Attempts to prepare Diels–Alder adducts of either oxime were unsuccessful.

Experimental

***syn*-9-Anthraldoxime.**—When 7 g. of hydroxylamine hydrochloride and 15 g. of 9-anthraldehyde were used as in Fieser and Hartwell's procedure,[3] 15.5 g. (96%) of *syn*-9-anthraldoxime was obtained, m.p. 160–165°. Recrystallization from ethanol gave long yellow needles, m.p. 165–166°, lit.[3] 165–165.5°. This compound was readily soluble in hot 5% sodium hydroxide.

***anti*-9-Anthraldoxime.**—A mixture of 5 g. (0.024 mole) of 9-anthraldehyde and 5 g. (0.073 mole) of hydroxylamine hydrochloride in 25 ml. of pyridine and 25 ml. of anhydrous ethanol was heated on the steam-bath for 1.5 hours. The pyridine and ethanol were then removed by heating on the steam-bath for 4 more hours while blowing a jet of air into the reaction flask. The solid residue was ground with 25 ml. of water, filtered and washed with 10 ml. of water. The crude product (m.p. 211–214°) was recrystallized from ethanol (750 ml. was necessary for complete solution). Upon cooling, 5.2 g. (97%) of product was obtained, m.p. 218–220°. When 2 g. of this material was heated on the steam-bath in 50 ml. of 5% sodium hydroxide for 0.5 hour only a trace of it dissolved.

Anal. Calcd. for $C_{15}H_{11}NO$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.46; H, 5.12; N, 6.04.

In a further experiment, 0.200 g. of *syn*-9-anthraldoxime, m.p. 165°, was placed in 10 ml. of ethanol containing 2 drops of concentrated hydrochloric acid and heated at 75° for 17 hours. Upon cooling, 0.150 g. of material (75%) was separated, m.p. and mixed m.p. with the *anti*-oxime 218–220°.

Treatment of I and II with Acetic Anhydride.—In an effort to compare the ease of dehydration of I and II, 0.22 g. of each was placed in 2 ml. of acetic anhydride and warmed on the steam-bath for 10 minutes. Each solution was then made basic with 2 g. of sodium carbonate in 10 ml. of water and heated on the steam-bath for 10 minutes, cooled, diluted with 20 ml. of water and filtered.

Compound I was converted to a material melting at 132–133°; Fieser and Hartwell[3] give the melting point of the oxime acetate as 131.5–132°. II was converted to a compound melting at 173–174° and a mixed m.p. with 9-cyanoanthracene gave no depression. Refluxing I for 15 minutes with acetic anhydride will also produce 9-cyanoanthracene.[3]

Treatment of I and II with Allyl Chloride.—A mixture of 1.1 g. (0.005 mole) of I, 0.5 ml. (0.005 mole) of allyl chloride and 0.2 g. (0.005 mole) of sodium hydroxide in 2 ml. of water and 10 ml. of ethanol was heated under a reflux condenser to 80° and then allowed to cool. Since the allyl chloride seemed to be evaporating, 0.5 ml. more was added, the mixture was heated to 70° and allowed to cool. A very small amount of precipitate formed so 25 ml. of water was added. A precipitate melting at 75–78° was then formed. Upon dissolving in hot ethanol, diluting with water to the cloud point and allowing to cool, the melting point of the yellow compound O-allyl-*syn*-9-anthraldoxime was raised to 85–86°.

Anal. Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79. Found: C, 82.70; H, 5.60.

About 0.4 g. of the above material was obtained along with a low melting, polymer-like material. Upon heating 0.1 g. of O-allyl-*syn*-9-anthraldoxime in an oil-bath at 200° for ten minutes, 0.04 g. was recovered unchanged, while the remainder of the material was converted to an oil which could not be made to crystallize.

A mixture of 1.1 g. (0.005 mole) of II, 2 ml. (0.02 mole) of allyl chloride and 0.2 g. (0.005 mole) of sodium hydroxide in 2 ml. of water and 50 ml. of ethanol was refluxed for 20 minutes. Ten milliliters of water was added to the hot solution and 0.90 g. of yellow crystals were obtained in three crops: 1st crop, 0.22 g., m.p. 167–173°; 2nd crop, 0.33 g., m.p. 135–155°; 3rd crop, orange-colored resin 0.35 g. Recrystallization of crops I and II gave only 9-cyanoanthracene as isolable products.

Attempted Diels–Alder Reactions.—Compound I gave little evidence of adduct formation when heated under a reflux condenser with allyl alcohol, acrylic acid in sodium hydroxide solution, allyl chloride or acrylyl chloride, and upon refluxing with acrylamide in xylene.

When 1.1 g. of I dissolved in 10 ml. of 5% sodium hydroxide and 6 ml. of allyl alcohol was refluxed for 21 hours almost 1.1 g. of solid, m.p. 175–176°, was obtained and was identified as 9-cyanoanthracene by its color and mixed melting point.

II gave no evidence of adduct formation in reactions under reflux conditions with allyl chloride and acrylyl chloride by heating in a sealed tube reaction with acrylonitrile, or by heating with acrylamide in xylene.

Acrylyl chloride led to 9-cyanoanthracene with both oximes.

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The Preparation and Decarboxylation of Some α-Alkyl-β,β-dimethylglycidates

BY HORTON H. MORRIS AND RAYMOND H. YOUNG, JR.[1]

RECEIVED JULY 28, 1955

The nature of the products obtained by thermal decarboxylation of various α-substituted glycidic acids has been the subject of previous reports[2] from this Laboratory. In order to further establish that ketones, and not aldehydes, result when glycidic acids containing alkyl groups in the α-position undergo decarboxylation, and in continuation of our study of the glycidic ester condensation, an homologous series of previously unreported ethyl α-alkyl-β,β-dimethylglycidates has been prepared, where the alkyl group varies from methyl through nonyl.

The presence of an unsaturated, hydroxy-containing contaminant was detected by means of the infrared spectra in the initial preparations of the α-hexyl, α-heptyl and α-octyl glycidic esters. A report by Johnson, *et al.*,[3] and work to be reported later from this Laboratory strongly suggests that the impurity is the corresponding ethyl α-hydroxy-α-alkyl-β-methyl-β,γ-butenoate. The preparations were repeated, taking special precautions to maintain anhydrous conditions, and the glycidic esters so obtained were easily purified and showed no trace of the contaminant.

The corresponding glycidic acids decarboxylated under the influence of heat to yield the expected 2-methyl-3-alkanones in yields of 50–75%. The structures of the ketones, several of which are new, have been established by alternate syntheses and the determination of mixed melting points of derivatives.

An empirical relationship between the reciprocal of the molecular weight of an organic liquid and its refractive index exists and has proved to be a useful tool in this Laboratory. The general equation is $n^{20}\text{D} = A/M + 1.4704 \pm 0.0006$, where A is a homology constant and M is the molecular weight. The A values for the homologous series reported

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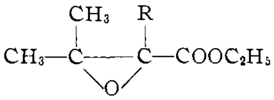
(1) From the thesis submitted by Raymond H. Young, Jr., in partial fulfillment of the requirements of the degree of Master of Science in Chemistry, June, 1955.

(2) H. H. Morris and C. J. St. Lawrence, THIS JOURNAL, **77**, 1692 (1955), and previous papers.

(3) W. S. Johnson, J. Belew, L. Chinn and R. Hunt, *ibid.*, **75**, 4995 (1953).

TABLE I

ETHYL α-ALKYL-β,β-DIMETHYLGLYCIDATES



$$CH_3-\overset{CH_3}{\overset{|}{C}}\underset{O}{\diagdown\!\!\diagup}\overset{R}{\overset{|}{C}}-COOC_2H_5$$

R	Yield, %	B.p. °C.	B.p. Mm.	$n^{20}D$	d^t_4	t, °C.	Carbon, % Found	Carbon, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.
CH_3[6]	63.8	60	4	1.4230	0.9897	20	60.74	61.16	8.92	9.20
					1.0105	0				
C_2H_5	61.4	74	4	1.4252	0.9748	20	62.40	62.71	9.3	9.57
					.9938	0				
C_3H_7	63.5	76	3	1.4289	.9597	20	65.01	64.49	9.60	9.74
					.9771	0				
C_4H_9	62.7	86	4	1.4306	.9510	20	66.28	65.97	9.86	10.07
					.9721	0				
C_5H_{11}	66.5	99	4	1.4331	.9385	20	67.22	67.26	10.36	10.35
					.9575	0				
C_6H_{13}	60.5	120	8	1.4354	.9341	20	68.15	68.38	10.28	10.60
					.9509	0				
C_7H_{15}	46.9	125	4	1.4378	.9257	20	69.13	69.38	10.45	10.82
					.9423	0				
C_8H_{17}	65.2	139	4	1.4388	.9217	20	70.42	70.27	10.51	11.01
					.9380	0				
C_9H_{19}	64.3	136	2	1.4406	.9144	20	71.20	71.07	11.35	11.18
					.9282	0				

here are −7.705 for the glycidic esters, −4.524 for the aliphatic α-bromo esters and −7.615 for the 2-methyl-3-alkanones. The relationship seems to be valid for at least ten other homologous series, the constants of which were obtained from the literature.[4]

Some of the glycidic esters reported here, as well as members of a previously reported series of glycidic esters[5] have shown activity against the fungus organisms causing stem rust of oats and late blight of potatoes. A detailed report of this work will be published at a later date by J. E. Livingston and M. T. Hilborn, Department of Plant Pathology of this university.

Experimental

Preparation of Intermediates.—The α-bromo esters were prepared by the Hell–Volhard–Zelinsky reaction and were purified by fractionation through a 10″ Vigreux column. Potassium *t*-butoxide was prepared as previously described[2,3] from potassium metal and *t*-butyl alcohol which had been purified by repeated partial crystallization.

Preparation of the Glycidic Esters.—The esters were prepared by means of a method reported earlier[2,3] which involved the addition of one mole of potassium *t*-butoxide in excess *t*-butyl alcohol to a cooled, well-stirred mixture of one mole of acetone and one mole of the appropriate α-bromo ester. After the usual heating period and washing procedure, the glycidic esters were distilled through a 10″ Vigreux column and then fractionated through a Todd precise fractionation assembly. Yields were calculated on the basis of material distilling within a 1° range and having refractive index varying no more than 0.0002 unit for all cuts. The physical constants and analyses of the esters are given in Table I.

As mentioned in the discussion, the initial preparation of the α-hexyl, α-heptyl and α-octyl glycidic esters gave products that were difficult to purify. The infrared spectra of the three impure preparations were quite similar and showed an absorption band at 2.8 μ and another at 6.2–6.3 μ. The preparations were repeated, especial care being taken to dry the *t*-butyl alcohol before use, and the three esters so obtained were easily purified. The infrared spectra of the α-heptyl and α-octyl esters were determined on the product from the second preparation and showed no evidence of a hydroxy group or of an alkene linkage.

Saponification and Decarboxylation of the Esters.—The saponification of the esters was accomplished by the method of Claisen which involved the use of one equivalent of sodium ethoxide in excess ethanol, followed by the addition of exactly one equivalent of water.

Most of the glycidic acids were obtained as viscous liquids that could not be induced to crystallize. The α-hexyl and α-heptyl substituted glycidic acids precipitated when the saponification mixtures were poured into an ice–HCl slurry and were recrystallized from petroleum ether to yield products with the properties and analyses given below.

α-*n*-Hexyl-β,β-dimethylglycidic Acid.—The acid was obtained in 99% yield as white platelets which melted at 67–68°. The material did not decolorize a solution of Br_2 in CCl_4 or a permanganate solution. It did not react with sodium metal and gave a negative test with a $FeCl_3$ solution.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.96; H, 10.06; neut. equiv., 200. Found: C, 65.94; H, 9.91; neut. equiv., 199 ± 4.

α-*n*-Heptyl-β,β-dimethylglycidic Acid.—This acid precipitated as white platelets when the saponification mixture was acidified. Recrystallization from petroleum ether gave a 93% yield of material which melted at 71–71.5° and which gave negative tests with Br_2 in CCl_4, permanganate solution, sodium metal and a $FeCl_3$ solution.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35, neut. equiv., 214. Found: C, 67.33; H, 10.54; neut. equiv., 213 ± 3.

The acids were decarboxylated by heating them at a temperature sufficient to cause the steady evolution of carbon dioxide for an 8–10 hr. period at atmospheric pressure. At the end of this time, the decarboxylation product was distilled through a 10″ Vigreux column and was then further purified by fractionation through the Todd assembly. Tables II and III list the physical properties, the yield and derivatives of the 2-methyl-3-alkanones so obtained.

When necessary, authentic samples of the ketones were prepared by the dialkyl cadmium ketone synthesis.[6a] The structure of the decarboxylation products was shown by the determination of mixed melting points of similar derivatives.

Analyses were performed by the Oakwold Laboratories, Alexandria, Va. The infrared spectra of the α-bromo esters, most of the glycidic esters, and most of the ketones were determined by the S. P. Sadtler Research Laboratories, 1517 Vine St., Philadelphia 3, Pa., and copies are available from them.

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(4) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. 4, Physico-Chemical Optics, Longmans, Green & Co., London, 1949.

(5) H. H. Morris and M. L. Lusth, THIS JOURNAL, **76**, 1237 (1954).

(6) G. Darzens, *Compt. rend.*, **141**, 766 (1905).

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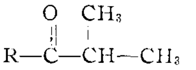
TABLE II

KETONES FROM DECARBOXYLATION OF α-ALKYL-β,β-DIMETHYLGLYCIDIC ACIDS,



$R-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-CH_3$

R	Yield, %	B.p. °C.	B.p. Mm.	$n^{20}D$	d^{t}_{4}	t, °C.	Carbon, % Found	Carbon, % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.
CH_3[7] [a]	..	96	Atm.	....	....	..	...	...	...	...
C_2H_5[8]	51	113	Atm.	1.3971	0.8105	20	...	...	...	...
					.8349	0				
C_3H_7[8]	57.5	133	Atm.	1.4042	.8091	20	...	...	...	...
					.8340	0				
C_4H_9[9]	40	158	Atm.	1.4115	.8163	20	...	...	...	...
					.8333	0				
C_5H_{11}[10]	69.5	72	20	1.4172	.8176	20	...	...	...	..
					.8340	0				
C_6H_{13}	51.5	77	4	1.4226	.8215	20	76.80	76.86	12.64	12.90
					.8369	0				
C_7H_{15}	61	79	3	1.4261	.8243	20	77.11	77.48	12.55	13.02
					.8387	0				
C_8H_{17}	75.5	94	4	1.4300	.8268	20	78.19	78.19	12.82	13.12
					.8419	0				
C_9H_{19}[11]	73.5	111	4	1.4340	.8293	20	78.55	78.72	13.19	13.21
					.8441	0				

[a] Isolated as the 2,4-dinitrophenylhydrazone.

TABLE III

DERIVATIVES OF THE 2-METHYL-3-ALKANONES

R	2,4-Dinitrophenylhydrazone M.p., °C.	Nitrogen, % Found	Nitrogen, % Calcd.	Lit. m.p. °C.	Semicarbazone M.p., °C.	Lit. m.p. °C.
CH_3	122	...	...	122[7]	113	113[7]
C_2H_5	110	...	...	109[8]	81	80[8]
C_3H_7	97.5	19.17	19.04	...	119	119[8]
C_4H_9	73	18.14	18.17	...	110	110[9]
C_5H_{11}	92.5	16.86	17.19	...	77	75[10]
C_6H_{13}	82	16.66	16.66	83[a]	Oil	Oil[a]
C_7H_{15}	103	15.70	15.96	Oil?[a]	Oil	Oil[a]
C_8H_{17}	125	15.77	15.38	125.5[a]	57[c]	..
C_9H_{19}	28	14.45	14.77	36,[11,b] 27[a]	Oil	Oil[a]

[a] Alternate synthesis product. Mixed melting point determinations showed no depression. [b] Apparently this value is incorrect. [c] Calcd.: N, 16.72. Found: N, 16.73.

Acknowledgment.—We wish to express our appreciation for the financial aid given us through a Frederick Gardner Cottrell grant from Research Corporation.

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Triphenylethylene Derivatives. II

BY TOYOYUKI NAGANO

RECEIVED MAY 9, 1955

Although triphenylhaloethylenes with estrogenic properties and triphenylethanes with low estrogenic activity are well known,[1] the estrogenic properties of triphenylhaloethanes have not been reported. The author has prepared some examples of the latter type in order to study their biological behavior.

1,2,2-Triphenylethanone, obtained by the Friedel–Crafts condensation of desyl bromide with benzene, was converted to the corresponding ethanol by reduction with sodium borohydride. The ethanol, on treatment with thionyl chloride, gave the desired 1,2,2-triphenyl-1-chloroethane.

Although diphenylacetic acid is converted to the crystalline acid chloride by treatment with phosphorus trichloride, only the acid anhydride was obtained in crystalline form from *p*-anisylphenylacetic acid by this treatment. The slow crystallization of the acid anhydride from a benzene–petroleum ether solution of the reaction product was accompanied by the faint, but continuous, evolution of hydrogen chloride. Presumably, the intermediate ketene was formed spontaneously and reacted with the trace of moisture present to give the acid anhydride.

Experimental

1,2,2-Triphenylethanone[2] **(I).**—Compound I was obtained by the condensation of desyl bromide with benzene in the presence of aluminum chloride in 85% yield, m.p. 136–138°.

1,2,2-Triphenylethanol (II).—Compound I (0.27 g., 0.001 mole) was dissolved in hot methanol (30 ml.). When the solution was cooled to 30°, sodium borohydride (0.05 g., 0.0013 mole in 1 ml. of water) was added dropwise with stirring. After standing for 30 minutes at room temperature, the reaction mixture was concentrated to 15 ml. on a water-bath and water (50 ml.) added. The precipitate which was collected after a few hours (0.27 g. of the crude product) was recrystallized from hot 60% acetic acid as colorless needles, m.p. 88–89°, reported m.p. 87°,[3] m.p. 87.5–88.5°.[4]

1,2,2-Triphenyl-1-chloroethane (III).—To a cold solution of II (0.27 g., 0.001 mole) in pyridine (0.15 ml., 0.0019 mole) was added thionyl chloride (0.1 ml., 0.0013 mole) with stirring. After the slurry had stood overnight at room temperature, water (10 ml.) was added and the solid material collected. The crude product (0.28 g.), on crystallization

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