titration for oxirane oxygen[16] at that time indicated the presence of 0.44 mole of that functional group. The yield of total epoxide was therefore 88% based on acrolein charged. Acidic by-product, measured by the consumption of 1 *N* alkali, amounted to 0.04 mole or 8%.

Glycidaldehyde from Acrolein. Procedure B.—To a 3-liter, 5-neck, round-bottom flask equipped as above were charged 300 ml. of distilled water and 15 g. (0.14 mole) of 30.5% hydrogen peroxide. The *p*H was adjusted to 8.0–8.5 with 3 *N* caustic and a solution of 335 g. (3.0 moles) of 30.5% hydrogen peroxide in 168 g. (3.0 moles) of acrolein (slight cooling required to hold the temperature below 30° during mixing of these two chemicals) was added with stirring over a period of 10 minutes at 40–45° using Dry Ice–acetone cooling. At the end of the addition, 45 ml. of 3 *N* sodium hydroxide had been used. After another 5 minutes at 45° and *p*H 8.0–8.5, 75 ml. had been consumed and the reaction mixture was cooled quickly to 15–20°. Iodometric titration indicated that 95% of the theoretical amount of peroxide had been consumed; titration for oxirane oxygen[16] showed the presence of 2.39 moles (80% yield) of that group.

Flashing of Glycidaldehyde.—The above reaction mixture was rapidly flashed at 65–70° and 200 mm. by means of a circulating evaporator,[17] using a wet ice trap and Dry Ice trap in series beyond the condenser to protect the vacuum pump. In less than 0.5 hr. the mixture was concentrated to a volume of about 150 ml.; the aqueous distillate (including that collected in the wet ice trap) was found to contain 2.04 moles of glycidaldehyde free of any acidic by-product (68% yield based on acrolein originally charged).

Anhydrous Glycidaldehyde.—The freshly flashed aqueous solution of glycidaldehyde (2.04 moles) was saturated with ammonium sulfate and immediately extracted with four 150-ml. portions of cyclohexanone. The combined extracts contained 0.69 mole of glycidaldehyde by titration. One more extraction with 500 ml. of cyclohexanone previously warmed to 70° resulted in the extraction of another 0.63 mole (total recovery, 1.32 moles or 68%). All extracts were combined and flashed through a 10-tray Oldershaw column at 50 mm. pressure until a head temperature of 70° was reached. The relatively concentrated solution of glycidaldehyde thus taken overhead was treated with 50 ml. of benzene, dried over magnesium sulfate, and distilled through the same column. After removal of benzene along with some water at 200 mm., the pressure was lowered to 100 mm. and anhydrous glycidaldehyde distilled, b.p. 57–58°, $n^{20}D$ 1.4198. The yield was 85 g. (40% based on acrolein originally charged). Infrared analysis showed carbonyl absorption at 5.75 μ and epoxide absorption at 8.15 and 11.76 μ.

Anal. Calcd. for $C_3H_4O_2$: C, 50.0; H, 5.6; oxirane oxygen, 22.2. Found: C, 50.1; H, 5.7; oxirane oxygen, 21.6.[16]

Glycidaldehyde 2,4-Dinitrophenylhydrazone.—To a boiling solution of 19.8 g. (0.10 mole) of 2,4-dinitrophenylhydrazine and 10 g. (0.16 mole) of acetic acid in 1400 ml. of ethanol was added 7.2 g. (0.10 mole) of anhydrous glycidaldehyde. After boiling on the steam-bath for one minute, the solution was cooled quickly to 50° and filtered to remove any insoluble solid. The filtrate was allowed to cool to room temperature over an hour period and then in an ice-bath overnight. Filtration, followed by washing with cold ethanol and vacuum drying, gave 13.9 g. (55% yield) of glycidaldehyde 2,4-dinitrophenylhydrazone, m.p. 96–98°, followed by resolidification and m.p. unsharp *ca.* 150°.

Anal. Calcd. for $C_9H_8N_4O_5$: C, 42.9; H, 3.2; N, 22.2. Found: C, 42.9; H, 3.2; N, 22.1.

When a 0.5-g. sample of this derivative was placed in a test-tube and heated on the steam-bath it *exploded*, sending carbon and a flame out the end of the test-tube.

The epoxy dinitrophenylhydrazone was converted to the corresponding **glyceraldehyde derivative** by dissolving 0.5 g. in 100 ml. of hot 0.1 *N* sulfuric acid. Hot filtration, precipitation at room temperature, isolation, and recrystallization from 50% aqueous methanol gave material melting at 164–165° (lit.[18] m.p. 167°), mixed m.p. not depressed.

Glycidaldehyde Oxime.—A solution of 36 g. (0.50 mole) of glycidaldehyde in 450 ml. of ether was treated with 41 g. (0.5 mole) of hydroxylamine sulfate and 43 g. (0.5 mole) of sodium bicarbonate. The mixture was stirred vigorously at 15–20° after adding 10 ml. of water to initiate the reaction. After 1.5 hr., carbon dioxide evolution was slow and the ether solution was decanted from insoluble salt and dried over magnesium sulfate. Concentration at room temperature followed by careful Claisen-distillation at 1 mm. afforded 15 g. of product, b.p. 48–49°, prior to sudden darkening in the kettle followed by a *violent* polymerization.

The epoxy oxime taken overhead was subsequently found to undergo slow polymerization to a water-soluble substance even when stored at 5°. When left at room temperature it very slowly warmed over a 1–2 hour period to the point where it polymerized *explosively*. In view of the hazard involved with this compound, no further attempt was made to handle it at room temperature in the absence of solvent.

The freshly distilled oxime was analyzed by a micro carbon and hydrogen technique, taking care to avoid polymerization by keeping the sample cold prior to combustion.

Anal. Calcd. for $C_3H_5O_2N$: C, 41.4; H, 5.8. Found: C, 41.4; H, 5.8.

Glycidaldehyde Oxime Acetate.—The preparation of oxime was carried out as described above except that the temperature was held at 10–15° and the time reduced to 1 hr. Crude oxime obtained by removal of ether at <10° amounted to 29 g. (66% yield). It was treated with 1.3 molar equivalents of acetic anhydride and the temperature then held at 35° by periodic cooling. After an overnight stand at room temperature, acetic acid and excess anhydride

(15) C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).

(16) Hydrochloric acid in aqueous magnesium chloride; see J. L. Jungnickel, E. D. Peters, A. Polgar and F. T. Weiss, "Organic Analysis," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1953, p. 134.

(17) D. T. Mitchell, P. Shildneck and J. Dustin, *Ind. Eng. Chem., Anal. Ed.*, **16**, 754 (1944).

(18) I. Neuberg and H. Collatz, German Patent 557,564 (1931).

were removed under vacuum below 50°. Claisen-distillation of the residue gave 28 g. of glycidaldehyde oxime acetate, b.p. 60–65° (1 mm.), $n^{20}D$ 1.4647. The yield was 44% over-all based on glycidaldehyde.

Anal. Calcd. for $C_5H_7NO_3$: C, 46.5; H, 5.5; N, 10.8; sapon. equiv., 129; oxirane oxygen, 12.4. Found: C, 46.5; H, 5.5; N, 10.8; sapon. equiv.,[19] 131; oxirane oxygen, 11.2.[20]

Glycidonitrile.—A 32.8-g. (0.25 mole) sample of oxime acetate was charged to a 100-ml. distillation kettle and attached to a 0.7 × 50 cm. glass spiral-packed column. The pressure was held at 50 mm. while heating with an oil-bath. Deacetylation started when the bath temperature reached 115–120°, but in order to obtain a satisfactory distillation rate it was necessary to hold the bath at 140–145°. Takeoff was adjusted to maintain a maximum head temperature of 70°. After 2.5 hr., 24.8 g. of a mixture of acetic acid and glycidonitrile had been collected and the rate of takeoff was very slow; by lowering the pressure to 1 mm. only 0.4 g. more material distilled as a separate fraction. The distillation residue was 5.0 g.

Careful distillation of the mixture of acid and nitrile through the same column afforded 7.3 g. (42% yield) of glycidonitrile, b.p. 47.5–48° (20 mm.), $n^{20}D$ 1.4094. Infrared analysis showed nitrile absorption at 4.43 μ and epoxide absorption at 8.05 and 11.98 μ.

Anal. Calcd. for C_3H_3NO: C, 52.2; H, 4.4; N, 20.3; oxirane oxygen, 23.2. Found: C, 52.2; H, 4.5; N, 20.0; oxirane oxygen, 22.1.[16]

The epoxy nitrile was also isolated by dissolving 69 g. of the mixture of acetic acid and glycidonitrile in 300 ml. of ether and washing out the acetic acid with a concentrated sodium bicarbonate solution. Distillation of the dried ether solution gave 21 g. of glycidonitrile with the above b.p.

Glyceraldehyde from Glycidaldehyde.—A freshly flashed aqueous solution containing 0.25 mole of glycidaldehyde in 200-ml. total volume was treated with 2 ml. of formic acid and allowed to stand at room temperature. The disappearance of epoxide was followed by titration[16] and after 2 weeks only 1% remained. The solution was concentrated under vacuum at <40° to a viscous residue and then triturated with 5 ml. of ethanol. After completion of the crystallization process (2–3 days), the solid mass was crushed and dried to a constant weight of 21.4 g. (95% yield), m.p. 125–130°. After trituration with warm acetone there remained 18.9 g. (84% yield) of glyceraldehyde dimer, m.p. 136–137°; a mixed m.p. with an authentic sample (Nutritional Biochemical Corp.) was not depressed.

Anal. Calcd. for $C_6H_{12}O_6$: C, 40.0; H, 6.7. Found: C, 39.8; H, 6.8.

α-Methylglycidaldehyde from Methacrolein.—To a 1-liter, 5-neck flask equipped as above were charged 300 ml. of water and 1.05 mole of 30% hydrogen peroxide. The mixture was stirred at 35–40° and 70 g. (1.0 mole) of methacrolein was added over 15 minutes at a *p*H of 8–8.5; the latter was maintained by the addition of 1 *N* sodium hydroxide. After an additional hour at the same temperature and *p*H, iodometric titration indicated the consumption of 0.96 mole of hydrogen peroxide; acidic by-product amounted to 0.08 mole as determined by alkali consumption. The yield of epoxide was 0.82 mole by titration for oxirane oxygen.[16]

The crude mixture was flashed as above, using an extra 100 ml. of water after the volume had been reduced to 50–100 ml. Recovery of volatile epoxide (α-methylglycidaldehyde) amounted to 0.79 mole in a total volume of 600 ml.

For the recovery of anhydrous epoxy aldehyde, the solution was saturated with 400 g. of ammonium sulfate and extracted with five 200-ml. portions of ether. Titration of the aqueous salt solution indicated the presence of 0.21 mole of epoxide, so the mixture was warmed to 35° and extracted with two more 200-ml. portions of ether. The combined ether extracts, containing 0.71 mole of epoxide by titration, were dried for 1 hour over 100 g. of anhydrous magnesium sulfate and finally over 100 g. of Drierite for 1 hour. The filtered solution was distilled through a 10-tray Oldershaw column to give a concentrate of 260 ml. This was further concentrated using a 0.7 × 50 cm. glass spiral-packed column until the kettle temperature reached 80°. Distillation under vacuum then afforded 55 g. (64% yield based on methacrolein) of α-methylglycidaldehyde, b.p. 52–53° (80 mm.). There was no pre-cut and virtually no residue.

Anal. Calcd. for $C_4H_6O_2$: C, 55.8; H, 7.0; oxirane oxygen, 18.6. Found: C, 55.5; H, 7.1; oxirane oxygen, 18.1.[16]

The 2,4-dinitrophenylhydrazone derivative was prepared exactly as described above, m.p. 137–138°.

Anal. Calcd. for $C_{10}H_{10}N_4O_5$: N, 21.0. Found: N, 21.1.

EMERYVILLE, CALIF.

(19) Sample allowed to stand for 0.5 hr. at room temperature with excess 0.1 *N* sodium hydroxide; back titration made with 0.1 *N* hydrochloric acid.

(20) Hydrochloric acid–dioxane method; see ref. 16, p. 135.

[CONTRIBUTION NO. 510 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Chemistry of Cyclobutanes. II. Cyclobutenes from 3-Methylenecyclobutane-1,2-dicarboxylic Anhydride

BY H. N. CRIPPS, J. K. WILLIAMS, V. TULLIO AND W. H. SHARKEY

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The adduct from allene and maleic anhydride, 3-methylenecyclobutane-1,2-dicarboxylic anhydride, has proved to be a versatile intermediate to a variety of functionally substituted cyclobutenes. Upon treatment with alkali, this anhydride is converted to 3-methyl-2-cyclobutene-1,2-dicarboxylic acid. Other functionally substituted cyclobutenes with ester, amide, nitrile, amine and hydroxyl groups have been obtained from this acid. The stereochemistry of the saturated dicarboxylic acids obtained by hydrogenation of 3-methyl-2-cyclobutene-1,2-dicarboxylic acid has been established.

The discovery of a convenient synthesis of substituted methylenecyclobutanes[1] has made compounds of this type readily accessible for the first time. Among these is 3-methylenecyclobutane-1,2-dicarboxylic anhydride (I) a compound that, because of its multiple functionality, appeared ideally suited as an intermediate to a variety of new four-membered ring compounds (Fig. 1). Our interest in I was greatly increased when it was found that treatment with excess alkali followed by acidification gave 3-methyl-2-cyclobutene-1,2-dicarboxylic acid (II) in 84% yield.

The structure of II was assigned on the basis of spectral data. Its infrared spectrum showed absorption at 5.85 μ for an unconjugated carboxyl group, at 5.92 μ for a conjugated carboxyl group, a shoulder at about 6.05 μ for the double bond and a band at 7.29 μ for the methyl group. The ultraviolet spectrum in ethanol had a maximum at 220 mμ (ε 8580) consistent with an α,β-conjugated

(1) H. N. Cripps, J. K. Williams and W. H. Sharkey, THIS JOURNAL, **80**, 757 (1958); **81**, 2723 (1959).