

was heated at 100° for 5 minutes. After three hours at room temperature, water was added and the product extracted with petroleum ether. The extract was washed with sodium carbonate solution and water, dried and concentrated. The residue (0.3 g., 12%) showed both before and after distillation (b.p. about 120° (0.1 mm.)) an infrared absorption of 1700 cm^{-1} and gave the yellow 2,4-dinitrophenylhydrazone of VII, m.p. 168–170°, after recrystallization from butanol.

When the dinitrophenylhydrazone of VII was kept with a methanolic solution of sodium hydroxide at room temperature for 3 hours, it was transformed into the 2,4-dinitrophenylhydrazone of II, m.p. 122°, but a great part was converted into an insoluble, amorphous product of unknown structure.

4-Phenylcycloheptanone (X).—To a solution of 15 g. of 4-phenylcyclohexanone in 50 ml. of 95% alcohol, 1 ml. of water and 50 ml. of ether, 10 g. of nitrosomethylurea was added, and the stirrer adjusted so that it only agitated the surface of the liquid, without affecting the solid nitroso derivative on its bottom. At 0°, a solution of 12 g. of potassium hydroxide in 40 ml. of 50% alcohol was added during 2.5 hours. The reaction mixture was then kept for 12 hours and 20 ml. of 2 *N* hydrochloric acid and 200 ml. of water added successively. The ether layer was separated, neutralized, dried and concentrated. The product boiled at 132–134° (3 mm.), 115–118° (0.5 mm.) and crystallized upon cooling; it had m.p. 23–25° and n_D^{20} 1.5381; the yield was 12.5 g. (80%); $\lambda_{\text{max}}^{\text{EtOH}}$ 247 (2.22), 253 (2.34), 258 (2.40), 264 (2.30), 267 μ (2.28); $\bar{\nu}_{\text{max}}^{\text{EtOH}}$ 1700 cm^{-1} (carbonyl) (2- and 3-phenylcycloheptanone: 1688 cm^{-1}).¹⁵

Anal. Calcd. for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 83.0; H, 8.5. Found: C, 82.6; H, 8.2.

The 2,4-dinitrophenylhydrazone crystallized from 1-butanol in yellow crystals of m.p. 158°, while for the 2- and the 3-isomers melting points of 171–172° and 145–146° have been recorded, respectively¹⁵; $\lambda_{\text{max}}^{\text{EtOH}}$ 260 (4.03), 378 μ (4.38).

2-Bromo-4-phenylcycloheptanone (XI).—To an ice-cold solution of 10 g. of X in 50 ml. of carbon tetrachloride, 10.2 g. of bromine in 75 ml. of the same solvent was added slowly. The reaction started after a brief inhibition period; the bromine was introduced so that a new portion was added after the previous one had been completely decolorized. After one hour, the solution was washed with water, sodium carbonate solution and water, dried and concentrated. The remaining oil was used for the further reactions. Distillation led to partial decomposition even under 1 mm. pressure (b.p. 180°) (the starting material boils at

115° (1 mm.)), and the distillate blackened quickly upon standing. Therefore, no satisfactory analysis could be secured, and the crude bromoketone was best characterized as the red 2,4-dinitrophenylhydrazone of m.p. 115° (see below).

anti-2,4-Dinitrophenylhydrazone.—At 0°, 0.5 g. of 2,4-dinitrophenylhydrazine in a mixture of 2 ml. of concd. sulfuric acid, 3 ml. of water and 10 ml. of alcohol was added to 0.5 g. of XI in 20 ml. of alcohol. The yellow product crystallized nicely from butanol; it melted at 76°. Upon standing and more quickly upon drying, it is transformed into the red *syn* compound; $\lambda_{\text{max}}^{\text{EtOH}}$ 260 and 363 μ ; quantitative data could not be obtained, as the product could not be dried without change.

syn-2,4-Dinitrophenylhydrazone.—The above reaction was repeated, but the mixture refluxed for 2 hours. The red product was recrystallized from nitromethane and melted at 115°; $\lambda_{\text{max}}^{\text{EtOH}}$ 262 (4.20), 395 μ (4.20).

Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{BrN}_4\text{O}_4$: C, 51.0; H, 4.4. Found: C, 51.9; H, 4.2.

4-Phenylcyclohept-3-en-1-one (XII).—A solution of 3 g. of XI in 30 ml. of collidine was refluxed for one hour. After cooling, the solid product was filtered off and washed with ether and the filtrate was diluted with water and ether. The ethereal extract was washed with dilute hydrochloric acid and water, dried and evaporated. The product boiled at 128–130° (3 mm.); its yield was 1.5 g. (75%); $\lambda_{\text{max}}^{\text{EtOH}}$ 253 μ (3.70); $\bar{\nu}_{\text{max}}^{\text{EtOH}}$ 1700 cm^{-1} (carbonyl, broad band).

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}$: C, 83.8; H, 7.5. Found: C, 83.4; H, 7.7.

The 2,4-dinitrophenylhydrazone formed yellow crystals of m.p. 136° after recrystallization from butanol; $\lambda_{\text{max}}^{\text{EtOH}}$ 250 (4.11), 365 μ (4.34).

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4$: C, 62.3; H, 4.9. Found: C, 62.4; H, 4.9.

4-Phenylcyclohept-2-en-1-one (XIII) 2,4-Dinitrophenylhydrazone.—The mixture of 1 g. of XI, 0.8 g. of 2,4-dinitrophenylhydrazine and 20 ml. of glacial acetic acid was heated for 5 minutes in a current of nitrogen. The product was precipitated by addition of water and recrystallized from butanol; red crystals of m.p. 107°; $\lambda_{\text{max}}^{\text{EtOH}}$ 258 (4.20), 375 μ (4.20).

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_4\text{O}_4$: C, 62.3; H, 4.9. Found: C, 62.3; H, 4.8.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, HEBREW UNIVERSITY]

Experiments in the 4-Arylcycloalk-2-en-1-one Series. II.¹ The Stobbe and Darzens Reactions of Ethyl β -Benzoylpropionate

BY ERNST D. BERGMANN, SAMUEL YAROSLAVSKY² AND HANNAH WEILER-FEILCHENFELD

RECEIVED OCTOBER 28, 1958

Ethyl β -benzoylpropionate condenses with diethyl succinate (Stobbe reaction) to give 4-carbethoxy-5-oxo-2-phenylcyclopent-1-enyl-acetic acid (VI) and with ethyl chloroacetate in the presence of sodium *t*-pentoxide (Darzens reaction) to yield diethyl 1,2-epoxy-2-phenyladipate (III). Some transformations of these two products are described, and some observations on the infrared spectra of glycidic esters reported.

A general method for the preparation of 4-aryl-cyclohexanones capable of extension to higher 4-arylated cycloalkanones appeared to consist in the application of the Stobbe and the Darzens reactions to ethyl β -aroylpropionates (I), according to schemes A and B.

To our best knowledge, the Darzens reaction has not been applied to any ketoester; as to the

Stobbe reaction, β -ketoesters fail to react³ and γ -ketoesters have not been studied. Only one δ -ketoester has been reported to react normally in the Stobbe reaction, *viz.*, ethyl γ -anisoylbutyrate.⁴

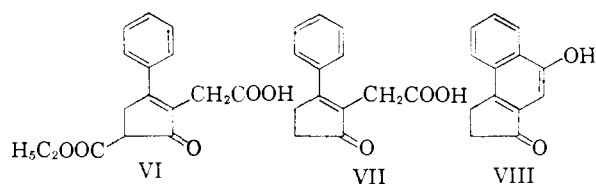
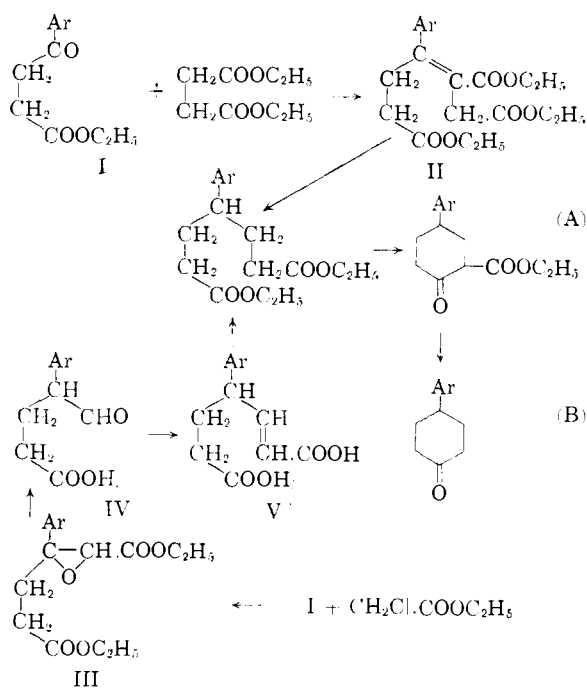
The condensation of ethyl β -benzoylpropionate (I) with 3 moles of diethyl succinate and 3 moles of sodium hydride gave a mixture of neutral and acidic products. The neutral products contained, apart

(1) Part I: E. D. Bergmann and J. Szmuszkowicz, *THIS JOURNAL*, **75**, 3226 (1953).

(2) Part of the M.Sc. Thesis, submitted to the Hebrew University, Jerusalem.

(3) W. S. Johnson, J. W. Petersen and C. D. Gutsche, *ibid.*, **69**, 2942 (1947).

(4) W. S. Johnson, A. R. Jones and W. P. Schneider, *ibid.*, **72**, 2395 (1950).



That the carboxylic and not the acetic acid side-chain is present in esterified form follows from the thermal stability of the substance; in the inverse case it would be a free β -keto acid. Already during esterification the β -carbomethoxy-group was largely eliminated and the ethyl ester of VII (λ_{\max} 270 $m\mu$, $\log \epsilon$ 4.38; 2,4-dinitrophenylhydrazone λ_{\max} 393 $m\mu$, $\log \epsilon$ 4.53) was formed. Its hydrolysis led to 5-oxo-3-phenylcyclopent-1-enylacetic acid (VII), (see Fig. 1) which is characterized by a red 2,4-dinitrophenylhydrazone (λ_{\max} 405 $m\mu$). The acid proved identical with a compound of formula VII obtained by Robinson⁹ by a different route. The identity was proved by conversion of the acid into 4-hydroxy-3'-oxo-1,2-cyclopentenaphthalene (VIII).⁹

When in the condensation of I with ethyl chloroacetate sodium ethoxide was used as catalyst, a yield of 6–8% of the desired glycidic ester III was obtained. With sodium *t*-amyloxide,¹⁰ the yield rose to 35%. The infrared spectrum of the product showed the ester frequency at 1710⁻¹; the frequencies at 1180 and 860 cm^{-1} can be attributed to the presence of the epoxide ring (see below). Hydrolysis of the ester III with sodium ethoxide and the theoretical quantity of water (Claisen's method^{11–13}) gave in 80% yield the acid corresponding to III. It showed infrared absorption at 860 and 1210 cm^{-1} , characteristic of the epoxide ring. The transformation of this acid into 4-carboxy-2-phenylbutyraldehyde (IV) was brought about in 75% yield by heating with copper powder.¹¹ Compound IV reduced Fehling solution readily and condensed with malonic acid in the presence of pyridine to 3-phenylpent-1-ene-1,5-dicarboxylic acid (V), which was isolated in 40% yield. Its infrared spectrum showed a broad band at 1700 cm^{-1} , probably due to the superposition of the frequencies of the saturated and the α,β -unsaturated carboxyl groups.

In connection with this work the infrared absorption characteristics of the ethyleneoxide ring in glycidic esters were studied systematically. Field, Cole and Woodford¹⁴ ascribed to the epoxide group a frequency at 1240–1260 cm^{-1} , whilst

from the excess of diethyl succinate, diethyl succinylsuccinate and a well-crystallized orange-red compound of the formula $C_{18}H_{12}O_8$, which has a very characteristic spectrum and is reduced catalytically to a colorless substance. No attempt was made to elucidate the structure of these compounds. The acidic fraction consisted almost entirely of the monoethyl ester of a dicarboxylic acid $C_{16}H_{16}O_5$. The fifth oxygen belongs to a carbonyl group; the infrared absorption band at 1700 cm^{-1} suggests that it is an α,β -unsaturated carbonyl in a five-membered ring.⁵ Also the ultraviolet absorption spectrum of the substance (275 $m\mu$, $\log \epsilon$ 4.02) as well as that of the red 2,4-dinitrophenylhydrazone (387 $m\mu$, $\log \epsilon$ 4.52) is best explained by the presence of the chromophore $C_6H_5\dot{C}=CCO$. Thus, for 3-phenylcyclopent-2-en-1-one, an absorption at 280 $m\mu$ ($\log \epsilon$ 4.40)⁶ and for 3,4-diphenyl-4-methyl-2-hydroxycyclopent-2-en-1-one a band at 286.5 $m\mu$ ($\log \epsilon$ 4.30)⁷ have been reported. Formula VI of 4-carboxy-5-oxo-2-phenylcyclopent-1-enylacetic acid is, therefore, proposed for the substance $C_{16}H_{16}O_5$. It is derived from the expected product II of the Stobbe reaction or rather its partial hydrolysis product (as it is likely to be formed in the Stobbe synthesis),⁸ by a Dieckmann reaction. The presence of a substituent in the α -position to the carbonyl is responsible for the slight hypsochromic effect observed in the ultraviolet spectrum. Yates, *et al.*,⁷ have made similar observations and have assumed that the substituent prevents the phenyl group from being coplanar with the five-membered ring.

(5) A second carbonyl band (at 1740 cm^{-1}) is due to the ester and carboxyl groups.

(6) A. L. Wilds and co-workers, *THIS JOURNAL*, **69**, 1985 (1947).

(7) P. Yates, N. Yula, W. Brown and B. Mann, *ibid.*, **80**, 202 (1958).

(8) See, for a review, W. S. Johnson and G. H. Daub, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 1.

(9) R. Robinson, *J. Chem. Soc.*, 1390 (1938); *cf.* for similar compounds, D. L. Turner, *THIS JOURNAL*, **71**, 612 (1949); G. S. Grinenko and V. J. Maksimov, *J. Obshchei Khimii*, **28**, 528 (1958) [*C.A.*, **52**, 14544 (1958)].

(10) This compound, which has proved efficient as, and easier to handle than, potassium *t*-butoxide in many Darzens reactions studied in this Laboratory, has been used as catalyst in other condensation reactions; G. Vavon and J. Conia, *Compt. rend.*, **223**, 157, 246 (1946); J. Conia, *Bull. soc. chim. France*, 533 (1950); 690, 943 (1954); 301 (1955); 1040, 1392 (1956); S. Julia, *ibid.*, 789 (1954).

(11) W. S. Johnson, J. S. Belew, I. J. Chinn and R. H. Hunt, *THIS JOURNAL*, **76**, 4995 (1953).

(12) H. H. Morris and C. J. St. Lawrence, *ibid.*, **77**, 1692 (1955).

(13) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 733.

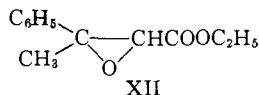
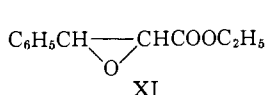
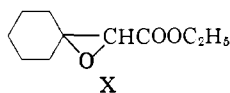
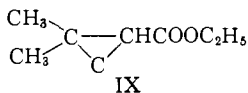
(14) J. E. Field, J. O. Cole and D. E. Woolford, *J. Chem. Phys.*, **18**, 1298 (1950).

TABLE I
 INFRARED SPECTRA OF SOME GLYCIDIC ESTERS

	Spectrum, cm. ⁻¹				
	820	880	1200	1260	1755 ^{a,b}
Ethyl 2,2-dimethylethyleneoxide-3-carboxylate (IX)					1755 ^{a,b}
Ethyl 2,2-pentamethylene-ethylenoxide-3-carboxylate (X)		840	1200	1250	1754 ^b
Ethyl 2-phenylethylenoxide-3-carboxylate (XI)	815	855	1200	1260	1713 ^b
Ethyl 2-phenyl-2-methylethyleneoxide-3-carboxylate (XII)		860	1200-1300		1755 ^b
Diethyl 1,2-epoxy-2-phenyladipate (III)		860	1180		1710 ^c
1,2-Epoxy-2-phenyladipic acid		860	1210 (broad)		1700-1760 ^d

^a In accord with the observations of H. H. Morris and R. H. Young (THIS JOURNAL, 79, 3408 (1957)) we found a second peak at 1724 cm.⁻¹ in XI, and a shoulder at 1724, 1730 and 1724 cm.⁻¹ in IX, X and XII, respectively. Cf. H. O. House, J. W. Blaker and D. H. Madden, *ibid.*, 80, 6386 (1958), and H. O. House and J. W. Blaker, *ibid.*, 80, 6389 (1958).
^b Liquid film. ^c Chloroform solution. ^d KBr pellet.

Shreve, Heether, Knight and Swern,¹⁵ who also observed this band in 1,2-epoxyalkanes, believe that a band at 917 — 882 and 833 — 829 cm.⁻¹ is the most characteristic one for *trans*- and *cis*-epoxides, respectively. Guenthard, Messikommer and Kohler¹⁶ did not find a 1250 cm.⁻¹ band in steroid epoxides, but discovered absorption between 900 and 800 cm.⁻¹ in most cases, and between 1050 and 1035 cm.⁻¹ in some of their compounds. Jones and Sandorfy¹⁷ summarize the evidence by stating that at 840-856 cm.⁻¹ the asymmetrical ring stretching vibration is situated—it is strong in the infrared—, at 1268 cm.⁻¹ the symmetrical one, which is strong in the Raman spectrum.¹⁸⁻²⁰ These two bands have been also found in the glycidic esters we studied; the results are summarized in Table I.



These data show that there is no significant effect of conjugation between the ethyleneoxide and the ester groups, which would have tended to reduce the frequency of both the ethyleneoxide and the carbonyl grouping. This situation is, thus, different from the case of cyclopropane which does enter into conjugation with carbonyl groups. Similar observations have been recorded by Jones and co-workers.²¹

Experimental

Ethyl β -benzoylpropionate (I) was prepared in 80% yield according to Kugel²²; b.p. 186° (24 mm.).

(15) O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Anal. Chem.*, **23**, 277 (1951).

(16) H. H. Guenthard, B. Messikommer and M. Kohler, *Helv. Chim. Acta*, **33**, 1809 (1950).

(17) R. N. Jones and C. Sandorfy, in A. Weissberger, "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, p. 433.

(18) The band in the 860 cm.⁻¹ region has also been observed by S. S. Skorokhodov, *C. A.*, **51**, 7149 (1957); see also the paper by J. Bomstein, *Anal. Chem.*, **30**, 544 (1958), which appeared after the conclusion of this study.

(19) For 3-phenyl-3-acetyleneoxide, a band at 1250 cm.⁻¹ has recently been observed by H. Kwart and L. G. Kirk (*J. Org. Chem.*, **22**, 116 (1957)).

(20) D. A. Rausch, A. M. Lovelace and L. E. Coleman (*ibid.*, **21**, 1328 (1956)) found bands at 1258 and 885 cm.⁻¹ for fluorine-substituted epoxides.

(21) R. N. Jones, P. Humphries, F. Herling and K. Dobriner, *THIS JOURNAL*, **74**, 2820 (1952).

(22) M. Kugel, *Ann.*, **299**, 50 (1898).

Stobbe Reaction of I.—In a 500-ml. flask, 10.3 g. (0.05 mole) of I, 26.1 g. (0.15 mole) of freshly distilled diethyl succinate, 3.6 g. (0.15 mole) of sodium hydride and 50 ml. of dry benzene were mixed, and the apparatus was flushed with nitrogen. The gas stream was only interrupted in order to add to the mixture 1 ml. of absolute alcohol which initiated the reaction (red coloration, evolution of hydrogen). The mixture was stirred for 2 hours and cautiously decomposed with 10.5 ml. of glacial acetic acid. Ether and water were added and the aqueous layer twice extracted with ether. The combined organic solutions were then extracted thoroughly with 5% sodium carbonate solution ("acidic product"), washed with water, dried and concentrated ("neutral products").

The "acidic product" was liberated by acidification of its solution with dilute hydrochloric acid and extracted with ether; crude yield, 10 g. (72%). Potentiometric titration indicated that one acidic group was present and that the molecular weight was that of 4-carbethoxy-5-oxo-2-phenylcyclopent-1-enylacetic acid (VI) (calcd., 288; found, 285); $\lambda_{\text{max}}^{\text{CHCl}_3}$ 275 m μ (log ϵ 4.02); $\bar{\nu}_{\text{max}}^{\text{KBr}}$ 1700-1740 cm.⁻¹ (superposition of carbonyl frequencies).

Anal. Calcd. for C₁₆H₁₆O₅: C, 66.6; H, 5.5. Found: C, 66.8; H, 5.7.

2,4-Dinitrophenylhydrazone, from butanol, dark-red crystals, m.p. 164°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ 263 m μ (4.48), 301 m μ (4.04), 387 m μ (4.52).

Anal. Calcd. for C₂₂H₂₀N₄O₈: C, 56.4; H, 4.3. Found: C, 56.8; H, 4.7.

Ethyl 5-Oxo-2-phenylcyclopent-1-enylacetate (as VII).—A mixture of 10 g. of VI, 50 ml. of anhydrous ethanol and 0.5 g. of concd. sulfuric acid was refluxed for 8 hours; b.p. 160-165° (0.7 mm.), yield 3.5 g. (32%), n_D^{20} 1.5535, $\lambda_{\text{max}}^{\text{EtOH}}$ 270 m μ (log ϵ 4.38). The analysis showed that the 4-carbethoxy group had been almost completely eliminated. This was confirmed by the preparation of the 2,4-dinitrophenylhydrazone.

Anal. Calcd. for C₁₅H₁₄O₃: C, 73.7; H, 6.6. Calcd. for C₁₅H₂₀O₃: C, 68.4; H, 6.3. Found: C, 72.6; H, 6.9.

2,4-Dinitrophenylhydrazone, from nitromethane and then butanol after repeated recrystallizations, dark-red crystals of m.p. 186°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ 268 m μ (4.36), 300 m μ (4.08), 393 m μ (4.53).

Anal. Calcd. for C₂₁H₂₀N₄O₆: C, 59.4; H, 4.7. Found: C, 59.7; H, 4.7.

5-Oxo-2-phenylcyclopent-1-enylacetic Acid (VII).—A mixture of 2 g. of the foregoing ester, 2 g. of sodium hydroxide and 30 ml. of water was refluxed for 5 hours, the solution acidified with dilute hydrochloric acid and the solid recrystallized from nitromethane or benzene; light-yellow crystals of m.p. 141° (lit.⁹ 141°), yield 1.2 g. (90%), $\lambda_{\text{max}}^{\text{EtOH}}$ 278 m μ (log ϵ 4.26), $\bar{\nu}_{\text{max}}^{\text{CHCl}_3}$ 1700 cm.⁻¹ (Figs. 1, 2).

Anal. Calcd. for C₁₃H₁₂O₃: C, 72.2; H, 5.5. Found: C, 72.2; H, 5.7.

The 2,4-dinitrophenylhydrazone, from xylene, red crystals of m.p. 272-273° (after darkening) (lit.⁹ 273°) is very slightly soluble in practically all solvents. Its spectrum was, therefore only measured qualitatively: maxima at 265, 302, 405 m μ (in chloroform).

The acid VII was converted according to the method of Robinson⁹ into 4-hydroxy-3'-keto-1,2-cyclopentenonaphthalene (VIII), which melted at 285-290° after recrystallization from glacial acetic acid and ethanol, and showed the characteristic green fluorescence in concentrated sulfuric acid solution.

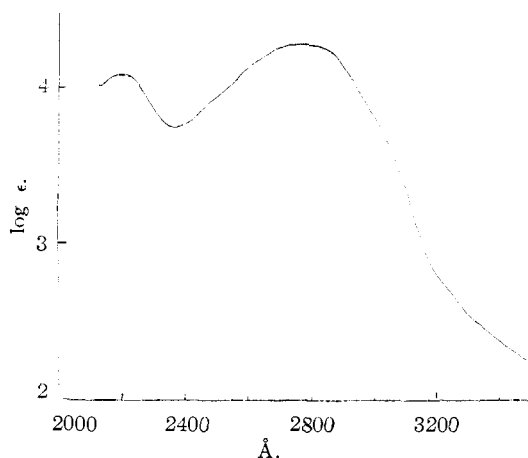


Fig. 1.—Ultraviolet spectrum of 5-oxo-2-phenyl-cyclopent-1-enylacetic acid (VII), in ethanol.

The neutral products of the Stobbe reaction formed a viscous oil, from which upon cooling 4 g. of a crystalline product separated slowly. (The liquid was identified as diethyl succinate.) The product was recrystallized slowly from anhydrous ethanol; thus 2.5 g. of almost colorless and 1.5 g. of orange-red prisms were obtained, which had to be separated mechanically. The colorless crystals were diethyl succinylsuccinate, from ethanol m.p. 126° (lit.²¹: 126°), $\lambda_{\text{max}}^{\text{EtOH}}$ 244 m μ (log ϵ 4.24).

2,4-Dinitrophenylhydrazone, from much butanol or from nitrobenzene, yellow crystals, m.p. 252°; $\lambda_{\text{max}}^{\text{CHCl}_3}$ 254 m μ (4.42), 358 m μ (4.47).

Anal. Calcd. for $\text{C}_{24}\text{H}_{24}\text{N}_4\text{O}_{12}$: C, 46.8; H, 3.9. Found: C, 47.2; H, 4.0.

The orange-red product melted, after recrystallization from butanol at 198° and had the formula $\text{C}_{15}\text{H}_{12}\text{O}_5$; it contains an ethoxy group; $\lambda_{\text{max}}^{\text{EtOH}}$ 255 m μ (4.24), 395 m μ (3.50); $\bar{\nu}_{\text{max}}^{\text{EtOH}}$ 700, 745, 805, 830, 905, 920, 940, 1130, 1220 (broad), 1340, 1450, 1500, 1630, 2350, 3110.

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_5$: C, 75.0; H, 5.0. Found: C, 75.1; H, 4.6.

Hydrogenation in ethyl acetate and in the presence of platinum oxide as catalyst gave a colorless compound which melted at 157° after recrystallization from toluene; $\lambda_{\text{max}}^{\text{EtOH}}$ 255 m μ (3.16), 385 m μ (2.26); $\bar{\nu}_{\text{max}}^{\text{EtOH}}$ 700, 735, 845, 885, 910, 935, 1050, 1130, 1190 (broad), 1320, 1400, 1450, 1475, 1630, 2400, 2950, 3450 cm^{-1} . Evidently, a hydroxyl group had formed in the reduction process.

Diethyl 1,2-Epoxy-2-phenyladipate (III).—In an atmosphere of nitrogen and with vigorous agitation, a mixture of 31.3 g. of I and 18.6 g. of ethyl chloroacetate was added to an ice-cooled solution of 3.5 g. of sodium in 150 ml. of *t*-amyl alcohol. The addition required 2 hours. The reaction mixture was stirred for two hours at 10–15° and for one further hour at 25°. Most of the amyl alcohol was then distilled off *in vacuo* and the residue treated with water and ether. The product boiled at 170–174° (1 mm.), yield 15 g. (35%), n_D^{20} 1.4948; $\bar{\nu}_{\text{max}}^{\text{CHCl}_3}$ 860, 1180, 1300, 1710 cm^{-1} .

Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_5$: C, 65.7; H, 6.8. Found: C, 65.8; H, 7.0.

1,2-Epoxy-2-phenyladipic Acid.—At 0°, 7 g. of III was added to a solution of 1.1 g. of sodium in 40 ml. of anhydrous alcohol. Then 0.80 ml. of water was added and the mixture left at room temperature for 12 hours. The salt of 1,2-epoxy-2-phenyladipic acid which crystallized during this period was filtered and immediately transferred into dilute hydrochloric acid. Extraction with ether gave 5 g. (90%) of a solid product which was recrystallized from nitromethane; m.p. 193° dec.; $\bar{\nu}_{\text{max}}^{\text{EtOH}}$ 860, 1210 (broad), 1700–1760, 3500 cm^{-1} .

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_5$: C, 61.0; H, 5.1. Found: C, 61.2; H, 5.2.

When the hydrolysis was carried out with aqueous sodium hydroxide or alcoholic potassium hydroxide, yields of 55 and 35–40% of the acid, respectively, were obtained.

(23) H. Ebert, *Ann.*, **229**, 45 (1885).

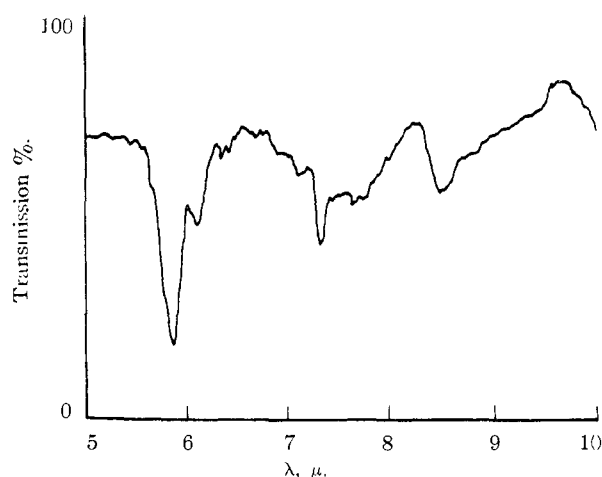


Fig. 2.—Infrared spectrum of 5-oxo-2-phenyl-cyclopent-1-enylacetic acid (VII), in chloroform.

4-Carboxy-2-phenylbutyraldehyde (IV).—A mixture of 5 g. of 1,2-epoxy-2-phenyladipic acid and 0.1 g. of copper powder was heated in a Claisen flask in a nitrogen atmosphere, just above the melting point of the acid. After one hour, the product was distilled; b.p. 150° (1 mm.), yield 3 g. (75%), n_D^{20} 1.5366.

Anal. Calcd. for $\text{C}_{11}\text{H}_{12}\text{O}_3$: C, 68.7; H, 6.2. Found: C, 68.5; H, 6.2.

3-Phenylpent-1-ene-1,5-dicarboxylic Acid (V).—A mixture of 1.35 g. of malonic acid, 2.5 g. of IV and 0.65 ml. of anhydrous pyridine was heated on the steam-bath for 2.5 hours. The mixture was cooled and diluted with a little water, and the solid obtained dissolved in concentrated ammonia solution. The filtered solution was acidified with 15% hydrochloric acid and kept at low temperature, and the acid filtered and recrystallized from nitromethane; m.p. 121°, yield 1.5 g. (40%); $\lambda_{\text{max}}^{\text{EtOH}}$ 215 m μ (4.14), 268 m μ (2.70); $\bar{\nu}_{\text{max}}^{\text{EtOH}}$ 1760 cm^{-1} .

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_4$: C, 66.6; H, 6.0. Found: C, 66.8; H, 5.9.

Ethyl 2,2-dimethylethylenoxide-3-carboxylate was prepared according to Newman, Magerlein and Wheatley²⁴ from anhydrous acetone, yield 40%. As the boiling point (168° (750 mm.)) was lower than that reported in the literature (182–184° (760 mm.)),²⁵ the purity of the substance was checked by analysis.

Anal. Calcd. for $\text{C}_7\text{H}_{12}\text{O}_3$: C, 58.3; H, 8.3. Found: C, 57.8; H, 8.2.

Ethyl 2-Pentamethyleno-ethylenoxide-3-carboxylate.—In an atmosphere of nitrogen, 9 g. of sodium metal was dissolved in 380 ml. of boiling anhydrous *t*-amyl alcohol. The solution was cooled, and at about –5° a mixture of 37.7 g. of cyclohexanone and 47 g. of ethyl chloroacetate added, with agitation, within 90 minutes. The stirring was continued at 0° for another 1.5 hours and at room temperature for two more hours. Most of the amyl alcohol was then removed *in vacuo* (oil-bath, 100–120°), water was added and the mass extracted with ether. The ethereal extract was washed with water and dilute acetic acid, dried and distilled; b.p. 138° (9 mm.) (lit.¹¹ 139–144° (27 mm.)), yield 64 g. (90%).

Ethyl 2-Phenylethylenoxide-3-carboxylate.—The method of Newman, *et al.*,²⁴ was used; yield 50%, b.p. 156° (18 mm.) (lit.²⁶ 279.5° dec.).

Ethyl 2-phenyl-2-methylethylenoxide-3-carboxylate was prepared, using sodamide as catalyst²⁷; yield 60%, b.p. 158° (18 mm.) (lit.²⁸, 153–159° (20 mm.)).

JERUSALEM, ISRAEL

(24) M. S. Newman, B. J. Magerlein and W. B. Wheatley, *THIS JOURNAL*, **68**, 2112 (1946).

(25) B. N. Rutowski and N. A. Dajew, *Ber.*, **64**, 693 (1931); *cf.* L. Claisen, *ibid.*, **38**, 693 (1905).

(26) C. Glaser, *Ann.*, **147**, 104 (1868).

(27) "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 727.