[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, TENNESSEE AGRICULTURAL AND INDUSTRIAL STATE COLLEGE]

Ozonization and Catalytic Hydrogenation of Cyclohexylketene Dimer and (ω-Cyclohexylalkyl)-ketene Dimers

BY CARL M. HILL, MARY E. HILL, HELEN I. SCHOFIELD AND LONNIE HAYNES

Five monosubstituted ketene dimers of the type: $[C_6H_{11}-(CH_2)_n-CHCO]_2$, where n is 0 to 4, have been treated with ozone and hydrogen under high pressure and in the presence of Raney nickel catalyst. The results of this investigation point to the β-lactone structure with an exocyclic carbon–carbon double bond as a most likely formulation for these ketene dimers.

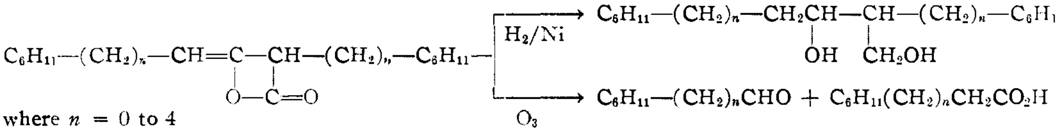
Recently, several investigators[1-4] have reported studies aimed at elucidation of the structure of monosubstituted ketene dimers. This paper describes ozonization and catalytic reduction of five ω-cyclohexyl substituted ketene dimers: namely, ketene, methyl-, β-ethyl-, γ-propyl- and δ-butylketene.

For this investigation, it was assumed that these ketene dimers were of the β-lactone structure. It was expected that ozone would add at the olefinic bond and that decomposition of the ozonide would yield the corresponding cyclohexyl substituted aldehyde and acid. The results of this study show that each of the five ketene dimers investigated reacted with ozone to give, upon distillation, the ω-cyclohexyl substituted aldehyde and fatty acid postulated from the β-lactone structure with an exocyclic carbon–carbon olefinic bond.

High pressure reduction of these dimers in the presence of Raney nickel catalyst opens the β-lactone ring at the oxygen–carbonyl bond forming ω-cyclohexyl substituted glycols which were believed to contain one primary and one secondary hydroxyl group. The glycols were low-melting white solids or colorless liquids and gave negative tests for unsaturation. Resistance of the glycols to cleavage by periodic acid indicated that the hydroxyl groups were separated by at least one carbon atom. Four of the glycols reacted smoothly with 3,5-dinitrobenzoyl chloride and phenyl isocyanate to give the dibenzoates and diurethans, respectively. The glycol from cyclohexylketene dimer indicated only one hydroxyl group as shown by hydroxyl determination and urethan formation. Proximity of the cyclohexyl ring to one of the postulated hydroxyl groups could conceivably exert a shielding or steric hindrance effect upon the reactivity of the hydroxyl.

The satisfactory yields of the glycols (with one exception) suggest that catalytic reduction might serve as a preparative procedure.

Formation of the ozonization and hydrogenation–hydrogenolysis products is illustrated by the scheme



where n = 0 to 4

Results of these ozonization and reduction studies are consistent with the β,γ-unsaturated β-lactone structure for these dimers.

Acknowledgment.—The authors express their appreciation to the Research Corporation for several Frederick Gardner Cottrell grants which assisted financially this investigation.

Experimental

Ketene Dimers.—The five monosubstituted ketene dimers used in this investigation were prepared and purified according to the procedure of Hill and Senter.[5]

Ozonization of Dimers.—A weighed sample (5 to 15 g.) of each dimer was dissolved in 150 ml. of dry petroleum ether and treated at 0° with 5% ozone stream until no more was absorbed. This required from 20 to 30 hours. The solvent was removed and the ozonide added dropwise and with stirring to a warm mixture of water, zinc and a trace of silver nitrate. The ozonolysis mixture was extracted several times with *n*-hexane and the combined extracts dried. After removal of the solvent, the residue was distilled from a modified Claisen flask. The final distillation products isolated are described in Table I. All observed melting points in this paper are corrected.

High Pressure Catalytic Reduction.—The Parr high pressure apparatus, serial number 136, with 3-A-169-H-C-5 bomb, was employed for reduction of the ketene dimers. The Raney nickel catalyst was prepared by the procedure of Mozingo[6] and stored under ethanol. Samples of the ketene dimers (10–15 g.) were dissolved in 25 ml. of a *n*-hexane–ethanol mixture, to which was added 2–3 g. of Raney nickel catalyst. Temperatures of 230 to 300° and hydrogen pressures of 2900 to 3700 p.s.i. were used. The desired bomb temperature and hydrogen pressure were attained within one hour, and maintained for one to two hours. The bomb was rocked during the period of reduction. The decrease in hydrogen pressure at the temperature and pressure of each experiment corresponded approximately to the absorption of three mole equivalents of hydrogen. The bomb was allowed to cool overnight and its contents filtered free of catalyst. The solvent was removed and the residue distilled under reduced pressure from a modified Claisen flask constructed for distillation of solid substances.

Physical constants and analytical data for the reduction products are given in Table II.

Determination of Number of Hydroxyl Groups.—The hydroxyl content of each of the hydrogenation–hydrogenolysis products was determined by the procedure of Siggia.[7] The results of these determinations are shown in Table II.

Attempted Cleavage by Periodic Acid.—A sample of each reduction product was treated with periodic acid by the method of Shriner and Fuson.[8] In each case the results were negative.

---

[1] F. A. Miller and S. D. Koch, Jr., THIS JOURNAL, **70**, 1890 (1948).

[2] A. T. Blomquist and F. H. Baldwin, *ibid.*, **70**, 29 (1948).

[3] J. D. Roberts, R. Armstrong, R. F. Trimble and M. Beng, *ibid.*, **71**, 843 (1949).

[4] C. D. Hurd and C. A. Blanchard, *ibid.*, **72**, 1461 (1950).

[5] C. M. Hill and G. W. Senter, *ibid.*, **71**, 364 (1949).

[6] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

[7] S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 4.

[8] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 115.

TABLE I

OZONIZATION PRODUCTS OF ω-CYCLOHEXYLKETENE DIMERS OF TYPE $[C_6H_{11}-(CH_2)_n-CHCO]_2$

	Aldehyde							
n	ω-Cyclohexyl	Yield, %	B.p. °C.	Mm.	$d^{20}{}_4$	$n^{20}{}_4$	*MRD* Found	Calcd.
0	Formaldehyde[a]	55	41–44	10	0.9035	1.4274	31.86	32.82
1	Acetaldehyde[b]	74	83–85	5	.9446	1.4520	35.99	37.44
2	Propionaldehyde[c]	90	40–42	92	.8201	1.4134	42.60	42.05
3	Butyraldehyde[d]	86	110–112	750	.8259	1.4180	46.99	46.67
4	Valeraldehyde[e]	46	145–148	750	.8846	1.4340	49.46	51.29

	Acid							
n	ω-Cyclohexyl	Yield, %	B.p. °C.	Mm.	$d^{20}{}_4$	$n^{20}{}_4$	*MRD* Found	Calcd.
0	Acetic[f]	87	122–125 (m.p., 30–31)	5	0.9335	1.4775	...	...
1	Propionic[g]	90	124–126	4	.9948	1.4770	44.31	43.57
2	Butyric[g]	24	135–137	5	.9491	1.4768	50.58	48.20
3	Valeric[g]	36	129–132	3	.9876	1.4754	52.49	52.81
4	Caproic[g]	26	134–136	1	.9626	1.4750	57.91	57.43

[a] Semicarbazone, m.p. 175–176°, reported m.p. 176° by L. Bouveault, *Chem. Centr.*, **74**, II, 1437 (1903); % nitrogen (found) 24.89, (calcd.) 24.85. [b] 2,4-Dinitrophenylhydrazone, m.p. 64–65°, reported m.p. 124–125° by H. Rupe, W. Messner and E. Kambli, *Helv. Chim. Acta*, 11, 449–462 (1928); % nitrogen (found) 17.95, (calcd.) 18.30. [c] Reported b.p. 40–42° (95 mm.) by Freendler, *Bull. soc. chim.*, [3] **35**, 544 (1906). [d] 2,4-Dinitrophenylhydrazone, m.p. 124–125°; semicarbazone, m.p. 181–182°; nitrogen (calcd.) 16.76, (found) 16.61; (calcd.) 19.89, (found) 19.56, respectively; C (calcd.) 77.92, (found) 77.42; H (calcd.) 11.68, (found) 11.56. [e] Semicarbazone, m.p. 78–79°; nitrogen (found) 19.01, (calcd.) 18.90. [f] Reported m.p. 29–30°, b.p. 116–117° (4 mm.) by G. S. Hiers and R. Adams, THIS JOURNAL, **48**, 2385 (1926). [g] Reported b.p. by G. S. Hiers and R. Adams, *ibid.*, **48**, 2385 (1926), 125–126° (4 mm.), 132–134° (3 mm.) 151–153° (5 mm.), and 157–158° (4 mm.), respectively.

TABLE II

CATALYTIC REDUCTION PRODUCTS OF ω-CYCLOHEXYLKETENE DIMERS OF TYPE $[C_6H_{11}-(CH_2)_n-CHCO]_2$

	Products						Analyses, %			
							Carbon		Hydrogen	
n	Formula	Yield, %	B.p. °C.	Mm.	M.p., °C.	No. OH	Calcd.	Found	Calcd.	Found
0	$C_{16}H_{30}O_2$	87	130–134	3	34–36	1.1	75.59	74.90	11.81	11.52
1	$C_{18}H_{34}O_2$	89	180–184	10	35–37	1.8	76.60	75.90	12.06	12.04
2	$C_{20}H_{38}O_2$	21	207–208	10	36–37	1.8	77.42	77.02	12.26	12.21
3	$C_{22}H_{42}O_2$	98	190–194	6	6–8	2.1	78.11	78.62	12.43	12.62
4	$C_{24}H_{46}O_2$	75	200–205	6	18–19	2.3	78.69	78.50	12.57	12.97

TABLE III

DERIVATIVES OF CATALYTIC REDUCTION PRODUCTS OF KETENE DIMERS

	3,5-Dinitrobenzoate					Phenylurethan								
				Nitrogen,[a] %					Nitrogen,[a] %		Carbon, %		Hydrogen, %	
n	Formula	Yield, %	M.p., °C.	Calcd.	Found	Formula	Yield, %	M.p., °C.	Calcd.	Found	Calcd.	Found	Calcd.	Found
0	$C_{30}H_{34}O_{12}N_4$	55	102–103	8.72	8.59	$C_{23}H_{35}O_3N$[b]	68	111–112	3.75	3.68	74.00	73.89	9.38	9.26
1	$C_{32}H_{38}O_{12}N_4$	96	149–150	8.36	8.61	$C_{32}H_{44}O_4N_2$	87	83–84	5.39	5.28				
2	$C_{34}H_{42}O_{12}N_4$	36	53–54	8.17	7.76	$C_{34}H_{48}O_4N_2$	68	141–142	5.10	4.99				
3	$C_{36}H_{46}O_{12}N_4$	56	151–152	7.55	7.56	$C_{36}H_{52}O_4N_2$	94	136–137	4.86	5.01	75.00	74.88	9.03	9.00
4	$C_{38}H_{50}O_{12}N_4$	49	152–153	7.43	7.46	$C_{38}H_{56}O_4N_2$	49	137–138	4.63	4.64	75.50	75.70	9.27	9.44

[a] Analyzed for nitrogen by micro Dumas method. [b] Determination of number of hydroxyl groups of the corresponding reduction product and nitrogen analysis indicated this compound to be the monourethan.

3,5-Dinitrobenzoates.—The benzoates were prepared according to a method described by McElvain,[9] using 0.5-g. samples of the reduction products. Physical constants and nitrogen analyses of the benzoates are shown in Table III.

Phenylurethans.—The urethans were prepared from 0.5-g. samples of the reduction products by the method of Shriner and Fuson.[8] Analytical data and melting points of the urethans are given in Table III.

NASHVILLE, TENNESSEE

RECEIVED MAY 28, 1951

---

(9) S. M. McElvain, "The Characterization of Organic Compounds." The Macmillan Company, New York. N. Y., 1947, p. 193.