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.

EVANSTON, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Rearrangement of Ethyl β-Phenylglycidate

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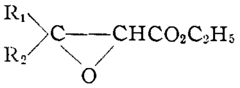
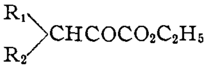
The acid-catalyzed (or thermal) rearrangement of ethyl β-phenylglycidate has been shown to yield ethyl phenylpyruvate and not ethyl α-formylphenylacetate, the isomerization product previously reported. Similarly, the acid-catalyzed rearrangement of ethyl β-methyl-β-phenylglycidate yielded ethyl α-keto-β-phenylbutyrate.

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.

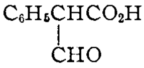


Ia, $R_1 = C_6H_5, R_2 = H$
b, $R_1 = C_6H_5, R_2 = CH_3$



$\begin{matrix}R_1\\R_2\end{matrix}\!>\!CHCOCO_2C_2H_5$

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



$C_6H_5\underset{\text{CHO}}{\underset{|}{C}}HCO_2H_5$

III

$C_6H_5COCH_2CO_2C_2H_5$

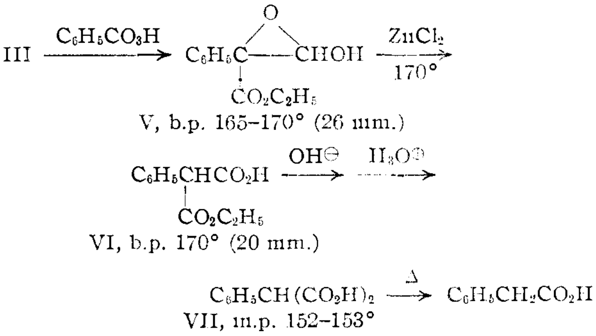
IV

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-

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(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).

ate readily when heated.[11] The characterization of the subsequent product, claimed to be phenylmalonic acid, rests on its melting point and its thermal decomposition to yield phenylacetic acid.[12] It should be noted that these properties also characterize phenylpyruvic acid, m.p. 150–154° dec.,[13] which when heated decomposes to yield phenylacetic acid and carbon dioxide as well as carbon monoxide.[14] Since the intermediate liquids in this degradation were not characterized and no yields were reported, it is not possible to decide what they might have been. However, it seems likely that the α-keto ester IIa either survived the first two steps in the sequence or, more probably, was formed in the second step (distillation over zinc chloride) by isomerization of some unchanged glycidic ester Ia present in the crude product. In any event the reported reaction sequence does not provide compelling evidence for structure III as the rearrangement product of the glycidic ester Ia.

We have investigated the rearrangement of the glycidic ester Ia in the presence of a benzene solution of boron trifluoride gas. The isomerization product, isolated as its 2,4-dinitrophenylhydrazone in 80% yield, proved to be the α-keto ester IIa. Neither of the isomeric esters III or IV could be detected in the crude reaction product. Similarly, the glycidic ester Ib afforded the α-keto ester IIb, isolated as its 2,4-dinitrophenylhydrazone derivative in 69% yield, as previously reported.[7] Thus, the rearrangement of ethyl β-phenylglycidate (Ia) is not anomalous, but rather is comparable to the rearrangements of other glycidic esters of type I.

Evidence discussed in the Experimental section of this paper and in an accompanying paper has led us to assign the *trans* stereochemistry to the glycidic ester Ia studied here. The glycidic ester Ib employed was found to be a mixture of both the *cis* and *trans* diastereoisomers.

Experimental[15]

The Isomeric Esters IIa, III and IV and Their Derivatives.—A redistilled sample [b.p. 147° (6 mm.), $n^{27}\text{D}$ 1.5273] of commercial ethyl benzoylacetate gave a red color with ethanolic ferric chloride, reduced Fehling solution and did not reduce Tollens reagent. A 1.0-g. (0.0052 mole) sample of the β-keto ester was treated with a solution 1.2 g. (0.006 mole) of 2,4-dinitrophenylhydrazine and 0.5 ml. of concentrated hydrochloric acid in 60 ml. of boiling ethanol and allowed to cool. The **2,4-dinitrophenylhydrazone of ethyl benzoylacetate** separated as yellow-orange needles, m.p. 165–166°, yield 1.73 g. (92%). The infrared spectrum[16] of the product exhibits absorption at 3300 cm.$^{-1}$ (N–H) and at 1730 cm.$^{-1}$ (ester C=O). The ultraviolet spectrum has maxima at 222 mμ (ϵ 14,700) and 372 mμ (ϵ 17,800).

Anal. Calcd. for $C_{17}H_{16}N_4O_6$: C, 54.84; H, 4.33; N, 15.05. Found: C, 54.51; H, 4.38; N, 15.07.

The product, m.p. 246–247°, previously reported[17] to be the 2,4-dinitrophenylhydrazone of ethyl benzoylacetate, was apparently acetophenone 2,4-dinitrophenylhydrazone formed by hydrolysis and decarboxylation of the starting β-keto ester.

Reaction of a 1.92-g. (0.01 mole) sample of the β-keto ester with a solution of 1.11 g. (6.01 mole) of semicarbazide hydrochloride and 1.5 g. of sodium acetate in 25 ml. of aqueous ethanol afforded the **semicarbazone of ethyl benzoylacetate** as fine, colorless needles, m.p. 126–127° dec. (lit.[18] 125° dec.), yield 1.55 g. (68%). The infrared spectrum[16] of the crude product had bands in the range 3250–3600 cm.$^{-1}$ (N—H), a shoulder at 1730 cm.$^{-1}$ (ester C=O) and a band at 1700 cm.$^{-1}$ (amide C=O). Recrystallization from water converted the semicarbazone to **5-phenyl-3-pyrazolone** which separated as colorless prisms, m.p. 242–243° dec. (lit.[19] 236° dec.), yield 1.05 g. (65%). The infrared spectrum[20] of the pyrazolone exhibits broad absorption bands at 1630 and 1600 cm.$^{-1}$ (C=O of conj. amide or C=N) and the ultraviolet spectrum has a maximum at 274 mμ (ϵ 17,000). The spectra suggest that the solid exists as the hydroxypyrazole rather than the pyrazolone. The product did not depress the melting point of an authentic sample prepared as previously described.[19]

Ethyl α-formylphenylacetate, b.p. 151° (30 mm.) [lit.[21] 144–145° (16 mm.)], gave a violet color with ferric chloride, reduced both Fehling and Tollens reagents, gave a copper complex as green needles from ether, m.p. 171–173° (lit.[22] 171–173°), and gave 1,4-diphenyl-5-pyrazolone as cream-colored needles, m.p. 194–196° (lit.[21] 195–196°). A sample of the aldehydo ester, regenerated from 200 mg. (0.00045 mole) of the copper complex, was converted to its semicarbazone as described previously. The derivative separated from aqueous ethanol as colorless plates, m.p. 130.5–131° (lit.[23] 130–131°), yield 120 mg. (50%). The infrared spectrum[20] exhibits bands in the region 3200–3500 cm.$^{-1}$ (N–H) and at 1730 cm.$^{-1}$ (ester C=O) and 1680 cm.$^{-1}$ (amide C=O).

Ethyl phenylpyruvate, b.p. 160° (20 mm.) [lit.[24] 154.5° (15 mm.)], gave a green color with ferric chloride solution and reduced Fehling solution but not Tollens reagent. The 2,4-dinitrophenylhydrazone of the α-keto ester, prepared in the usual manner, crystallized from ethanol as yellow-orange plates, m.p. 132–133° (lit.[25] 132.5–133°), yield 92%. The infrared spectrum[16] of the derivative has absorption at 1695 cm.$^{-1}$ (ester C=O); the ultraviolet spectrum has a maximum at 360 mμ (ϵ 26,000). The α-keto ester formed a semicarbazone which crystallized from aqueous ethanol as colorless prisms, m.p. 166–167° (lit.[26] 167°). The infrared spectrum[20] of the derivative has bands at 1730 cm.$^{-1}$ (ester C=O) and 1655 cm.$^{-1}$ (broad, amide C=O); the ultraviolet spectrum has a maximum at 287 mμ (ϵ 5380).

Ethyl β-Phenylglycidate (Ia).—Condensation of 26.4 g. (0.25 mole) of benzaldehyde with 43.8 g. (0.25 mole) of ethyl chloroacetate in the presence of potassium *t*-butoxide[27] prepared from 10.2 g. (0.26 gram-atom) of potassium and 220 ml. of *t*-butyl alcohol afforded 41.4 g. (86%) of the crude glycidic ester, b.p. 97–105° (1–2 mm.), $n^{25.7}\text{D}$ 1.5131–1.5160. Fractional distillation of the crude product through an 18 in. spinning-band column afforded a series of fractions, b.p. 142–145° (8 mm.), $n^{29}\text{D}$ 1.5133–1.5152, which gave no color with ferric chloride solution and no precipitate with 2,4-dinitrophenylhydrazine reagent. However, each fraction gave a slight positive Beilstein test for halogen. To effect further purification, a solution of 9.6 g.

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(11) E. J. Corey, THIS JOURNAL, **74**, 5897 (1952).

(12) Although this decomposition was said (ref. 7) to yield both the aforementioned acid and carbon dioxide, there was no indication that the gas was characterized.

(13) R. M. Herbst and D. Shemin, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 519.

(14) C. D. Hurd and H. R. Raterink, THIS JOURNAL, **56**, 1348 (1934).

(15) All melting points are corrected and all boiling points are uncorrected. The ultraviolet spectra were determined in 95% ethanol with a Cary recording spectrophotometer, model 11 MS. The infrared spectra were determined either with a Perkin-Elmer, model 21, or with a Baird, model B, infrared recording spectrophotometer fitted with a sodium chloride prism. The microanalyses were performed by Dr. S. M. Nagy and his associates.

(16) Determined in chloroform solution.

(17) G. D. Johnson, THIS JOURNAL, **75**, 2720 (1953).

(18) A. Michael, *ibid.*, **41**, 424 (1919).

(19) T. Curtius, *J. prakt. Chem.*, [2] **50**, 515 (1894).

(20) Determined as a suspension in a potassium bromide pellet.

(21) W. Wislicenus, *Ber.*, **20**, 2930 (1887).

(22) W. Wislicenus, *Ann.*, **389**, 265 (1912).

(23) K. Börner, Dissertation (Wurtzberg), 1899; *Chem. Zentr.*, **71, I,** 123 (1900).

(24) H. Gault and R. Weick, *Bull. soc. chim. France*, [4] **31**, 867 (1922).

(25) C. D. Gutsche and M. Hillman, THIS JOURNAL, **76**, 2236 (1954).

(26) J. Bougault, *Compt. rend.*, **162**, 760 (1916).

(27) W. S. Johnson, J. S. Belew, L. J. Chinn and R. H. Hunt, THIS JOURNAL, **75**, 4995 (1953).

(0.05 mole) of the ester Ia in 25 ml. of ethanol containing 0.05 mole of sodium ethoxide was treated with 0.9 ml. (0.05 mole) of water. The precipitate of sodium β-phenylglycidate, which separated immediately, was collected and recrystallized from aqueous ethanol. The sodium salt separated as colorless plates, m.p. 265° dec.,[28] yield 5 g. (54%). The infrared spectrum[20] of the salt has a single intense band at 1595 cm.$^{-1}$ (carboxylate anion) in the 6 μ region. The cautious acidification of a cold, aqueous solution of the salt with cold, aqueous sulfuric acid afforded β-phenylglycidic acid as a white crystalline solid, m.p. 85° dec. (lit.[29] 83–84° dec.), which decomposed rapidly on standing. Treatment of a solution of 3 g. (0.016 mole) of the sodium salt in 20 ml. of water with 20 ml. of a 10% aqueous solution of silver nitrate precipitated silver β-phenylglycidate which was collected on a filter, washed with ethanol and ether and dried. The crude salt, m.p. 165–166° dec., yield 3.7 g. (86%), was mixed with 25 g. (0.136 mole) of ethyl iodide and the mixture was heated under reflux for 30 min. The resultant mixture was diluted with ether and filtered. After the filtrate had been dried over magnesium sulfate and concentrated, distillation of the residue afforded 1.7 g. (65%) of pure ethyl β-phenylglycidate (Ia), b.p. 96° (0.5 mm.), n^{28}D 1.5131 [lit.[27] b.p. 168–172° (28 mm.), n^{25}D 1.5126].

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.71; H, 6.30. Found: C, 68.67; H, 6.39.

The purified product gave a negative Beilstein test for halogen. The infrared spectrum[30] exhibits no absorption in the 3 μ region attributable to a hydroxyl function and has partially resolved bands at 1751 and 1737 cm.$^{-1}$ attributable to the carbonyl group of a glycidic ester.[31] This spectrum is essentially identical with the spectrum of the crude ester prior to purification *via* the silver salt. The ultraviolet spectrum of the product exhibits only end absorption and a series of low intensity bands in the region 260–270 mμ (nonconjugated phenyl group). The nuclear magnetic resonance spectrum[32,33] of the glycidic ester has the following peaks (expressed as cycles per second relative to the proton resonance of water, a positive shift denoting a shift in the direction of increasing resonance frequency at constant magnetic field strength): a triplet with its center at −159 sec.$^{-1}$ (CH_3 adjacent to CH_2); a singlet at −65 sec.$^{-1}$ (>CH–O– grouping adjacent to an aromatic ring or a carbonyl group); a series of bands in the region −35 to −40 sec.$^{-1}$ attributable to a singlet (>CH–O– grouping adjacent to an aromatic ring or a carbonyl group) and a quadruplet (CH_2 adjacent to CH_3 and an oxygen atom); and a broad band at +86 sec.$^{-1}$ (aromatic C–H). The lack of duplicity of bands (*cf.* the spectrum of ethyl β-methyl-β-phenylglycidate[31]) suggests that this glycidic ester sample is predominantly one diastereoisomer. The fact that the bands (−40 and −65 sec.$^{-1}$) attributable to hydrogen atoms bonded to the oxirane ring of the glycidic ester Ia appear as singlets suggested that the diastereoisomer obtained has the *trans* configuration. In this configuration the hydrogen atoms are held far enough apart that the expected splitting of each band might not be resolved. The relative intensities of the two infrared bands attributable to the carbonyl function of the ester Ia are also in accord with this configurational assignment.[31] Finally, the fact that the *trans* isomer of the structurally related benzalacetophenone oxide is the more stable[34] is consistent with the assignment of the *trans* configuration to the glycidic ester Ia isolated here.

Ethyl β-Methyl-β-phenylglycidate (Ib).—Condensation of 42 g. (0.35 mole) of acetophenone with 43 g. (0.35 mole) of ethyl chloroacetate in the presence of potassium *t*-butoxide[27] prepared from 13.6 g. (0.35 gram-atom) of potassium and 325 ml. of *t*-butyl alcohol yielded 58.5 g. (82%) of the glycidic ester Ib, b.p. 138° (6 mm.), n^{27}D 1.5027 [lit.[27] b.p. 92–99° (0.5–0.6 mm.), n^{25}D 1.5109]. Fractional distillation of the crude product afforded a series of fractions, b.p. 127–135° (7 mm.), n^{27}D 1.4989–1.5077, which were shown[31] to be mixture of diastereoisomers of structure Ib of varying composition. The isomer mixture obtained by ordinary distillation was used for the rearrangement studies reported here.

Rearrangement of Ethyl β-Phenylglycidate (Ia).—A solution of 0.5 g. (0.0026 mole) of the glycidic ester in 75 ml. of benzene was saturated with boron trifluoride gas and allowed to stand at room temperature for 30 min. The resulting solution was washed with a saturated, aqueous solution of sodium chloride, dried over magnesium sulfate and concentrated. The residue, which gave a green color with ethanolic ferric chloride and did not reduce Tollens reagent, was treated with a boiling, ethanolic solution of 0.6 g. (0.003 mole) of 2,4-dinitrophenylhydrazine as described previously. The cold solution deposited 0.50 g. (53%) of the 2,4-dinitrophenylhydrazone of ethyl phenylpyruvate, m.p. 131–132°. Chromatography of the residue from the mother liquor on alumina afforded an additional 0.25 g. (27%) of the same product. The product was identified with an authentic sample by a mixed melting-point determination and by comparison of the infrared spectra of the two samples.

Rearrangement of Ethyl β-Methyl-β-phenylglycidate (Ib).—A solution of 0.509 g. (0.0025 mole) of the glycidic ester in 50 ml. of benzene was saturated with boron trifluoride gas over a 30-min. period. The resulting solution was washed with saturated, aqueous sodium chloride, dried over magnesium sulfate and concentrated. Reaction of the residue with an ethanolic solution of 2,4-dinitrophenylhydrazine produced the 2,4-dinitrophenylhydrazone of ethyl α-keto-β-phenyl-butyrate which crystallized from ethanol as yellow-orange plates, m.p. 161–162°, yield 0.51 g. (53%). An additional 0.15 g. (16%) of the same product was obtained by chromatography of the residue from the mother liquors. The infrared spectrum[16] of the product has bands at 3350 cm.$^{-1}$ (N—H) and 1730 cm.$^{-1}$ (ester C=O). The ultraviolet spectrum has a maximum at 355 mμ (ϵ 22,000).

Anal. Calcd. for $C_{18}H_{18}N_4O_6$: C, 55.95; H, 4.70; N, 14.50. Found: C, 56.22; H, 4.92; N, 14.59.

In a second experiment the product was isolated as the semicarbazone (crude yield 0.55 g. or 85%, m.p. 143–153°) which crystallized from ethanol as colorless plates, m.p. 162–162.1° dec. (lit.[7] m.p. 162–163°), yield 0.25 g. (40%). The infrared spectrum[16] of the product has a series of bands in the region 3200–3500 cm.$^{-1}$ (N–H) as well as bands at 1720 cm.$^{-1}$ (ester C=O) and 1690 cm.$^{-1}$ (amide C=O).

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(28) The value of this decomposition point was dependent on the rate of heating.

(29) W. Dieckmann, *Ber.*, **43**, 1035 (1910).

(30) Determined in carbon tetrachloride solution.

(31) The spectra of glycidic esters are discussed elsewhere [H. O. House and J. W. Blaker, THIS JOURNAL, **80**, 6389 (1958)].

(32) Determined as a pure liquid.

(33) Determined with a Varian Associates high-resolution nuclear magnetic resonance spectrometer, Model V4300B. The radio signal used had a frequency of 40 mc.

(34) H. H. Wasserman and N. E. Aubrey, THIS JOURNAL, **77**, 590 (1955); see also H. O. House and R. S. Ro, *ibid.*, **80**, 2428 (1958).