entirely suitable for synthetic purposes. Recrystallization from carbon tetrachloride gave pure product in 75–80% yields.

The sulfenyl bromide may be stored indefinitely in a dark bottle without noticeable decomposition; but it decomposes rapidly if exposed to bright sunlight.

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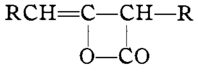
The Catalytic Hydrogenation of Alkylketene Dimers

BY CARL M. HILL, LONNIE HAYNES AND MARY E. HILL

In an earlier paper[1] experiments describing the ozonization and catalytic hydrogenation of five cyclohexyl substituted alkylketene dimers were reported. Ozonization data were in agreement with the work of Hurd and Blanchard[2] and structure I was accepted for the dimers. Hydrogenation yielded glycols, $RCH_2–CHOH–CHR–CH_2OH$.



$$\begin{array}{l} RCH{=}C{-}CH{-}R \\ \quad\;\; | \quad\; | \\ \quad\;\; O{-}CO \end{array}$$

I

TABLE I

GLYCOLS FORMED, $RCH_2—CHOH—CHR—CH_2OH$

R	Formula	B.p. °C.	Mm.	Yield, %	No. OH	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
C_2H_5	$C_8H_{18}O_2$[b]	82–85	16	80	2.1	65.75	66.06	12.33	12.31
n-C_3H_7	$C_{10}H_{22}O_2$[c]	98–100	12	56	1.9	68.96	68.81	12.64	12.56
n-C_4H_9	$C_{12}H_{26}O_2$[d]	125–127	12	28	1.8	71.30	71.66	12.90	13.04
n-C_5H_{11}[a]	$C_{14}H_{30}O_2$[e]	128–130	23	63	1.8	73.04	73.47	13.04	13.06
n-$C_{10}H_{21}$	$C_{24}H_{50}O_2$	M.p. 175–176		43	2.2	77.84	77.34	13.51	13.59
n-$C_{12}H_{25}$	$C_{28}H_{58}O_2$	M.p. 167–168		94	2.1	78.87	78.96	13.62	13.76

[a] Physical constants for new ketene dimer where R is *n*-pentyl: b.p. 128–130° (8 mm.); n^{20}_D 1.4330; d^{20}_4 0.8463. Calcd. C, 75.00; H, 10.71. Found: C, 75.41; H, 10.81. Identity, further established by conversion to 2-*n*-pentyl-1,3-nonanediol.[e] [b] Reported b.p. 133–134° (15 mm.) d^{15}_4 0.9367, n^{15}_D 1.4535 by V. Grignard and M. Fluchaire, *Ann. chim.*, **9**, 5 (1928). Observed d^{20}_4 0.9130, n^{20}_D 1.4230; *MR*D (calcd.) 42.19, (found) 41.00. [c] Reported b.p. 138–139° (1 mm.), d^{28} 0.9203, n^{28} 1.4442 by M. S. Kulpinski and F. F. Nord, *J. Org. Chem.*, **8**, 256 (1943). Observed d^{20}_4 0.8919, n^{20}_D 1.4265; *MR*D (calcd.) 51.43, (found) 50.40. [d] Literature b.p. 128–129° (1 mm.), d^{25} 0.9184, n^{25} 1.4570 reported by M. S. Kulpinski and F. F. Nord, footnote *c;* observed n^{20}_D 1.4270. [e] Reported b.p. 125–127° (0.5 mm.), d^{23} 0.8984, n^{23} 1.4545 by M. S. Kulpinski and F. F. Nord, footnote *c;* observed d^{20}_4 0.8653, n^{20}_D 1.4350; *MR*D (calcd.) 69.90, (found) 69.50.

TABLE II

DERIVATIVES OF THE GLYCOLS

	3,5-Dinitrobenzoate[a]					Phenylurethan[a]				
R	Formula	Yield, %	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found	Formula	Yield, %	M.p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
C_2H_5	$C_{22}H_{22}O_{12}N_4$	49	165–166	10.50	10.80	$C_{22}H_{28}O_4N_2$	53	124–125	7.29	7.00
n-C_3H_7	$C_{24}H_{26}O_{12}N_4$	90	160–161	9.96	9.94	$C_{24}H_{32}O_4N_2$	59	198–200 dec.	6.80	6.90
n-C_4H_9	$C_{26}H_{30}O_{12}N_4$	75	164–165	9.50	9.52	$C_{26}H_{36}O_4N_2$	50	220–222 dec.	6.36	6.02
n-C_5H_{11}	$C_{28}H_{34}O_{12}N_4$	74	163–164	9.06	9.05	$C_{28}H_{40}O_4N_2$	43	223–224	5.98	5.79
n-$C_{10}H_{21}$	$C_{38}H_{54}O_{12}N_4$	88	160–162	7.39	7.32	$C_{38}H_{60}O_4N_2$[b]	26	218–220 dec.	4.61	4.87
n-$C_{12}H_{25}$	$C_{42}H_{62}O_{12}N_4$	63	164–165	6.89	6.71	$C_{42}H_{68}O_4N_2$[c]	33	229–230	4.22	4.21

[a] % Nitrogen determined by micro Dumas method. [b] *Anal.* Calcd.: C, 71.62; H, 9.87. Found: C, 72.00; H, 9.75. [c] *Anal.* Calcd.: C, 75.90; H, 10.24. Found: C, 75.62; H, 10.10.

In the present work, the hydrogenation experiments were extended to six more alkylketene dimers, all prepared by the general method of Sauer.[3] Experimental details were the same as in reference 1 except that ethanol was used as solvent in place of ethanol–hexane, and hydrogen pressures and temperatures were different.

Samples of 3–4 g. of dimer and 25 ml. of ethanol were used. Glycols were formed as before, and derivatives (3,5-dinitrobenzoates and phenylurethans) were prepared as previously reported. The solid glycols were purified by recrystallization from ethanol. Results are described in Tables I and II.

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(1) C. M. Hill, M. E. Hill, H. I. Schofield and L. Haynes, THIS JOURNAL, **73**, 166 (1952).

(2) C. D. Hurd and C. A. Blanchard, *ibid.*, **72**, 1461 (1950).

(3) J. C. Sauer, *ibid.*, **69**, 2444 (1947).

Constituents of *Heliopsis* Species. II. Synthesis of Compounds Related to Scabrin[1]

BY MARTIN JACOBSON

RECEIVED DECEMBER 1, 1951

The isolation of scabrin, the major insecticidal component of the roots of *Heliopsis scabra* Dunal., was reported in the first paper[2] of this series. It was found to be the N-isobutylamide of an unsaturated 18-carbon straight-chain acid, containing 5 double bonds which are situated in the acid fragment in one of 4 possible combinations—namely, 2,4,8,10,14-, 2,4,8,12,14-, 2,6,8,10,14- and 2,6,10,-12,14.

In view of the high toxicity of scabrin to house flies,[2] it was decided to prepare the N-isobutylamides of several of the more readily available C_{18} acids for insecticidal testing. The acids chosen as starting materials were *cis*-9-octadecenoic (oleic), *trans*-9-octadecenoic (elaidic), 9,12-octadecadienoic (linoleic), 9,12,15-octadecatrienoic (linolenic), α- and β-9,11,13-octadecatrienoic (eleostearic) and 10,12,-14-octadecatrienoic (pseudo-eleostearic).

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(1) Report of a study made under the Research and Marketing Act of 1946.

(2) M. Jacobson, THIS JOURNAL, **73**, 100 (1951).

Although Bauer[3] stated that "oxalyl chloride is the only reagent capable of converting the higher unsaturated fatty acids to their acid chlorides in reasonably good yields," we were able to prepare the acid chlorides of the above acids in 83–90% yields by treating the acid in petroleum ether with an excess of thionyl chloride overnight at room temperature. The acid chlorides of the eleostearic and pseudo-eleostearic acids were not isolated since it was feared that considerable decomposition would occur if their distillation were attempted.

The N-isobutylamides were prepared in excellent yield by addition of the acid chloride to a cold ether solution of excess isobutylamine. The isobutylamides of oleic, linoleic and linolenic acids were viscous oils at room temperature, and the others were solids. The α- and β-forms of eleostearic acid gave only the β-form of the isobutylamide, isomerization probably occurring during preparation of the acid chloride. The α-form of eleostearic acid and its derivatives isomerizes rather readily to the β-form.[4]

In contrast to scabrin, all the isobutylamides described in this paper proved to be inactive when tested at high concentration against house flies,[5] showing little knock-down or mortality.

TABLE I

YIELDS AND PROPERTIES OF ACID CHLORIDES

Acid chloride	Yield, %	B.p. °C.	B.p. Mm.	$n^{25}D$	Chlorine, % Calcd.	Chlorine, % Found
Oleic	84	135	0.3[a]	1.4598	11.78	11.75
Elaidic	83	150	.3[a]	1.4595	11.78	11.80
Linoleic	86	148	.3[b]	1.4680	11.87	11.89
Linolenic	90	142	.2	1.4800	11.95	12.02

[a] F. Krafft and F. Tritschler, *Ber.*, **33**, 2580 (1900), report b.p. 213° (13.5 mm.) for oleoyl chloride and b.p. 216° (13 mm.) for elaidoyl chloride. [b] P. E. Verkade, *Rec. trav. chim.*, **62**, 393 (1943), reports b.p. 167–168° (2.3 mm.) for linoleoyl chloride.

Oleic, elaidic, linoleic and linolenic acids and their isobutylamides all showed blue fluorescence in ultraviolet light, while the eleostearic acids and pseudo-eleostearic acid and their isobutylamides did not possess this property. This is especially interesting in view of the fact that *Heliopsis scabra* roots have been shown to contain, in addition to scabrin, an as yet unidentified blue-fluorescing component with considerable activity against house flies.[2]

TABLE II

YIELDS AND PROPERTIES OF N-ISOBUTYLAMIDES

N-Isobutylamide	Yield, %	B.p. °C.	B.p. Mm.	M.p., °C.	$n^{25}D$	Hydrogen uptake, moles	Nitrogen, % Calcd.	Nitrogen, % Found
Oleic	93	185	0.2	21.0–22.0	1.4645	0.97	4.15	4.16
Elaidic[a]	97	...	..	54.5–55.0	....	1.00	4.15	4.15
Linoleic	88	203	0.3	4.0–5.0	1.4710	1.98	4.18	4.19
Linolenic	91	196	0.25	....	1.4816	3.00	4.23	4.24
α-Eleostearic[b]	80[d]	...	..	78.0–79.0[e]	....	2.95	4.23	4.20
β-Eleostearic[b]	86[d]	...	..	78.0–79.0[e]	....	2.99	4.23	4.21
Pseudo-eleostearic[c]	81[d]	...	..	90.0–91.0	....	3.00	4.23	4.20

[a] Colorless needles from petroleum ether (b.p. 30–40°). [b] Colorless needles from hexane. [c] Colorless needles from 90% ethanol. [d] Based on quantitative yield of acid chloride. [e] Mixed m.p. with isomeric form, 78.0–79.0°.

Experimental[6]

Materials.—Oleic, linoleic and linolenic acids were obtained from Hormel Foundation, Austin, Minn. The oleic acid was of 98.3% purity and had m.p. 13°, b.p. 151° (0.2 mm.), $n^{25}D$ 1.4580.[7] The linoleic acid was of 99.4% purity and had b.p. 152° (0.2 mm.), $n^{25}D$ 1.4675.[8] The linolenic acid was of 99.5% purity and showed b.p. 155° (0.2 mm.), $n^{25}D$ 1.4780.[9] Elaidic acid of 99% purity, m.p. 43.7–43.9°, was kindly supplied by Dr. D. Swern, Fats and Oils Division, Eastern Regional Research Laboratory, U. S. Department of Agriculture, Philadelphia, Pa. α-Eleostearic acid, m.p. 48°, was obtained from commercial tung oil fatty acids by the method of Thomas and Thomson.[10] β-Eleostearic acid, m.p. 71–72°, was obtained by isomerization of the α-acid in petroleum ether using ultraviolet light and a trace of iodine (Thomas and Thomson, ref. 10, give m.p. 70–71° for this acid). Pseudo-eleostearic acid, m.p. 79–81°, was obtained from commercial linseed fatty acids by the ethylene glycol procedure of Kass and Burr.[11]

Acid Chlorides.—The acid chlorides were prepared by allowing an anhydrous petroleum ether (b.p. 30–40°) solution of the acid and 50% excess of thionyl chloride (purified by distillation over quinoline and boiled linseed oil) to stand at room temperature overnight and then removing the solvent and excess thionyl chloride under reduced pressure (temperature below 40°). Both β-eleostearic acid and pseudo-eleostearic acid were insoluble in petroleum ether, but went into solution gradually as the reaction proceeded. The acid chlorides of α- and β-eleostearic and pseudo-eleostearic acids were not isolated by distillation, the crude products being used directly for the preparation of the isobutylamides, assuming quantitative conversion of the acids. The pure acid chlorides of oleic, elaidic, linoleic and linolenic acids were obtained as colorless liquids by distillation under reduced pressure, and their properties are summarized in Table I.

N-Isobutylamides.—To an ice-cold solution of 100% excess of isobutylamine in anhydrous ether an anhydrous ether solution of the acid chloride was added slowly with stirring. After the mixture had stood at room temperature for one hour, the precipitated amine hydrochloride was dissolved by the addition of dilute hydrochloric acid, and the ether layer was washed with water, 5% potassium hydroxide solution, and water, then dried and evaporated. The residue was then distilled under reduced pressure or recrystallized.

The isobutylamide of both α- and β-eleostearic acids proved to be the β-isomer. The isobutylamides of oleic, elaidic, linoleic and linolenic acids exhibited strong blue fluorescence in ultraviolet light, as did the parent acids and acid chlorides. Although all the isobutylamides prepared, except that of elaidic acid, were rather unstable at room temperature, N-isobutyleleostearamide and N-isobutylpseudo-eleostearamide were particularly unstable owing to

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[3] S. T. Bauer, *Oil and Soap*, **23**, 1 (1946).

[4] A. W. Ralston, "Fatty Acids and Their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 137, 139.

[5] These tests were made by W. A. Gersdorff and N. Mitlin of this Bureau.

[6] All melting points are corrected; boiling points are uncorrected.

[7] A. W. Ralston, ref. 4, p. 109 gives m.p. 13°, b.p. 200-201° (1.2 mm.), and $n^{20}D$ 1.45823 for pure natural oleic acid.

[8] A. W. Ralston, ref. 4, p. 129 gives b.p. 202° (1.4 mm.), and $n^{21.5}D$ 1.4683 for linoleic acid.

[9] A. W. Ralston, ref. 4, p. 136 gives b.p. 157–158° (0.001–0.002 mm.) and $n^{20}D$ 1.4795 for linolenic acid.

[10] A. W. Thomas and J. C. Thomson, THIS JOURNAL, **56**, 898 (1934).

[11] J. P. Kass and G. O. Burr, *ibid.*, **61**, 3292 (1939).

their conjugation. However, they could all be kept indefinitely under nitrogen at 5°.

Hydrogenation of the isobutylamides in ethanol solution using platinum oxide catalyst, gave in each case N-isobutylstearamide, m.p. 77–78°, undepressed by admixture with an authentic sample, m.p. 77–78°.[2]

The properties of the isobutylamides are summarized in Table II.

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The Alkaline and Neutral Hydrolysis of 2-Methoxyethyl Iodide

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RECEIVED OCTOBER 25, 1951

This work was undertaken to determine whether or not the Hinshelwood, Laidler and Timm theory[1] would again[2] predict the correct qualitative trend in activation energy for the neutral hydrolysis of another organic iodide. The alkaline hydrolysis was studied in order to show that the formation of ethylene iodohydrin by reaction in basic solution is associated with the fact that there is a hydrogen which is easily ionizable[3] in the iodohydrin, whereas, when this hydrogen is replaced by methyl, the ordinary replacement of OH for I is obtained.

Experimental

The 2-methoxyethyl iodide was prepared from 2-methoxyethyl chloride. This latter compound was obtained by the reaction of methyl cellosolve with thionyl chloride in dimethylaniline.[4] The 2-methoxyethyl iodide was obtained by treating the corresponding chloride, obtained above, with sodium iodide in 95% ethanol.[5] The product of this reaction was purified by vacuum distillation. The boiling point at 35 mm. pressure was 53.5°. Pressure fluctuations caused the constancy of boiling point not to be indicative of purity. Powdered silver was used to keep iodine from distilling over. An analysis of the final product was made by completely hydrolyzing a weighed sample and titrating iodide by a potentiometric method described below. The analysis showed the product was 99% pure.

The 1,4-dioxane was Eastman Kodak Co. Best Grade. It was further purified by refluxing over metallic sodium, followed by distillation. The final product was not appreciably alkaline, as shown by titration with standard acid.

The neutral hydrolysis kinetics experiments were carried out in sealed tubes immersed in an oil thermostat which held to ± 0.05°. An approximately 0.02 *N* stock solution of 2-methoxyethyl iodide was made up before each run. A magnetic stirrer was employed to quicken the solution. Reaction tubes of about 25-cc. capacity were filled with this solution, sealed off, and placed in the thermostat for known lengths of time. Care was exercised to make the gas space above the solution as low as possible (~ 1 cc.) since appreciable amounts of the organic iodide would have accumulated there. Reproducible results were obtained even though the small gas space was varied by a factor of 2 or 3. The tubes were removed from the thermostat, cooled quickly, and a 20.00-ml. sample was titrated with silver nitrate to determine the amount of I^- formed. This was assumed to equal the amount of 2-methoxyethyl iodide which had been hydrolyzed. The end-point was obtained potentiometrically, using a silver electrode, sealed in the tip of the buret containing the silver nitrate, *vs.* a silver–silver iodide electrode in the solution being titrated.[6] The concentration of the 2-methoxyethyl iodide stock solution was obtained by letting a sample stay in the thermostat or, in some cases, boiling water, until the reaction was at least 99.9% completed.

The temperatures were determined by an N.B.S. platinum resistance thermometer and a Mueller bridge.

The alkaline hydrolysis was carried out in polyethylene bottles, since considerable difficulty with silica formation was experienced in Pyrex tubes when the temperature was above 60°.

The product of the alkaline hydrolysis of 2-methoxyethyl iodide in pure water was established as methyl cellosolve by extraction of the product from the aqueous phase by chloroform. The chloroform layer was dried with potassium carbonate, followed by magnesium sulfate. Comparison of the infrared spectrum of this solution and that of a synthetic solution of methyl cellosolve showed the same strong absorption at 9.1 microns. The general shape of the absorption band was sufficient to identify the reaction product as methyl cellosolve. A Baird Infrared Spectrophotometer was used for the analysis.

Experimental Results

The Neutral Hydrolysis.—The neutral hydrolysis in all cases followed the usual first order plot of concentration of 2-methoxyethyl iodide *vs.* time, showing the absence of appreciable salt effects and giving confidence that the starting reactant was pure and that the reaction was not catalyzed by the presence of small amounts of I_2 which appeared during the course of the reaction from the air oxidation of I^-.

The velocity constants were determined from the slope of the line obtained by plotting the log of the concentration of the 2-methoxyethyl iodide in the various tubes withdrawn at different times as a function of the time withdrawn. Duplicate runs gave satisfactory checks as seen in Table I. The percentages are given by weight.

TABLE I

Temp., °C.	Solvent	k(hr.$^{-1}$)	k(average)
91.06	Water	2.99×10^{-2}	2.98×10^{-2}
91.06	Water	2.97×10^{-2}	
91.06	20.8% EtOH	1.90×10^{-2}	1.91×10^{-2}
91.06	20.8% EtOH	1.92×10^{-2}	
91.06	44.1% EtOH	1.21×10^{-2}	1.23×10^{-2}
91.06	44.1% EtOH	1.25×10^{-2}	
99.76	Water	7.19×10^{-2}	7.22×10^{-2}
99.76	Water	7.25×10^{-2}	
107.89	Water	1.50×10^{-1}	1.58×10^{-1}
107.89	Water	1.66×10^{-1}	

The Alkaline Hydrolysis.—The alkaline hydrolysis showed second order kinetics as shown by linearity of the plot of $\log b - x/a - x$ *vs.* t. From the slope of this line the velocity constant was calculated from, slope $= 2.303/k(a - b)$.[7] At the low temperatures the reaction was followed to about 30% completion, while at the higher temperatures to about 80% completion. The kinetic results are summarized in Table II. Preliminary experiments in ethanol–water mixtures are not reported in the table because the precision of the results does not warrant it. However, it was found that in a 33.3% by volume ethanol-water solution at 70°, the k was 1.2, while k was 0.8 in a

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(1) C. N. Hinshelwood, H. J. Laidler and E. W. Timm, *J. Chem. Soc.*, 848 (1938).

(2) H. D. Cowan, C. L. McCabe and J. C. Warner, THIS JOURNAL, **72**, 1194 (1950).

(3) C. L. McCabe and J. C. Warner, *ibid.*, **70**, 4031 (1948).

(4) G. M. Bennett and F. Heathcoat, *J. Chem. Soc.*, 270 (1929).

(5) L. C. Swallen and C. E. Boord, THIS JOURNAL, **52**, 665 (1930).

(6) H. H. Willard and A. W. Boldyreff, *ibid.*, **51**, 471 (1929).

(7) Samuel Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., p. 1056.