thoquinonoid, it would be possible to prepare a symmetrical benzdifuroxan upon pyrolysis of 1,4-dinitro-2,5-diazidobenzene (V) or 4-nitro-5-azidobenzfuroxan (VI). Both of these compounds upon prolonged heating above 90° decomposed without giving any recrystallizable material. Heating below this temperature, V gave 4-nitro-5-azidobenzfuroxan (VI) while further heating resulted in total decomposition.

Benzfurazan, 5-Methylbenzfurazan, 5-Chlorobenzfurazan, 4,6-Dimethylbenzfurazan, 4-Nitrobenzfurazan, and 5-Methoxybenzfurazan.—These compounds were all prepared according to the method described by Zincke and Schwarz[9] by reduction of the parent furoxan with hydroxylamine followed by steam distillation of the alkaline solution, except for the 4-nitrobenzfurazan which was obtained by nitration of benzfurazan with mixed acid as described above. For example, in the preparation of 5-methoxybenzfurazan, 5 g. of methoxybenzfuroxan was dissolved in 75 cc. of alcohol and 7.5 g. of hydroxylamine hydrochloride in a minimum amount of water was added. An aqueous 25% sodium hydroxide solution was then added till gas evolution ceased. The alcohol was evaporated and the residue made alkaline and steam distilled. The 5-methoxybenzfurazan was obtained in 75% yield.

Anal. Calcd. for $C_7H_6N_2O_2$: C, 56.00; H, 4.00; N, 18.66. Found: C, 56.21; H, 4.22; N, 18.62.

DOVER, NEW JERSEY

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[9] T. Zincke and P. Schwarz, *Ann.*, **307**, 40 (1899).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

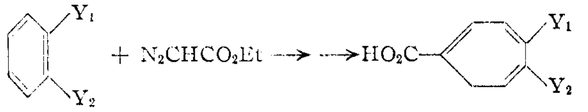
Reactions of Ethyl Diazoacetate with Aromatic Compounds Containing Hetero Atoms Attached to the Benzyl Carbon

BY C. DAVID GUTSCHE AND MANNY HILLMAN[1]

RECEIVED OCTOBER 17, 1953

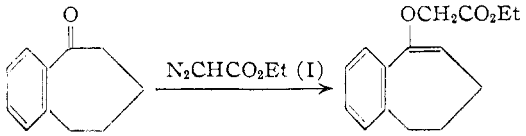
The reactions of ethyl diazoacetate with various aromatic compounds containing hetero atoms attached to the benzyl carbon have been studied, and in all cases the benzyl position was found to be involved in preference to the aromatic nucleus. Thus, benzosuberone yielded ethyl 6,7-dihydro-5H-cycloheptabenzene-9-oxyacetate (II), benzal chloride yielded ethyl α-chlorocinnamate (III), 2-phenyl-1,3-dioxolane yielded both stereoisomeric forms of ethyl 3-phenyl-2-*p*-dioxanecarboxylate (IV), and 2-phenyl-2-methyl-1,3-dioxolane yielded ethyl 3-methyl-3-phenyl-2-*p*-dioxanecarboxylate (XI). The last two reactions are unusual in that a ring enlargement of a 1,3-dioxolane ring to a *p*-dioxane ring is involved. In addition to the dioxane XI, 2-phenyl-2-methyl-1,3-dioxolane also yielded a very small amount of acetylcycloheptatrienecarboxylic acid (XIII), the product resulting from attack of the ethyl diazoacetate on the phenyl nucleus.

The present investigation had its inception in our search for a method of preparation of cycloheptatrienes carrying actual or potential aldehydo or acyl groups. It was hoped that the well-known ring enlargement of benzene by means of ethyl diazoacetate might be applicable and that conversions of the type shown below might be effected



In only one of the four cases studied, however, was any of the desired product isolated, and it was produced in such small amount as to be impractical from the synthetic standpoint. In all instances the main reaction involved the nuclear substituent Y rather than the benzene nucleus itself.

Ethyl Diazoacetate and Benzosuberone (Y_1,Y_2 = $-CO(CH_2)_4-$).—Benzosuberone reacted smoothly with ethyl diazoacetate (I) at 120–160° to give a product in 50.5% yield whose chemical behavior is best rationalized in terms of the enol ether II. This material reacted with semicarbazide and with 2,4-dinitrophenylhydrazine under acidic conditions to form the semicarbazone and 2,4-dinitrophenylhydrazone of benzosuberone. Treatment with *p*-nitrobenzaldehyde resulted in no reaction unless preceded by an acid hydrolysis, in which case the product was the *p*-nitrobenzylidene derivative of benzosuberone. This acid lability is characteristic of enol ethers. The formation of an amide possessing the correct analysis, the permanganate oxidation to γ-(2-carboxyphenyl)-butyric acid and the ultraviolet spectrum which showed a strong absorption at 250 mμ[2] further substantiated the postulated structure.



II

Reactions have been reported between ethyl diazoacetate and various carbonyl compounds including benzaldehyde,[3,4] halogenated aliphatic aldehydes,[5] *n*-heptaldehyde,[4] alloxans,[6] diphenylketene,[7] acetone and cyclohexanone.[8] Of these, acetone and cyclohexanone are reported to yield enol ethers, in correspondence with the results obtained with benzosuberone.

Ethyl Diazoacetate and Benzal Chloride (Y_1 = $CHCl_2$, Y_2 = H).—Benzal chloride and ethyl diazoacetate reacted at 160–175° to yield 24% of a product which proved to be ethyl α-chlorocinnamate (III). The structure proof is based on the conversion to the known amide, the formation of 3-phenylpyrazolone-5 upon treatment with hydrazine, saponification to α-chlorocinnamic acid, and

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[1] du Pont predoctoral fellow 1952–1953.

[2] D. S. Horn and W. S. Rapson, *J. Chem. Soc.*, 2421 (1949), report the ultraviolet spectrum of 6,7-dihydro-5H-cycloheptabenzene as ϵ_{max} 254 mμ (15,600).

[3] E. Buchner and T. Curtius, *Ber.*, **18**, 2371 (1885); T. Curtius, *J. prakt. Chem.*, **38**, 394 (1888).

[4] W. Dieckmann, *Ber.*, **43**, 1024 (1910).

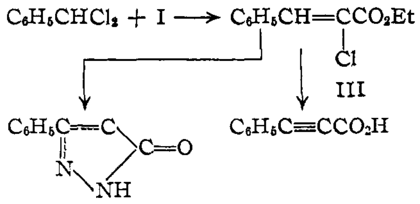
[5] F. Schlotterbeck, *ibid.*, **40**, 3000 (1907); **42**, 2565 (1909).

[6] H. Biltz and E. Kramer, *Ann.*, **436**, 154 (1924).

[7] H. Staudinger and T. Reber, *Helv. Chim. Acta*, **4**, 3 (1921).

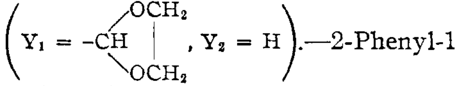
[8] M. S. Kharasch, T. Rudy, W. Nudenberg and G. Buchi, *J. Org. Chem.*, **18**, 1030 (1953). We are indebted to one of the referees for calling our attention to this paper which appeared after our work had been completed and which we had overlooked.

saponification and dehydrohalogenation to phenylpropiolic acid. At the time that this investigation



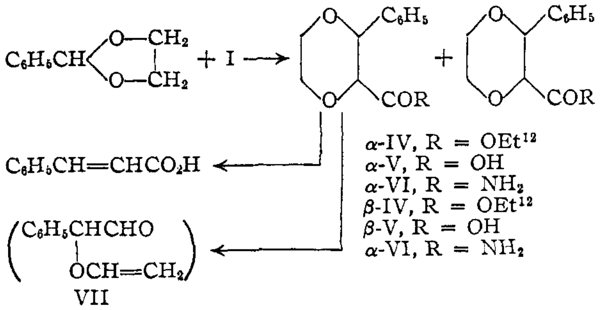
was carried out there were no clear-cut cases of the reaction of a diazoalkane with a compound of the type $R_1R_2CCl_2$ although there were indications that diazomethane reacted with carbon tetrachloride.[9] Recently, however, Urry and Eiszner[10] have reported that diazomethane reacts with carbon tetrachloride, chloroform, and other halogen-containing compounds to give well-defined products.

Ethyl Diazoacetate and 2-Phenyl-1,3-dioxolane



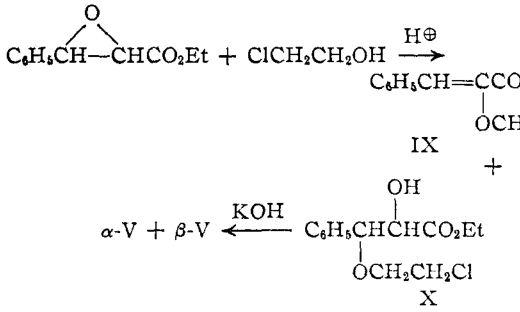
$\left(Y_1 = -CH\begin{matrix}OCH_2\\ |\\ OCH_2\end{matrix},\ Y_2 = H\right)$.—2-Phenyl-1,3-dioxolane and ethyl diazoacetate reacted at 130–150° to yield 48.5% of a product which could be separated into a solid fraction and a liquid fraction. The data indicated that the liquid, although probably not a pure entity, contained a compound stereoisomeric with the solid material and that these isomeric compounds are best represented by the structure IV, the solid designated as α-IV and the liquid as β-IV. The considerations upon which this structure assignment is based are detailed below.

The presence in the molecule of an ester group was indicated by the formation of amides, hydrazides and acids upon treatment with ammonia, hydrazine and base, respectively. That the ester group was attached to a carbon atom carrying at least one hydrogen atom was indicated by the saponification data. Saponification of β-IV yielded a mixture of a solid acid and an oily acid, while saponification of α-IV yielded only an oil from which no solid could be isolated; treatment of α-IV with ammonia, however, gave a mixture of amides from which both α-VI and β-VI could be isolated. Carbon and hydrogen analyses of α-IV, β-V, α-VI and β-VI, were all compatible with the $C_{13}H_{16}O_4$ formula that would be expected from the combination of one molecule of 2-phenyldioxolane and one molecule of ethyl diazoacetate with elimination of nitrogen. An indication that the attack had not been at the benzene nucleus was obtained from the ultraviolet spectra of compounds IV–VI, all of which possessed the characteristic bands associated with the phenyl ring.[11] The possibility that the product was ethyl 2-phenyl-1,3-dioxolane-2-acetate was ruled out by a comparison of authentic derivatives of this compound with those actually obtained. In fact, the absence of a 1,3-dioxolane ring was indicated by failure to undergo hydrolysis in the presence of dilute acid; the starting dioxolane was readily hydrolyzed under these conditions. Information concerning the location of the oxygen atoms was obtained from (a) treatment with hot, 57% hydriodic acid which gave cinnamic acid and (b) pyrolysis of the free acid at atmospheric pressure which gave an aldehyde, tentatively formulated as VII. Both of these reactions



are easily interpreted in terms of the *p*-dioxane structure IV. Cleavage of the *p*-dioxane ring with hydriodic acid should yield the unstable α,β-diiodocinnamic acid which would then lose iodine to form cinnamic acid; pyrolysis of α-methoxy acids is known to give aldehydes,[13a] and the present case is simply an extension of this general reaction.[13b] On the basis of these chemical properties, physical properties and modes of degradation the products of the reaction of phenyldioxolane and ethyl diazoacetate are formulated as the dioxane derivatives IV.

Conclusive proof for the dioxane structure of IV was acquired through an independent synthesis. From the reaction of ethyl β-phenylglycidate and ethylene chlorohydrin in the presence of a small amount of sulfuric acid there was obtained a mixture of two products which, on the basis of rather meager evidence, are thought to possess structures IX and X. The lower-boiling compound IX had



an ultraviolet spectrum similar to that of cinnamic acid, and yielded the 2,4-dinitrophenylhydrazone of ethyl phenylpyruvate upon treatment with 2,4-dinitrophenylhydrazine and hydrochloric acid. The higher-boiling compound X had only the ultraviolet spectrum of the benzene nucleus, formed a solid amide with the correct analysis, and yielded a mix-

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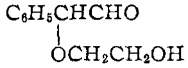
(9) O. Pauli, Dissertation, Marburg, 1935, footnote 10, p. 20.

(10) W. H. Urry and J. R. Eiszner, THIS JOURNAL, **74**, 5822 (1952).

(11) T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, *ibid.*, **69**, 880 (1947).

(12) The *cis* and *trans* designations are used to differentiate the α- and β-isomers and do not necessarily represent the actual configurations.

(13) (a) G. Darzens and A. Levy, *Compt. rend.*, **196**, 348 (1933). (b) The product that might actually be expected is VIII. However, the carbon and hydrogen analyses of the aldehyde and of its 2,4-dinitrophenylhydrazone are more compatible with the dehydration product VII (or an isomer). Furthermore, the infrared spectrum of the aldehyde has only a very weak band in the OH region, and an active hydrogen determination showed only 0.26% (calcd. for VIII 0.63%).

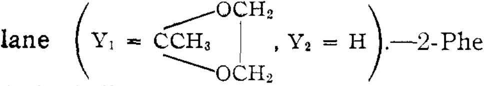


$$\begin{matrix}C_6H_5CHCHO\\ |\\ OCH_2CH_2OH\end{matrix}$$

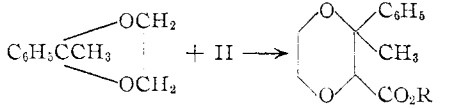
VIII

ture of the α- and β-isomers of the dioxane V upon refluxing with aqueous alcoholic potassium hydroxide.

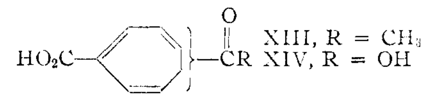
Ethyl Diazoacetate and 2-Phenyl-2-methyl-1,3-dioxolane



$\left(Y_1 = \overset{OCH_2}{\underset{OCH_2}{CCH_3}}\,,\ Y_2 = H\right)$.—2-Phenyl-2-methyl-1,3-dioxolane reacted very sluggishly with ethyl diazoacetate, and even when it was used in fourfold excess the conversion was low. From a reaction mixture worked up directly by fractional distillation there was isolated 6.5% of a solid compound thought to be the *p*-dioxane derivative XI. The structure assignment is based on the ultraviolet spectrum which shows only the bands associated with the benzene ring, on the carbon and hydrogen analysis, on the saponification to a solid acid (XII) with the correct analysis, and on the pyrolysis to an aldehyde. From a reaction mixture that was subjected to saponification before fractional distillation there was obtained 11.5% of a semi-solid from which 1.1% of pure material was isolated. That this product is an acetylcycloheptatrienecarboxylic acid (XIII) is indicated by the carbon and hydrogen analysis, by the formation of a 2,4-dinitrophenylhydrazone, and by the hypobromite oxidation to a dicarboxylic acid, probably a cycloheptatrienedicarboxylic acid (XIV).



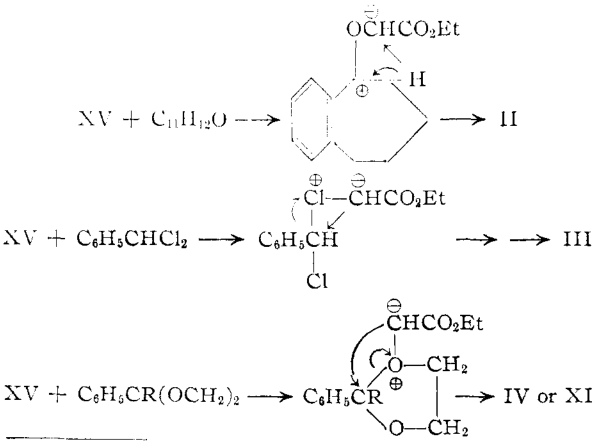
XI, R = Et
XII, R = H



XIII, R = CH_3
XIV, R = OH

Mechanism of Reactions.—A mechanism which accommodates all of the reactions discussed in this paper involves[14]: (a) decomposition of ethyl diazoacetate to carbethoxycarbene,[15] (b) coördination of the carbene with an electron rich center such as an oxygen or chlorine atom, (c) decomposition of the intermediate so formed by the routes

$$N_2CHCO_2Et \longrightarrow \underset{XV}{:CHCO_2Et} + N_2$$



Similar explanations have been advanced for the reactions of ethyl diazoacetate with acetone and cyclohexanone to form the enol ethers.[8]

As a result of the discovery of the ring enlargement reaction of dioxolanes to dioxanes it would be interesting to study in more detail the reaction between diazomethane and tetrahydrofuran, reported by Meerwein, *et al.*[16] These workers assumed, from boiling point data and carbon and hydrogen analyses, that the product consisted of a mixture of 2-methyl- and 3-methyltetrahydrofuran; in view of our results it seems equally possible that some or all of the product was tetrahydropyran.

Experimental[17]

Ethyl 6,7-Dihydro-5H-cycloheptabenzene-9-oxyacetate (II).—An 87.6-g. (0.547 mole) sample of α-benzosuberone (b.p. 99–100° at 1.2 mm.) was mixed with 2 g. of copper powder, heated to 120°, and treated over a period of 1 hour, with 16.2 g. (0.142 mole) of ethyl diazoacetate. The reaction mixture was then heated for an additional hour at 175°. The copper was removed by filtration, and the product was fractionally distilled in a Claisen flask. After removal of the excess benzosuberone, the major fraction boiled at 126.5–133° (0.7 mm.) and contained 17.6 g. (50.5% based on ethyl diazoacetate) of a colorless oil. Redistillation gave material with b.p. 129–130° (0.65 mm.), $n^{20}\text{D}$ 1.5405, $\lambda_{\max}^{\text{EtOH}}$ (ε) 250 mμ (6440).

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.14; H, 7.67. Found: C, 72.14; H, 6.98.

Treatment of the product described above with semicarbazide hydrochloride in the usual manner yielded the semicarbazone of benzosuberone, m.p. 208.5–209.5°. Similarly, treatment with 2,4-dinitrophenylhydrazine yielded the **2,4-dinitrophenylhydrazone of benzosuberone**, m.p. 211–212° dec.

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.74. Found: C, 59.92; H, 4.53.

Treatment of II with hot concentrated hydrochloric acid followed by *p*-nitrobenzaldehyde yielded the *p*-nitrobenzylidene derivative of benzosuberone, m.p. 172–174°. Similarly the amide of II (described below) yielded the same derivative.

6,7-Dihydro-5H-cycloheptabenzene-9-oxyacetamide.—A small sample of II was allowed to react with ammonium hydroxide in a sealed tube for several days at room temperature. Filtration yielded crystalline material which was purified by several recrystallizations from Solvent C[18]; m.p. 127.5–128.5°.

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96. Found: C, 71.76; H, 6.68.

Permanganate Oxidation of II.—A 1.00-g. (0.004 mole) sample of II was oxidized with 7.1 g. (0.045 mole) of potassium permanganate in 140 ml. of water to yield 0.173 g. of white crystals, m.p. 127–135°. Recrystallization from water yielded colorless needles, m.p. 138–139°, which showed no depression in m.p. upon admixture with authentic γ-(2-carboxyphenyl)-butyric acid.[19]

Ethyl α-Chlorocinnamate (III).—To 100 g. (0.62 mole) of benzal chloride heated to 160° there was added dropwise, over a period of 30 minutes, 20 g. (0.175 mole) of ethyl diazoacetate. The temperature was then raised to 170° and maintained there for 1 hour after which the reaction mixture was fractionally distilled through an 11-inch column packed with glass helices. The first fraction consisted of 1.9 g. of diethyl fumarate (or maleate), the second fraction consisted of 85.9 g. of benzal chloride, and the third fraction consisted of 8.8 g. (24% based on ethyl diazoacetate) of a colorless oil, b.p. 80–127° but mainly at 80–83° (0.7 mm.).

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(14) We are indebted to one of the referees for suggesting this mechanism.

(15) W. von E. Doering and L. H. Knox, Abstracts of Papers, 119th Meeting of the Am. Chem. Soc., April, 1951, p. 2M.

(16) H. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942).

(17) All melting points are corrected; all boiling points are uncorrected. Analyses were performed by W. L. Parr and J. Warnhoff of this Laboratory, by Micro-Tech Laboratories of Skokie, Ill., and by Weiler and Strauss of Oxford, England.

(18) Solvent C will be used as a designation for a mixture of ethyl acetate-petroleum ether (b.p. 88–98°).

(19) We are indebted to Dr. F. A. Hoyer for the preparation of this material.

α-Chlorocinnamamide.—Treatment of the oil described above with aqueous ammonia for 2 days yielded 66% of a crystalline amide (m.p. 81–106°), which after recrystallization from petroleum ether (b.p. 88–98°), existed as colorless plates, m.p. 120.5–121.5° (lit.[20] 121°).

Anal. Calcd. for C_9H_8ClNO: C, 59.51; H, 4.44. Found: C, 59.38; H, 4.30.

3-Phenyl-5-pyrazolone was prepared from III by treatment with hydrazine and was obtained as colorless needles, m.p. 243.5–244.5° (lit.[21] 236°). Upon admixture with 3-phenylpyrazolone-5, m.p. 245–246°, prepared from ethyl benzoylacetate, no depression in m.p. was observed.

Anal. Calcd. for $C_9H_8N_2O$: C, 67.07; H, 5.00. Found: C, 66.87; H, 4.98.

Saponification of III. (a) **With Dehydrohalogenation.**—A 1.0-g. sample of III was refluxed for 2 hours with aqueous alcoholic sodium hydroxide to yield 0.28 g. (40%) of phenylpropiolic acid which after two recrystallizations from Solvent C[18] was obtained as colorless needles, m.p. 136–137° (lit.[22] 135–136°). A mixed m.p. with an authentic sample of phenylpropiolic acid prepared from phenylacetylene showed no depression in m.p.

(b) **Without Dehydrohalogenation.**—A 0.92-g. sample of III was refluxed for 0.5 hour with aqueous potassium hydroxide to yield 38% of α-chlorocinnamic acid which after sublimation at atmospheric pressure followed by two recrystallizations from petroleum ether (b.p. 88–98°) was obtained as colorless needles, m.p. 139–139.5° (lit.[20] 137–138°). A sample of α-chlorocinnamic acid prepared by dehydrohalogenation of cinnamic acid dichloride showed no depression in m.p. upon admixture with this material.

Ethyl 3-Phenyl-2-*p*-dioxanecarboxylate (IV).—A 100-g. sample (0.667 mole) of 2-phenyl-1,3-dioxolane was heated to 130–140° and was treated dropwise over a period of 4 hours with 20.0 g. (0.175 mole) of ethyl diazoacetate. The temperature was then slowly raised to 150° over the course of an additional 3 hours. Distillation of the reaction mixture through an 11-inch glass-helix packed column gave 85 g. of unreacted 2-phenyldioxolane and 20 g. (48.5% based on ethyl diazoacetate, 85% based on unrecovered 2-phenyldioxolane) of crude product, b.p. 104–132° (1 mm.). Redistillation through a Piros–Glover column gave 11 arbitrary fractions from 83 to 105° (0.07 mm.). Fractions 3 through 11 were seeded with previously obtained solid isomer of IV and allowed to stand in the refrigerator for several days. Filtration of the several fractions yielded a total of 8.62 g. of solid material (α-isomer) and 6.01 g. of liquid (β-isomer). The solid isomer was recrystallized several times from petroleum ether (b.p. 33–58°) to yield colorless needles, m.p. 69–70°; $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 252 mμ (182), 257 mμ (220), 261 mμ (157), 263 mμ (175), 267 mμ (100).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83; sapn. equiv., 236. Found: C, 66.03; H, 7.10; sapn. equiv., 230.

A reaction carried out for 9 days at room temperature in the environment of 365 mμ irradiation yielded *ca.* 80 g. of recovered dioxolane and 8.8 g. of crude product. Fractional distillation of the latter through a Piros–Glover column gave 1.0 g. of an oil (possibly ethyl O-benzoylglycolate), b.p. 98–99° (0.4 mm.), 0.70 g. of the α-isomer of IV and 3.70 g. of the β-isomer of IV.

3-Phenyl-2-*p*-dioxanecarboxylic Acid. (a) **By Saponification of Ethyl 3-Phenyl-2-*p*-dioxanecarboxylate (IV).**—Saponification of the liquid isomer (β-IV) with aqueous alcoholic potassium hydroxide yielded 34% of a solid acid and 26% of an oily acid. The former was recrystallized from Solvent C[18] and was obtained in the form of colorless long needles, m.p. 144–144.5°; $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 252 mμ (190), 258 mμ (235), 261 mμ (180), 264 mμ (195), 268 mμ (124).

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.80; neut. equiv., 208. Found: C, 63.31; H, 5.71; neut. equiv., 210.

Saponification of the solid isomer (α-IV) under the same conditions yielded 93.5% of an oil from which no solid was obtained; neut. equiv. 230 (calcd. 208); $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 252 mμ (194), 257 mμ (238), 263 mμ (207).

(b) **From Ethyl β-Phenylglycidate.**—A mixture of 39.5 g. (0.205 mole) of ethyl β-phenylglycidate (b.p. 142–147° at 10 mm.), 16.7 g. (0.208 mole) of ethylene chlorohydrin and 8 drops of concentrated sulfuric acid was heated on a steam-bath for 4 hours. The cooled reaction mixture was taken up in ether, the ether was washed with sodium bicarbonate solution and with water, and the ether was then removed leaving a 48-g. residue. Distillation from a Claisen flask yielded 8.6 g. of an oil with b.p. 93–115° (0.3 mm.) and 16.9 g. of an oil with b.p. 115–125° (0.3 mm.). The lower boiling fraction had $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 248 mμ (17,500), and is thought to consist mainly of **ethyl α-(2-chloroethoxy)-cinnamate (IX)**; upon treatment with 2,4-dinitrophenylhydrazine and hydrochloric acid in methanol the **2,4-dinitrophenylhydrazone of ethyl phenylpyruvate** was obtained, m.p. 132.5–133°.

Anal. Calcd. for $C_{17}H_{16}N_4O_6$: C, 54.84; H, 4.33. Found: C, 54.75; H, 4.40.

The higher-boiling fraction was redistilled in a Claisen flask and 10.9 g. (17%) of a middle fraction, assumed to be relatively pure ethyl α-hydroxy-β-(2-chloroethoxy)-β-phenylpropionate (X), was collected, b.p. 118–122° (0.25 mm.); $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 252 mμ (522), 258 mμ (522), 264 mμ (488), 268 mμ (460). Treatment of a sample of fraction b with ammonium hydroxide gave the amide of X, which was purified by recrystallization from ethyl acetate and was obtained as colorless needles, m.p. 166–167°.

Anal. Calcd. for $C_{11}H_{14}ClNO_3$: C, 54.21; H, 5.79; N, 5.75. Found: C, 54.40; H, 5.84; N, 5.68.

A mixture of 3.95 g. of ethyl α-hydroxy-β-(2-chloroethoxy)-β-phenylpropionate (X) (b.p. 118–122° at 0.25 mm.), 8 g. of potassium hydroxide, 8 ml. of water and 8 ml. of alcohol was refluxed for 4 hours. The product was worked up in the usual fashion to yield 1.76 g. (58.5%) of a bicarbonate-soluble fraction consisting of a mixture of the α- and β-isomers of 2-carboxy-3-phenyldioxane (V). After standing for three months at room temperature the product partially crystallized, and filtration yielded 0.15 g. of a solid, m.p. 135–140°. Two recrystallizations from Solvent C[18] yielded colorless needles, m.p. 143.5–145°, which showed no depression in m.p. upon admixture with the material obtained previously.

3-Phenyl-2-*p*-dioxanecarboxamide. (a) **α-Isomer.**—The solid isomer of ethyl 3-phenyl-2-*p*-dioxanecarboxylate (α-IV) was converted in 21% yield to an amide which, after three recrystallizations from Solvent C[18], was obtained as colorless, small needles, m.p. 138–139°; $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 252 mμ (180), 258 mμ (225), 264 mμ (185), 267 mμ (100).

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.39; N, 6.76. Found: C, 63.83; H, 6.24; N, 6.83.

(b) **β-Isomer.**—The liquid isomer of ethyl 3-phenyl-2-*p*-dioxanecarboxylate (β-IV) was converted in 29% yield to an amide which, after two recrystallizations from chloroform or ethyl acetate, was obtained as colorless, small plates, m.p. 229–230°; $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 252 mμ (137), 258 mμ (200), 264 mμ (175), 268 mμ (110).

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.39; N, 6.76. Found: C, 63.90; H, 6.40; N, 6.88.

A mixture of the α- and β-amides described above was obtained from 3-phenyl-2-*p*-dioxanecarboxylic acid (from saponification of the solid isomer of ethyl 3-phenyl-2-*p*-dioxanecarboxylate) by conversion to the acid chloride followed by treatment with ammonium hydroxide. Crystallization of the crude product from ethyl acetate yielded the higher-melting amide, m.p. 225–226°, and addition of petroleum ether (b.p. 88–98°) gave the lower-melting amide, m.p. 136–138°. Similarly, a mixture of amides was obtained from the sample of 3-phenyl-2-*p*-dioxanecarboxylic acid prepared from ethyl β-phenylglycidate.

3-Phenyl-2-*p*-dioxanecarboxylic Acid Hydrazide. (a) **α-Isomer.**—From the solid isomer of the ester (α-IV) there was prepared a hydrazide which, after three recrystallizations from Solvent C,[18] was obtained as colorless, hard prisms, m.p. 149.5–150°.

Anal. Calcd. for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35. Found: C, 59.81; H, 5.95.

(b) **β-Isomer.**—From the liquid isomer of the ester (β-IV) there was similarly obtained a hydrazide as colorless, waxy needles, m.p. 140–141°.

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(21) Th. Curtius, *J. prakt. Chem.*, [2] **50**, 515 (1895).

(22) T. W. Abbott, "Organic Syntheses," Coll. Vol. II, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 515.

Anal. Calcd. for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35. Found: C, 59.78; H, 6.07.

Acid Treatment of IV and V. (a) Hydrochloric Acid.—Treatment of either the liquid isomer or the solid isomer of 3-phenyl-2-*p*-dioxanecarboxylic acid (β-V) with a refluxing mixture of 1:1 hydrochloric acid in dioxane for 2 hours gave only starting material in almost quantitative yield.

(b) **Hydriodic Acid.**—A mixture of 0.55 g. of the solid isomer of ethyl 3-phenyl-2-*p*-dioxanecarboxylate (α-IV) was refluxed for 2 hours with 10 ml. of glacial acetic acid and 10 ml. of 57% hydriodic acid in an atmosphere of carbon dioxide. From the bicarbonate-soluble portion of the product there was obtained 0.040 g. (12%) of cinnamic acid, m.p. 132–133°.

Pyrolysis of 3-Phenyl-2-*p*-dioxanecarboxylic Acid (V).—A 1.65-g. sample of the solid isomer of the acid (β-V) was distilled at atmospheric pressure (bath temperature 370°) in the presence of a small amount of copper powder. The crude distillate (0.65 g.) was taken up in ether, the ether solution was washed with sodium bicarbonate solution, the ether was removed by evaporation, and the residue was distilled from a Claisen flask. A middle fraction with b.p. 80–104° (10 mm.) consisted of 0.36 g. (21%) of a pale yellow oil, $n^{20}\mathrm{D}$ 1.5235; $\lambda_{\max}^{\mathrm{CHCl_3}}$ in cm.$^{-1}$ 3440, 3030, 2950, 2870, 2730, 1945, 1875, 1724, 1700, 1680, 1650, 1624, 1603, 1580, 1491, 1450, 1425, 1394, 1355, 1308, 1260, 1130, 1076, 1029, 990, 906, 836 and 818.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.49; H, 7.04; active H, 0.26.

A 2,4-dinitrophenylhydrazone was prepared from this material and, after three recrystallizations from Solvent C,[18] was obtained as orange plates, m.p. 117–117.5°.

Anal. Calcd. for $C_{16}H_{14}N_4O_5$: C, 56.14; H, 4.12. Found: C, 55.95; H, 3.98

Pyrolysis of the liquid isomer of the acid (α-V) under the same conditions yielded an oil which, on the basis of the infrared spectrum, appeared to be identical with the aldehyde described above.

2-Phenyl-1,3-dioxolane-2-acetamide was obtained in 28% yield from ethyl 2-phenyl-1,3-dioxolane-2-acetate as colorless needles, m.p. 139.5–140.5°. A mixed m.p. with the α-isomer of 3-phenyl-2-*p*-dioxanecarboxamide (α-VI), m.p. 137–138°, was 114–127°.

Anal. Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.54; H, 6.16; N, 6.96.

2-Phenyl-1,3-dioxolane-2-acethydrazide was obtained in 56% yield from ethyl 2-phenyl-1,3-dioxolane-2-acetate as colorless needles after three recrystallizations from petroleum ether (b.p. 88–98°); m.p. 93.5–94°.

Anal. Calcd. for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35. Found: C, 59.66; H, 6.18.

Ethyl 3-Methyl-3-phenyl-2-*p*-dioxanecarboxylate (XI).—A 332-g. (2.02 moles) sample of 2-phenyl-2-methyl-1,3-dioxolane was heated to 150–160° and was treated with 60 g. (0.525 mole) of ethyl diazoacetate over a period of 0.7 hour. The temperature was then raised to 170–180° and heating was continued for 3 hours. The resulting product was distilled through an 11-inch, glass-helix packed column to yield (a) 298 g. of unreacted starting dioxolane, (b) 6.26 g. with b.p. 153–164° (10 mm.), (c) 16.26 g. with b.p. 164–172° (10 mm.), (d) 15.47 g. with b.p. 172–219° (10 mm.). Fraction c was semi-solid and upon filtration yielded 7.2 g. of a yellow oil and 8.2 g. of a colorless solid, m.p. 62–69°. After several recrystallizations from petroleum ether (b.p. 33–58°) colorless, stout needles were obtained, m.p. 72–72.5°; $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 246 mμ (182), 251 mμ (198), 258 mμ (228), 264 mμ (173).

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 66.96; H, 7.23.

3-Methyl-3-phenyl-2-*p*-dioxanecarboxylic Acid (XII).—Saponification of ethyl 3-methyl-3-phenyl-2-*p*-dioxanecarboxylate (m.p. 70–72°) with aqueous alcoholic potassium hydroxide yielded 56% of colorless material, m.p. 95–97°, which was recrystallized several times from ethyl acetate–petroleum ether (b.p. 63–69°) and obtained as colorless needles, m.p. 97–97.5°; $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ) 251 mμ (186), 258 mμ (226), 264 mμ (181).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.08; H, 6.43.

Pyrolysis of 3-Methyl-3-phenyl-2-*p*-dioxanecarboxylic Acid.—A 1.35-g. sample of the acid (XII) was distilled at atmospheric pressure (bath temperature 290–360°) in the presence of a small amount of copper powder. The product was worked up as described above to yield 0.41 g. (35%) of distillate as a colorless oil, b.p. 112–115° (11 mm.), $n^{20}\mathrm{D}$ 1.5180. This material was converted in 91% yield to a 2,4-dinitrophenylhydrazone, m.p. 110–113°, which after three recrystallizations from Solvent C[18] was obtained as orange plates, m.p. 134.5–135.5°.

Anal. Calcd. for $C_{17}H_{16}N_4O_5$: C, 57.30; H, 4.54. Found: C, 57.28; H, 4.35.

Acetylcycloheptatrienecarboxylic Acid (XIII).—A reaction between 97.5 g. (0.59 mole) of 2-phenyl-2-methyl-1,3-dioxolane and 20 g. (0.175 mole) of ethyl diazoacetate was carried out as described above. The product was treated with 70 g. of sodium hydroxide, 80 ml. of water and 100 ml. of methanol and the mixture was refluxed for 4 hours. From the neutral fraction there was recovered 77 g. of starting dioxolane, and from the acidic fraction there was isolated a brown oil which was refluxed for 2 hours with a mixture of 5% hydrochloric acid and ethanol. Distillation of the material so obtained through a Claisen flask yielded 3.5 g. of a yellow-green, semi-crystalline material, b.p. 113–174° (2 mm.). Separation by filtration yielded 0.33 g. of acetylcycloheptatrienecarboxylic acid which was recrystallized several times from Solvent C[18] to give colorless needles, m.p. 116–117°; $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ), 241 mμ (12,000), 278 mμ (1020).

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.29; H, 5.65.

A **2,4-dinitrophenylhydrazone of acetylcycloheptatrienecarboxylic acid** was prepared in 100% yield, m.p. 130–135°. Several recrystallizations from Solvent C[18] yielded orange plates, m.p. 156–156.5°.

Anal. Calcd. for $C_{16}H_{14}N_4O_6$: C, 53.63; H, 3.94. Found: C, 53.80; H, 4.22.

Cycloheptatrienedicarboxylic Acid (XIV).—A sodium hypobromite oxidation, carried out according to the directions of Johnson, *et al.*,[23] yielded 65% of cycloheptatrienedicarboxylic as a pale yellow solid of indefinite m.p. After four recrystallizations from water a sharp-melting product was obtained, m.p. 257.5–258.5° dec.; $\lambda_{\max}^{\mathrm{EtOH}}$ (ϵ), 226 mμ (20,500), 298 mμ (4890).

Anal. Calcd. for $C_9H_8O_4$: C, 59.94; H, 4.48. Found: C, 60.14; H, 4.56.

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[23] W. S. Johnson, C. D. Gutsche and R. D. Offenhauer, THIS JOURNAL, 68, 1648 (1946).