80% recovery by ether extraction of the solution resulting from treatment of aqueous sodium glycidate with dilute nitric acid at −5°. Further purification was achieved by distillation followed by recrystallization. Pure glycidic acid is a crystalline hygroscopic solid melting at 36–38° and having a pK_a of 3.4.

Hydration of the epoxide group of sodium glycidate was accomplished in dilute aqueous solution at reflux for eight hours. Treatment of the resulting solution with calcium chloride led to the precipitation of calcium glycerate in 83% overall yield.

EXPERIMENTAL

Sodium glycidate hemihydrate. Procedure A. To a 1-l., five-neck, round bottom flask equipped with stirrer, dropping funnel, thermometer, and *p*H electrodes connected to a Beckman *p*H meter, was added 108 g. (1.50 moles) of anhydrous glycidaldehyde.[2] With stirring and ice bath cooling at 35–40° was added 1.60 moles of 30% hydrogen peroxide over a 10-min. period. The wet ice bath was then replaced with an efficient Dry Ice–acetone bath, and a solution of 60 g. (1.50 moles) of sodium hydroxide in 200 ml. of water was added as rapidly as possible at 40–45° and an initial *p*H of 8.5–9.0. After part of the alkali had been added, it was possible to control the *p*H at 9.0 ± 0.1. After completion of the addition (*ca.* 30 min.), the mixture was allowed to stir for an additional 15 min. The final *p*H was about 7.

The reaction mixture was concentrated at 100 mm. and <40° by means of a circulating evaporator.[3] When the volume had been reduced to about 250 ml., the concentrate was diluted with 1600 ml. of ethanol. Sodium glycidate hemihydrate started to precipitate immediately. After 12 hr. in the cold, the solid product was recovered by filtration, washed with ethanol, and vacuum-dried at room temperature. The weight of white crystalline product was 115 g. (65% yield). Titration for oxirane oxygen indicated a minimum purity of 94%.

Anal. Calcd. for $C_3H_3O_3Na\cdot{}^1/_2H_2O$: Oxirane oxygen, 13.4. Found: Oxirane oxygen, 12.6.[4]

The salt was best recrystallized by dissolving 10.0 g. in 20 ml. of water and adding this solution to 200 ml. of boiling ethanol. On cooling to room temperature there was recovered 8.0 g. having a minimum purity of 98%.

Anal. Calcd. for $C_3H_3O_3Na\cdot{}^1/_2H_2O$: C, 30.3; H, 3.4; Na, 19.3; oxirane oxygen, 13.4 Found: C, 30.3; H, 3.4; Na, 19.1 oxirane oxygen, 13.1.[4]

Procedure B. To the same flask was added 100 ml. of water and 1.10 moles of 30% hydrogen peroxide. With stirring and cooling at 30–35° was added dropwise 72 g. (1.0 mole) of glycidaldehyde. A solution of 40 g. (1.0 mole) of sodium hydroxide in 150 ml. of water was then added dropwise at 30–35° at such a rate as to maintain a *p*H of 8.5–9.0. After about one half of the alkali had been added, the *p*H was controlled at 9.0 ± 0.1. Alkali addition was complete in 1.25 hr. and stirring was continued for 15 min. longer as the *p*H fell to 7–8.

The reaction mixture was concentrated under vacuum at 15–20° to a volume of 150–200 ml. Some crystalline sodium salt precipitated. Dilution with 1500 ml. of ethanol then afforded 78 g. (65%) of sodium glycidate hemihydrate having an oxirane oxygen content of 12.7.[4]

Glycidic acid from sodium glycidate hemihydrate. A solution of 23.8 g. (0.20 mole) of sodium salt in 50 ml. of water was stirred at −5° as 37 ml. of 5.17*N* nitric acid (0.19 equiv.) was added dropwise over 1 hr. The resulting solution was saturated with ammonium sulfate and extracted with ten 75-ml. portions of ether. After drying over magnesium sulfate, the combined ether extract was concentrated on the steam bath until the internal temperature reached 45°. This concentrate was then pumped at 2 mm. pressure to a constant weight of 13.3 g. (80% yield) of colorless liquid. A minimum purity of 93% was indicated by titration for oxirane oxygen.

Anal. Calcd. for $C_3H_4O_3$: oxirane oxygen, 18.2; neut. equiv., 88. Found: oxirane oxygen, 16.8;[4] neut. equiv., 93.

Claisen distillation of an 11.3 g. portion gave 4.3 g. of distillate, b.p. 55–60° (0.5 mm.), n_D^{25} 1.4424, and 6.9 g. of polymeric residue. Analysis of the glycidic acid indicated a minimum purity of 97% (found: oxirane oxygen, 17.6; neut. equiv., 89).

In another experiment, carried out as above except that 2*N* sulfuric acid was used in place of nitric acid, there was obtained a 53% over-all recovery of distilled glycidic acid. Its purity was 94% by titration for oxirane oxygen. That material, on crystallization from benzene-hexane, gave analytically pure glycidic acid, m.p. 36–38°.

Anal. Calcd. for $C_3H_4O_3$: C, 40.9; H, 4.6. Found: C, 40.8; H,4.6.

Calcium glycerate. A solution of 10.0 g. (0.084 mole) of sodium glycidate hemihydrate in 100 ml. of water was allowed to reflux for 8 hr. To the warm solution was then added a solution of 5.1 g. (0.046 mole) of calcium chloride in 25 ml. of water. The clear solution, on standing at 50°, deposited crystals which, on filtration, washing with 50% alcohol and drying, amounted to 7.4 g. of calcium glycerate dihydrate. An additional 2.5 g. was recovered from the original mother liquor for a total yield of 83%.

Anal. Calcd. for $C_6H_{10}O_8.2H_2O$: C, 25.2; H, 4.9; Ca, 14.0; H_2O, 12.6; α-glycol value, 0.70 mole/100 g. Found: C, 25.0; H, 5.0; Ca, 13.9; H_2O, 13.9; α-glycol value, 0.70 mole/100 g.[5]

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[2] G. B. Payne, *J. Am. Chem. Soc.*, 81, 4901 (1959).

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

[4] Hydrochloric acid in aqueous magnesium chloride; see J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, *Org. Anal.*, Vol. 1, Interscience, New York, 1953, p. 134.

[5] Modification of the procedure of V. C. Mehlenbacher, *Org. Anal.*, Vol. 1, Interscience, New York, 1953, p. 45.

A Case of Nonstereospecificity in the Simmons-Smith Procedure for Preparation of Cyclopropanes[1]

D. W. SETSER[2] AND B. S. RABINOVITCH

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In connection with studies of the unimolecular isomerization of cyclopropanes, we have attempted the preparation of the *trans*-dideutero (I), all *cis* (II), and *cis*-dideutero-*trans*-methyl (III) isomers of 1,2-dideutero-3-methylcyclopropane. Use of the Simmons-Smith reaction appeared feasible since addition to 1,2-disubstituted olefins proceeds stereospecifically to yield 1,2-disubstituted cyclopropanes of corresponding configuration.[3] In our

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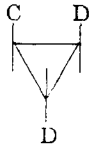
[1] Work supported by a grant from the National Science Foundation.

[2] N.S.F. Predoctoral Fellow.

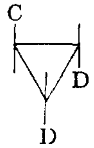
[3] H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, 81, 4256 (1959).

experiments addition to ethylene-d_2 was found to be nonstereospecific.

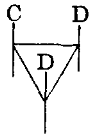
The *cis*- and *trans*-propene-1-*d* used had average composition of 98% *cis*-propene-1-*d*, 2% propene and of 87% *trans*-propene-1-*d*, 4% *cis*-propene-*d* and 9% propene, respectively. Methylene-*d* iodide was of 99.5% isotopic purity. The Simmons-Smith reaction at 60° with *cis*-propene-1-*d* and methylene-*d*-iodide yielded products of average composition 97% methylcyclopropane-d_2 and 3% methylcyclopropane-*d* (IV); the product from *trans*-propene-1-*d* reactant had average composition of 90% methylcyclopropane-d_2, 10% IV. *Stereospecific* addition occurred with formation of an equal mixture of I and II (assumed) from *cis*-propene-1-*d*, and with formation of an equal mixture of I and III (assumed) from *trans*-propene-1-*d*. The infrared spectrum of each mixture (2–15 μ) revealed, in addition to bands in common, characteristic bands absent in the other mixture.[4] Thermal homogeneous geometrical isomerization of the I–II mixture at 400° gave rise to the characteristic infrared bands of the I–III mixture, with diminution of intensity of the original characteristic bands; further details will appear elsewhere. The unchanged propene underwent no isomerization.



I



III



II

The preparation of pure I was attempted at 60° with ethylidene iodide reagent and *trans*-ethylene-d_2 of 99.3% isotopic purity. Extensive decomposition of the reagent to light ethylene occurred (as well as coupling to *cis*- and *trans*-butene-2) and it was found desirable to use large excess of ethylene-d_2 to prevent excessive contamination (for purposes of kinetic studies) of the product by light methylcyclopropane. The methylcyclopropane product had a composition of 10% $-d_0$ and 90% $-d_2$. Infrared analysis showed that a *nonstereospecific* dideutero product had been obtained which had the composition of the equilibrium mixture, 50% *trans*, 25% *cis*, 25% *cis-trans;* the spectrum was identical with that of a 50–50 mixture made from the products of the two earlier preparations with propene-1-*d*. *The recovered trans-ethylene-d_2 was isomerically pure.* A similar experiment at 60° with methylene iodide and *trans*-ethylene-d_2 in 2:1 proportions gave a partially stereospecific addition product of 75% *trans*- and 25% *cis*-cyclopropane-d_2, as determined from known infrared spectra[5]. Repetition of this experiment at 25° (and longer reaction time) showed somewhat greater stereospecificity (88% *trans*, 12% *cis*). *The unchanged ethylene-d_2 underwent no cis-trans isomerization.*

To this point our results invited several possible alternative explanations of which we need mention only two: A catalytic effect with ethylene could be occurring in the presence of the copper-zinc reagent; or the data might reflect a delicate balance in the stability of an intermediate ring, such as VI of Simmons and Smith,[3] influenced here by temperature change and electron density at the reaction site. That the former explanation applies was shown by duplicate experiments with *trans*-ethylene-d_2 and methylene iodide, wherein excess metal was removed after formation of the organometallic reagent, and before reaction with olefin in the usual way at 60°. Completely stereospecific addition to give *trans*-cyclopropane-d_2 occurred, but in low yield. No isomerization of the recovered deuteroethylene occurred and no light ethylene appeared. Similar experiments with ethylidene iodide unfortunately yielded negligible amounts of product.

The occurrence of a catalytic effect is understandable as a *post facto* finding. First, possible unusual catalytic effects of zinc-copper metal have been previously encountered.[6] Second, it is well known that ethylene is more strongly absorbed on transition metal catalysts than are its higher homologs.

EXPERIMENTAL

Preparation of reagents. cis- and *trans*-Propene-1-*d* were prepared by appropriate reduction procedures[6] applied to propyne-1-*d* of 98% isotopic purity. *trans*-Ethylene-d_2 was prepared by the procedure previously described.[7]

Methylene-*d*-iodide was made in 99.5% isotopic purity by reduction of deuteriodoform, obtained from exchange of iodoform with sodium deuteroxide solution. A 70-g. sample of iodoform in 280 ml. of anhydrous benzene was stirred for 6 hr. with two successive 40-ml. portions of 0.5*N* sodium deuteroxide, in the dark under a nitrogen atmosphere. The organic layer was washed with several 30-ml. portions of 47% hydriodic acid solution. The degree of exchange was followed by infrared analysis. Reduction of the deuteroiodoform to methylene *d*-iodide was effected by a conventional white phosphorus–hydriodic acid treatment. Based on iodoform, the yield was 15%.

Cis-trans ratios were measured with a calibrated Beckman IR 5 infrared spectrometer. Isotopic analyses were by low-voltage parent peak data obtained on a Consolidated 21-103 mass spectrograph.

Reaction of propenes and ethylene with methylene iodide. In a typical experiment giving 65% yield based on olefin, 0.02 mole of methylene-*d*-iodide, 2.0 g. of copper-zinc

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[4] The composition of the product mixture from *cis*-propene reagent was estimated statistically as 48.5% I, 48.5% II, 3% IV; that from the *trans*-propene reagent was estimated as 45.5% I, 2% II, 43% III, and 10% IV; the infrared absorption of the 2% II was scarcely detectable in this mixture.

[5] E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960). Thermodynamic equilibrium of the cyclopropane-d_2 isomers was found to correspond to a 50:50 *cis-trans* mixture.

[6] B. S. Rabinovitch and F. S. Looney, *J. Am. Chem. Soc.*, **75**, 2652 (1953).

[7] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, **23**, 315 (1955).

catalyst,[3] 0.01 mole of propene-1-*d*, a trace of iodine, and 8 ml. of anhydrous ether were sealed in a 25-ml. Pyrex vessel and shaken for 20 hr. at 60° Methylcyclopropane was recovered by distillation of the reaction mixture and was purified on a preparative GLPC column.

Similar technique with *trans*-ethylene-d_2 and methylene iodide (molar ratio of 1:2) gave yields based on olefin of 35% at 60° and 7% at 35° (50-hr. reaction time). Reactions employing methylene iodide gave side products of ethylene, resulting from reagent coupling, as well as cyclopropane from subsequent addition to the ethylene.

In two experiments, the organometallic reagent was prepared in the absence of olefin by stirring 0.02 mole of zinc-copper catalyst, 0.01 mole of methylene iodide, and a trace of iodine in anhydrous ether at reflux temperature for 4 hr.; the reaction with ethylene was completed in the normal manner at 60° after removal of the excess catalyst by filtration and addition of 0.003 mole of *trans*-ethylene-d_2. Pure *trans*-cyclopropane-d_2 was obtained in 2% and 4% yield.

Reaction of ethylene with ethylidene iodide. The following procedure minimized the undesirable side reactions of ethylene formation through rearrangement, and butene production from coupling, of the ethylidene iodide. *trans*-Ethylene-d_2 (0.02 mole), ethylidene iodide (0.007 mole), a trace of iodine, catalyst (0.015 mole), and 8 cc. of ether were sealed in a Pyrex vessel of volume such that, ignoring the solubility in the ether, the ethylene pressure would have been 35 atm. Explosions were prevented by filling the reaction vessel at liquid nitrogen temperature and placing it within a small diameter iron pipe which was pressurized to 15 atm. before the assembly was permitted to warm. The reaction was then completed by shaking in an oil bath at 60° for 10 hr. Methylcyclopropane was recovered and purified in the previously described manner. The yield of methylcyclopropane was 12% based on iodide and was 90%-d_2 and 10% light. 5% of the ethylidene iodide coupled to give butene and the remainder gave light ethylene.

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The Reaction of Lactones with Pyrones in the Presence of Trifluoroacetic Acid

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This report is part of a continuing study of the fundamental chemistry of the 4-pyrones and is a portion of the investigation of the reaction of pyrones in the presence of the powerful solvating agent, trifluoroacetic acid.[2-4]

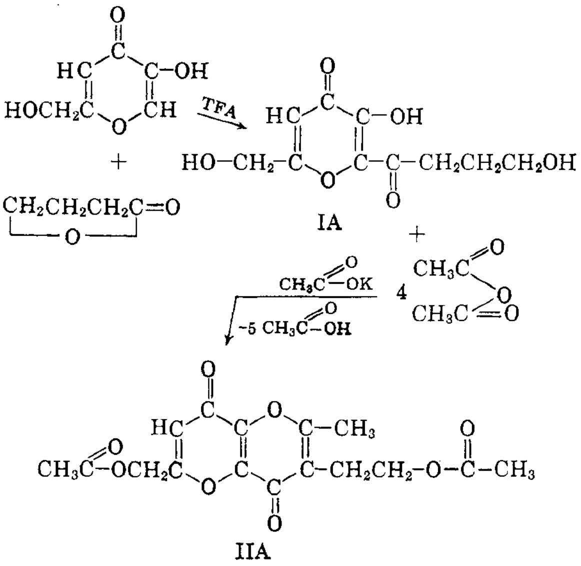
The reaction of lactones with pyrones gives good yields and requires only a short period of time for completion. Table I lists the various pyrones used in the experiment. Coumarin and 6-methyl-2-pyronone were tried to ascertain if the generalized method was applicable to pyrones other than 4-pyrones. Only coumarin gave a product which could be isolated under the conditions employed.

The point of attachment of the hydroxy-acyl radical to the ring was ascertained by converting all those pyrones having a 5-hydroxy group to the corresponding pyrano[3,2,-b]pyran-6-methyl-4,8-diones given in Table II.

As I_A upon conversion to II_A gave a poor analysis, compound III was prepared as added confirmation of its structure.

EXPERIMENTAL[4]

Preparation of members of I_{A-G} *series.* A mixture consisting of 0.1 mole of the pyrone, 0.1 mole of the lactone and 10 ml. of trifluoroacetic acid was refluxed for 1 hr. The resulting material was cooled somewhat, diluted with about 40 ml. of absolute ethanol and chilled. In the case of coumarin, only 20 ml. of ethanol was used.



The chilled solutions were filtered and dried in air to give the crude yields reported in Table I.

Analytical samples were obtained by two further recrystallizations from ethanol.

All the 5-hydroxy compounds gave red colorations with ferric chloride.

Preparation of members of (IIa-d) *series.* A 100-ml. flask containing 3 g. of the hydroxy-acylated pyrone of the I_{A-G} series, 3 g. of fused potassium acetate, and 10 ml. of acetic anhydride was connected with an air cooled condenser and immersed in a Fisher Hi Temp oil bath and heated at 130° for 2 hr. The melt was then diluted with 30 ml. of water, cooled, neutralized with sodium bicarbonate, chilled in the freezing compartment of the refrigerator, and filtered. The air dried compound was recrystallized twice from heptane to give the analytical sample.

Preparation of compound III. Two grams of compound Ia was allowed to react with 5 ml. of ammonium hydroxide overnight in a stoppered flask. The mixture was evaporated to dryness to give the pyridone of 2-hydroxymethyl-5-hydroxy-6-(γ-hydroxybutyryl)-4-pyrone.

The brown solid was converted, without purification, to

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(1) The authors express their gratitude to the Robert A. Welch Foundation for the support of this investigation.

(2) L. L. Woods and P. A. Dix, *J. Org. Chem.*, **24**, 1126 (1959).

(3) L. L. Woods, *J. Org. Chem.*, **24**, 1804 (1959).

(4) L. L. Woods and H. L. Williams, *J. Org. Chem.*, **25**, 1052 (1960).

(5) All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J., and all melting points were determined on a Fisher-Johns melting point assembly.