[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Elimination Reactions. X. Pyrolysis of Xanthate and Sulfite Esters of *erythro*- and *threo*-3-*p*-Tolylthio- and 3-*p*-Tolylsulfonyl-2-butanols

BY F. G. BORDWELL AND P. S. LANDIS[1]

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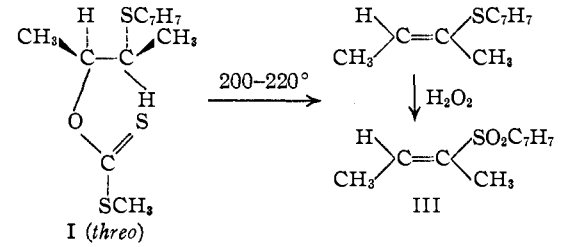
Pyrolysis of the S-methyl xanthates of *dl-threo*- and *dl-erythro*-3-*p*-tolylthio-2-butanols gave *cis*- and *trans*-2-*p*-tolylthio-2-butenes, respectively (stereoselective *cis* eliminations). In contrast, pyrolysis of the S-methyl xanthates of *dl-threo*- and *dl-erythro*-3-*p*-tolylsulfonyl-2-butanols gave the same product, *cis*-2-tolylsulfonyl-2-butene (the more stable isomer). The latter results are interpreted in terms of a stepwise mechanism involving a dipolar intermediate, which can undergo rotation prior to forming olefin. The methyl sulfites of *dl-threo*- and *dl-erythro*-3-*p*-tolylsulfonyl-2-butanols both gave *cis*-2-*p*-tolylsulfonyl-2-butene on pyrolysis, probably by a similar mechanism. The methyl sulfites of *dl-threo*- and *dl-erythro*-3-*p*-tolylthio-2-butanols also gave essentially the same pyrolysis product, but this is believed to be due to an acid-catalyzed rearrangement of one of the olefins.

It is generally agreed that the Chugaev reaction and related ester pyrolyses usually proceed by way of a concerted path involving simultaneous removal of the ester grouping and a *cis*-β-hydrogen.[2] However, only one example demonstrating the stereoselective *cis* nature of ester pyrolyses in acyclic systems appears to have been recorded thus far.[2,3] In preceding papers in this series we have shown that *cis*-2-*p*-tolylthiocyclohexyl S-methyl xanthate and methyl sulfite undergo pyrolysis to give predominantly 3-*p*-tolylthio-1-cyclohexene, the expected *cis* elimination product.[4] In contrast, *cis*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate and methyl sulfite undergo first-order decompositions on heating to give 1-*p*-tolylsulfonyl-1-cyclohexene, the *trans* elimination product. It was suggested that the latter reactions occurred by a stepwise process involving a dipolar intermediate in preference to a concerted mechanism. It was of interest to extend this study to an acyclic system, since it would be anticipated on the basis of these results that in comparable open-chain compounds the analog containing the C_7H_7S group would pyrolyze by the usual concerted mechanism (stereoselective *cis* elimination), whereas the analog containing the $C_7H_7SO_2$ group would decompose by a stepwise mechanism in which stereoselectivity would not be mandatory.

The synthesis of the *erythro* and *threo* forms of $CH_3CHOHCH(CH_3)SC_7H_7$ and $CH_3CHOHCH(CH_3)SO_2C_7H_7$, and establishment of their structures has been described previously.[5] The same method was used except that in the first step of the synthesis it was found that the *cis*- and *trans*-2-butenes could be converted in high yield to the corresponding bromohydrins by reaction with N-bromosuccinimide in an aqueous suspension at 0°.[6] The S-methyl xanthates and methyl sulfites were prepared in the usual manner.

The S-methyl xanthates of *dl-threo*- and *dl-erythro*-3-*p*-tolylthio-2-butanol (I and II, respectively) each decomposed smoothly when heated under vacuum at 200–220°. The olefins were oxidized to the corresponding sulfones which were identified by infrared analysis.[5] The product from pyrolysis of the *threo* isomer I after oxidation was *cis*-2-*p*-tolylsulfonyl-2-butene (III), whereas *trans*-2-*p*-tolylsulfonyl-2-butene (IV) was obtained from the *erythro* isomer II under similar conditions. The analyses indicate that no more than 5% of IV can be present in the product from I. Similarly, II appears to have given only IV, but it would be difficult to detect the presence of even as much as 10% of III in this product. The eliminations are therefore strongly stereoselective although they may not be stereospecific.[7]



I (*threo*) III

The stereoselective *cis* pyrolytic eliminations for I and II are to be expected on the basis of concerted mechanism involving a quasi six-membered ring.[2] They resemble Cram's[3] results on the pyrolysis of the S-methyl xanthates of 3-phenyl-2-butanol except that the pyrolysis of the *threo* isomer was less stereoselective in his system, and about 20% of 1-olefin was formed in each pyrolysis. The absence of bands in the 10.1 and 11.2 μ region of the infrared spectra of III and IV indicate that little or none of the 1-olefin is formed in the pyrolysis of I or II. It would appear that the acidity of the α-hydrogen and conjugative effects promoting formation of the 2-olefin are stronger in these pyrolyses than for the S-methyl xanthates of 3-phenyl-2-butanol.

In contrast to the highly stereoselective pyrolytic eliminations of I and II, the corresponding sulfones, the S-methyl xanthates of *dl-threo*- and *dl-erythro*-3-*p*-tolylsulfonyl-2-butanol (V and VI, respectively), both pyrolyzed to give predominantly the *cis*-olefin III. For the *threo* isomer V this is a *cis* elimination which may be concerted, but for which we prefer to write the stepwise mechanism shown.[4] For the *erythro* isomer VI the over-all result is *trans* elimination.

(1) Socony-Mobil Predoctoral Fellow, 1955–1958.

(2) See the discussion by D. J. Cram in Chapter 6 of "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956.

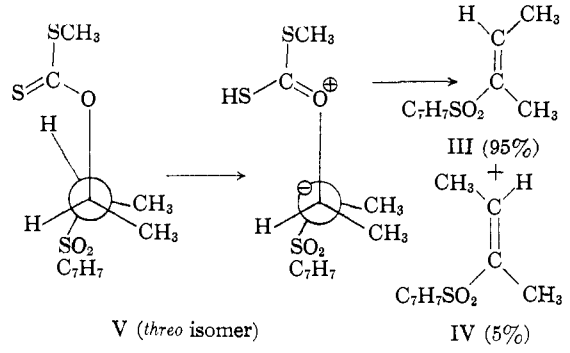
(3) D. J. Cram, THIS JOURNAL, **71**, 3883 (1949); D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5828 (1952).

(4) F. G. Bordwell and P. S. Landis, *ibid.*, **80**, 2450, 6379 (1958).

(5) F. G. Bordwell and P. S. Landis, *ibid.*, **79**, 1593 (1957).

(6) C. O. Guss and R. Rosenthal, *ibid.*, **77**, 2549 (1955).

(7) It seems advisable to reserve the term stereospecific for reactions which can be demonstrated to be nearly completely stereoselective (*i.e.*, 99 ± 1%).

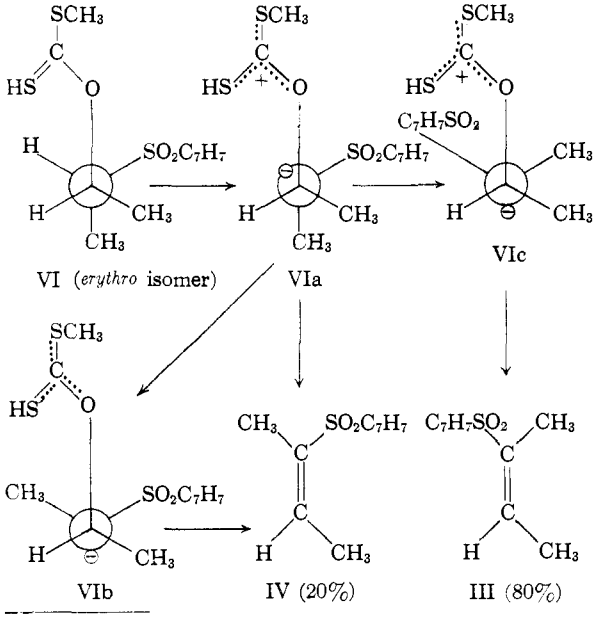


V (*threo* isomer) IV (5%) III (95%)

The formation of III from VI occurs by a primary reaction and not by rearrangement of the *cis* elimination product IV, since IV fails to rearrange to III when treated for as long as 108 hr. with concd. hydrochloric acid in aqueous dioxane and also remains essentially unchanged when mixed with the *threo*-xanthate V and the mixture pyrolyzed. It was also established that rearrangement did not occur during xanthate formation, since it was shown that the *threo* and *erythro* isomers could be converted to potassium salts and recovered unchanged on hydrolysis.

Heating IV with one-twentieth equivalent of potassium *t*-butoxide in *t*-butyl alcohol at 80° for 30 min. converted it to a mixture of about 80% III (*cis*) and 20% IV (*trans*). After an additional 30 min. IV was converted completely to the *cis* isomer. A separate sample of III remained unchanged on treatment with potassium *t*-butoxide solution. The greater thermodynamic stability of the *cis* isomer III is expected, since the sulfonyl group is known to be large.[8]

The formation of III from VI (over-all *trans* elimination) is not unexpected in view of the fact that *cis*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate undergoes *trans* elimination on pyrolysis *in preference* to *cis* elimination.[2] The present results



VI (*erythro* isomer) VIa VIc VIb IV (20%) III (80%)

(8) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5184 (1951); *ibid.*, **79**, 916 (1957); E. L. Eliel and R. S. Ro, *ibid.*, **79**, 5995 (1957).

support the previous suggestion that when the β-hydrogen is activated by a strong electron-withdrawing group ($C_7H_7SO_2$) a dipolar ion intermediate may be formed. A comparable dipolar intermediate (VIa) from VI could undergo direct decomposition to give IV (which might be preceded by inversion and 60° rotation to give VIb) or could rotate 120° to VIc prior to elimination which would give III. The observed products therefore can be explained in terms of a carbanion intermediate which rotates prior to elimination. The intermediates from V and VI are apparently not identical since the proportions of III and IV from the two reactions are somewhat different. This may mean that carbanions are formed from both V and VI[9] (with several paths each to III and IV), or it may mean that V decomposes by a concerted mechanism and VI by a stepwise mechanism. The similarity in the rates of decomposition of I, II, V and VI and of the corresponding *cis* and *trans* isomers in the cyclohexyl series[4] argues for the first possibility.

Although attempts to crystallize I, II, V and VI were unsuccessful, rate measurements on the crude xanthates gave reasonably good first-order plots. These data support the postulated mechanism since they show that the decompositions must be intramolecular. The first-order rate constants determined graphically from runs made at 165 ± 2° are: 5.3×10^{-5} sec.$^{-1}$ for I, 4.2×10^{-5} sec.$^{-1}$ for II, 4.2×10^{-5} sec.$^{-1}$ for V and 8.5×10^{-5} for VI. The rate constants for V and VI are slightly greater than for the cyclohexyl analogs.[4] It is interesting to note that the sulfone xanthate VI, which is believed to decompose by a stepwise process, pyrolyzes twice as rapidly as does the corresponding sulfide xanthate II where the reaction is believed to be concerted. Evidently the ease of formation of the dipolar intermediate from VI wins out over the concerted process, despite the energetic economy of the latter and the fact that oxidation of the sulfur greatly increases the steric effect of the sulfur grouping. In pyrolytic *cis* eliminations the advantages of the concerted mechanism are always offset to some extent by the increased repulsions arising by the requirement of coplanarity for the maximum assistance of bond-making to bond-breaking. These repulsions are probably often large enough to necessitate a compromise between these two factors. The stepwise mechanism derives no benefit from coplanarity of the groups, and a staggered conformation may be used for the transition state. This may be an important factor in making the rate of decomposition of VI faster than that of II. Since the stepwise mechanism provides an advantage for the decomposition of VI relative to II, it seems probable that V will also utilize this mechanism (as shown) in preference to the concerted one. The 8-fold and 5-fold rate advantages of V and I, respectively, over VI, can be attributed to the increased importance of steric hindrance in the decomposition of VI.

(9) Such carbanions would probably maintain a tetrahedral configuration since there is evidence that there is little or no angular requirement for conjugation involving a sulfonyl group (pd overlap) [see S. Oae and C. C. Price, *ibid.*, **80**, 4938 (1958), and references cited therein].

In the preceding paper in this series[4] it was shown that methyl sulfites often parallel S-methyl xanthates as to products formed on pyrolysis, and it was proposed that the two reactions proceeded by similar mechanisms. However, acidic by-products are formed in methyl sulfite pyrolyses and sensitive olefins may be rearranged during the pyrolysis, whereas S-methyl xanthates rarely, if ever, give rise to rearrangement products. Pyrolysis of the methyl sulfite of *dl-threo*-3-*p*-tolylthio-2-butanol and oxidation gave III (stereoselective *cis* elimination). However, unlike the xanthate, the methyl sulfite of *dl-erythro*-3-*p*-tolylthio-2-butanol also gave predominantly III (75%) (*trans* elimination product) under these conditions. From our previous experience[4] it seems highly probable that rearrangement has occurred in this instance, the unoxidized form corresponding to III being the more stable product (according to this assumption).

The results of the pyrolysis of the methyl sulfites of *dl-threo*- and *dl-erythro*-3-*p*-tolylsulfonyl-2-butanols paralleled those from the corresponding S-methyl xanthates. Since the sulfone IV has been shown to be very resistant to acid-catalyzed rearrangement (see above) these sulfites are probably decomposing by the stepwise mechanism utilized by the sulfone S-methyl xanthates. This is not surprising since *cis*-2-*p*-tolylsulfonylcyclohexyl methyl sulfite was found to undergo stepwise *trans* elimination even more rapidly than did the corresponding xanthate.[4,10]

Experimental

Preparation and Pyrolysis of *dl-threo*-3-*p*-Tolylthio-2-butyl S-Methyl Xanthate (I).—*dl-threo*-3-*p*-Tolylthio-2-butanol (9.8 g., 0.05 mole) was added to a stirred suspension of 1.95 g. (0.05 g. atom) of metallic potassium in 100 ml. of dry benzene. The mixture was stirred for 2 hr. at room temperature and then for 2 hr. at 50–55°. All the potassium appeared to have reacted at the end of this period. Carbon disulfide (15 ml.) was added, the solution was refluxed for 8 hr. and 20 ml. of methyl iodide was added. The solution was stirred overnight, filtered and washed thoroughly with water. After drying over anhydrous sodium sulfate, the solution was filtered and the solvent removed, first on a steam-bath, then under vacuum. The residual oil weighed 13.5 g. (94%). The crude xanthate (7.0 g., 0.022 mole), was placed in a 25-ml. vacuum distillation flask fitted with a 3-inch Vigreux head. The flask was heated at 200° for 30 min., vacuum was applied slowly and the product was distilled at 0.1 mm. keeping the pot temperature at 200–220°. In this way 3 g. (77%) of an oil, b.p. 135–147° at 0.1 mm., was collected. One gram of the sulfide was oxidized with 10 ml. of 30% hydrogen peroxide in 20 ml. of acetic acid at 80°. The resulting sulfone melted at 35–45° Its infrared spectrum indicated that the product was *cis*-2-*p*-tolylsulfonyl-2-butene containing less than 5% of the *trans* isomer, since the strong 14.7 μ peak characteristic of the *trans* isomer[5] was absent.

Preparation and Pyrolysis of *dl-erythro*-3-*p*-Tolylthio-2-butyl S-Methyl Xanthate (II).—Using quantities and procedure similar to that described for the *threo* isomer, 13.8 g. (96%) of crude S-methyl xanthate was obtained. Pyrolysis of 9 g. (0.0314 mole) of this xanthate gave 3.2 g. (58%) of olefin, b.p. 120–130° (0.5 mm.). Oxidation of a small sample gave a colorless solid, m.p. 45–47°. Infrared analysis[6] indicated that the compound was primarily *trans*-2-*p*-tolylsulfonyl-2-butene, although as much as 10% of *cis* isomer could escape detection.

Preparation and Pyrolysis of *dl-threo*-3-*p*-Tolylsulfonyl-2-butyl S-Methyl Xanthate.—Using a procedure similar to that described above, 12.4 g. (95%) of a viscous xanthate was obtained from 8.5 g. (0.037 mole) of alcohol, 1.8 g. of potassium, 50 ml. of dry benzene and excess carbon disulfide and methyl iodide. Decomposition of the xanthate gave 3.2 g. (58%) of material, b.p. 145–155° (0.5 mm.). Infrared analysis indicated that the product was primarily *cis*-2-*p*-tolylsulfonyl-2-butene containing no more than 5% of the *trans* isomer.

Preparation and Pyrolysis of *dl-erythro*-3-*p*-Tolylsulfonyl-2-butyl S-Methyl Xanthate.—Decomposition of 6.0 g. of crude xanthate, prepared as described above, gave 3.2 g. of an oil b.p. 145–175° (2 mm.). This sample was chromatographed over activated silica gel using hexane and benzene as successive eluents. Fractions 9 and 10, representing 82% of the sample and an over-all 48% yield, were identified by infrared analysis as mixtures of about 80% *cis*-2-*p*-tolylsulfonyl-2-butene and 20% of the *trans* isomer.

Pyrolysis of *threo*-3-*p*-Tolylsulfonyl-2-butyl S-Methyl Xanthate in the Presence of Added *trans*-2-*p*-Tolylsulfonyl-2-butene.—Pyrolysis of 6.5 g. of the xanthate in the presence of 2.0 g. of *trans*-2-*p*-tolylsulfonyl-2-butene gave 5.3 g. of a mixture containing about 40% of *trans*-olefin. Theoretically 50% of *trans*-olefin should have been present barring rearrangement or formation of *trans*-olefin during the pyrolysis.

Failure of Rearrangement of *threo*- or *erythro*-3-*p*-Tolylsulfonyl-2-butanol on Treatment with Potassium.—The potassium salts of the alcohols (2.7 g.) were prepared in benzene medium, as described above. The mixture consisting of brown granular potassium salt suspended in benzene was transferred to a separatory funnel and shaken with 30 ml. of 10% hydrochloric acid. The benzene layer was washed with water, dried over anhydrous magnesium sulfate and the solvent removed on the steam-bath. The infrared spectrum of the residue (80% recovery) from the *erythro* isomer gave no evidence for the presence of the *threo* isomer, which has two strong doublets at 10.18, 10.38 and 10.85, 11.05 μ. Similarly, the strong band at 9.98 μ, which is characteristic of the *erythro*-alcohol, was absent in the spectrum of the recovered *threo*-alcohol.

Rearrangement of *trans*-2-*p*-Tolylsulfonyl-2-butene.—Five hundred milligrams of *trans*-2-*p*-tolylsulfonyl-2-butene was refluxed for 30 minutes with a solution of 20 ml. of *t*-butyl alcohol to which had been added 5 mg. of metallic potassium. The cooled solution was poured into 50 ml. of water and extracted with chloroform. The chloroform extract was washed thoroughly with water, dried over anhydrous sodium sulfate, filtered and the solvent removed on a steam-bath. The resulting solid, 385 mg., was established by infrared analysis to be a mixture of 80% *cis*- and 20% *trans*-2-*p*-tolylsulfonyl-2-butenes. Further treatment of this product (80% *cis*- and 20% *trans*-olefin) with 20 ml. of *t*-butyl alcohol containing 5 mg. of potassium followed by isolation as previously described gave 260 mg. of pure *cis*-olefin. Similar treatment of *cis*-2-*p*-tolylsulfonyl-2-butene with potassium *t*-butoxide solution gave only unchanged *cis*-olefin.

Kinetic Measurements.—The kinetic runs were made in a series of tared erlenmeyer flasks heated to 165 ± 2° in an oil-bath, as described previously.[4] The method is essentially that of O'Connor and Nace.[11]

Preparation and Pyrolysis of Methyl *erythro*- and *threo*-3-*p*-Tolylthio-2-butyl Sulfites.—The methyl sulfite was prepared by a procedure similar to that described in the preceding paper.[4] Pyrolysis of 6.1 g. (0.0223 mole) of crude *erythro*-methyl sulfite under vacuum at 200–220° gave 3.9 g. (97%) of distillate. A 3.8-g. sample was oxidized with hydrogen peroxide to give material melting at 35–43°. Infrared analysis indicated about 25% of *trans*-2-*p*-tolylsulfonyl-2-butene and 75% of *cis* isomer to be present. The strong 14.7 μ band of the *trans* isomer was absent in a comparable olefin sample obtained by pyrolysis of the *threo*-methyl sulfite.

Pyrolysis of Methyl *erythro*- and *threo*-3-*p*-Tolylsulfonyl-2-butyl Sulfites.—A 6.1-g. (0.02 mole) sample of crude *erythro*-sulfite was heated under nitrogen for 30 min. at 170° and then the product was vacuum distilled (with concurrent decomposition) using a pot temperature of 180–190°. In one

(10) As pointed out by a Referee, it is also possible to interpret the results of the sulfide methyl sulfite pyrolyses using ion pair mechanisms [see E. L. Eliel, J. W. McCoy and C. C. Price, *J. Org. Chem.*, **22**, 1533 (1957) and our previous paper[4]] to account for the lack of stereoselectivity.

(11) G. L. O'Connor and H. R. Nace, THIS JOURNAL, **74**, 5454 (1952).

hour 3.8 g. (91%) of material was obtained, b.p. 160–164° (0.4 mm.). Since the infrared spectrum showed a weak hydroxyl band, the product was chromatographed over silica gel using hexane as the solvent and benzene as the eluent. In this way 2.6 g. (62%) of olefinic product was obtained which consisted of about 15% of *trans*-2-*p*-tolylsulfonyl-2-butene and 85% of the *cis* isomer. The pyrolysis of the *threo*-methyl sulfite and product isolation were carried out as described for the *erythro* isomer. The product obtained contained about 10% of *trans*-2-*p*-tolylsulfonyl-2-butene and 90% of the *cis* isomer.

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The Rearrangement of Ethyl β-Phenylglycidate

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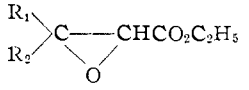
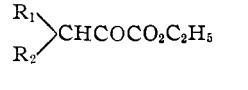
The acid-catalyzed (or thermal) rearrangement of ethyl β-phenylglycidate has been shown to yield ethyl phenylpyruvate and not ethyl α-formylphenylacetate, the isomerization product previously reported. Similarly, the acid-catalyzed rearrangement of ethyl β-methyl-β-phenylglycidate yielded ethyl α-keto-β-phenylbutyrate.

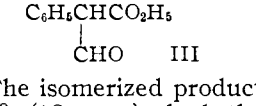
Examples of the acid-catalyzed isomerization of substituted glycidic esters I to substituted pyruvic esters II have been reported by a number of workers.[2–6] The example most often cited of a glycidic ester rearrangement which does not follow this pattern is the conversion of ethyl β-phenylglycidate (Ia) to ethyl α-formylphenylacetate (III) reported by Tiffeneau and Levy.[7] This conversion, effected by passing the glycidic ester vapor over either an alumina-containing clay or infusorial earth at temperatures of 250-300°, was judged to occur with migration of the phenyl group. However, the similarly constituted glycidic ester, ethyl β-methyl-β-phenyl-glycidate (Ib), was converted to the pyruvic ester IIb by the same reaction conditions.[7] Also, the isomerization of β-phenylglycidic acid in the presence of hydrochloric acid yielded phenylpyruvic acid.[8] The seemingly anomalous behavior of ethyl β-phenylglycidate (Ia) prompted us to reconsider the structure III assigned its rearrangement product.



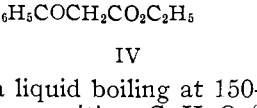
Ia, $R_1 = C_6H_5$, $R_2 = H$
b, $R_1 = C_6H_5$, $R_2 = CH_3$



IIa, $R_1 = C_6H_5$, $R_2 = H$
b, $R_1 = C_6H_5$, $R_2 = CH_3$



III



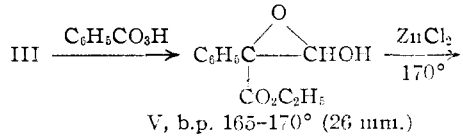
IV

The isomerized product, a liquid boiling at 150-151° (18 mm.), had the composition $C_{11}H_{12}O_3$.[9] Among other properties, the rearranged material reduced Fehling solution, gave a green color with ferric chloride and formed a semicarbazone melting at 162–165°. Also, the sequence of reactions, shown in the accompanying equations, was reported[7] as a structure proof for the rearranged product. It is instructive to compare the properties of the isomerized product with the properties (Table I) of the three possible rearrangement products IIa, III and IV of the glycidic ester Ia. Comparison of these data leaves no doubt that the isomerization product described by Tiffeneau and Levy was the α-keto ester IIa and not the α-formyl ester III as they had supposed.

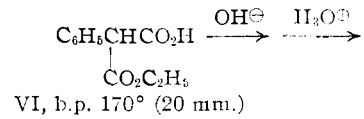
TABLE I

PROPERTIES OF POSSIBLE ISOMERIZATION PRODUCTS

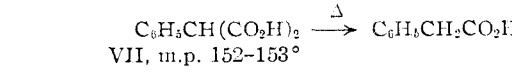
	IIa	III	IV
B.p., °C. (mm.)	160 (20)	151 (30)	147 (6)
Color with $FeCl_3$	Green	Violet	Red
M.p. semicarbazone, °C.	166–167	130.5–131	126–127
Reduces Fehling solution	Yes	Yes	Yes



V, b.p. 165–170° (26 mm.)



VI, b.p. 170° (20 mm.)



VII, m.p. 152–153°

However, structure III for the isomerized product could not be entirely discarded until the validity of the alleged structure proof was examined. The first step in the reported sequence is not unreasonable, although the open-chain tautomer of the proposed structure V is more probable.[10] Irrespective of what might be expected in the subsequent zinc chloride-catalyzed rearrangement, the structure VI is most unlikely since the monoethyl ester of phenylmalonic acid has been shown to decarboxyl-

(1) National Science Foundation Predoctoral Fellow, 1956–1958.

(2) R. Pointet, *Compt. rend.*, **148**, 417 (1909).

(3) E. P. Kohler, N. K. Richtmyer and W. F. Hester, THIS JOURNAL, **53**, 205 (1931).

(4) S. Ecary, *Ann. chim.* (*Paris*), [12] **3**, 447 (1948). The rearrangement of ethyl β,β-diphenylglycidate during distillation was shown to be an acid-catalyzed process rather than a thermal rearrangement as supposed by previous workers (ref. 2 and 3).

(5) E. Vogel and H. Schinz, *Helv. Chim. Acta*, **33**, 116 (1950).

(6) F. F. Blicke and J. A. Faust, THIS JOURNAL, **76**, 3156 (1954).

(7) M. Tiffeneau and J. Levy, *Anales soc. quim. Argentina*, **16**, 144 (1928).

(8) E. Erlenmeyer, *Ber.*, **33**, 3001 (1900). Since this isomerization may have involved a chlorohydrin intermediate, the results obtained with ester under different reaction conditions need not be comparable.

(9) Apparently, the presence of the starting glycidic ester Ia in the product was not excluded. The liquid was said to be a mixture of products of similar boiling point which were judged to be the tautomeric forms of structure III.

(10) For a discussion of the reaction of enolizable β-dicarbonyl compounds with peracids accompanied by leading references see H. O. House and W. F. Gannon, *J. Org. Chem.*, **23**, 879 (1958).