[Contribution from Department of Chemistry, Tennessee A. and I. State University]

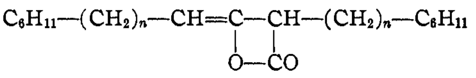
The Lithium Aluminum Hydride Reduction of Cyclohexylketene Dimer and (ω-Cyclohexylalkyl)-ketene Dimers

By Alfred S. Spriggs, Carl M. Hill and Gilbert W. Senter

Five ω-cyclohexyl substituted alkylketene dimers of the type $[C_6H_{11}-(CH_2)_n-CHCO]_2$, where $n = 0$ to 4, have been treated with lithium aluminum hydride. The reduction products isolated were β-hydroxy ketones. Attempts to reduce the fourth member of this series were unsuccessful.

The versatility of lithium aluminum hydride as a reducing agent for various types of chemical systems has been demonstrated by several workers.[1-3] The reagent normally has no action on double bonds, but some examples are cited in which olefinic-bond reduction occurs.[1] Studies have been reported on ring opening of epoxy and lactone systems.[1] Various mechanisms have been proposed to account for the products resulting from the application of this reagent to the systems mentioned.[3,4]

Hill, *et al.*,[5] of this Laboratory have indicated by ozonization and catalytic hydrogenation studies that certain ketene dimers exist chiefly in the β,γ-unsaturated β-lactone structure.



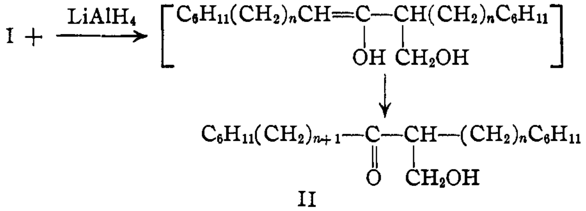
$$C_6H_{11}-(CH_2)_n-CH{=}\underset{\displaystyle O-}{C}-\underset{\displaystyle CO}{CH}-(CH_2)_n-C_6H_{11}$$

I

It was thought that the behavior of these dimers toward lithium aluminum hydride would provide further evidence of their structure.

The ketene dimers used in this study were prepared by dehydrohalogenation of the corresponding ω-cyclohexyl substituted fatty acid chlorides.[6]

The reduction products isolated were β-hydroxy ketones which indicated ring opening of the β-lactone structure at the oxygen–carbonyl bond with subsequent reduction of the carbonyl group and isomerization of the enol form.

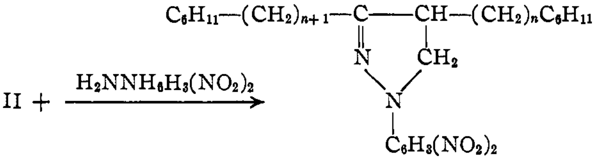


$$I + \xrightarrow{LiAlH_4} \left[C_6H_{11}(CH_2)_nCH{=}\underset{\displaystyle OH}{C}-\underset{\displaystyle CH_2OH}{CH}(CH_2)_nC_6H_{11}\right] \longrightarrow C_6H_{11}(CH_2)_{n+1}-\underset{\displaystyle O}{\overset{}{C}}-\underset{\displaystyle CH_2OH}{CH}-(CH_2)_nC_6H_{11}$$

II

The hydroxy ketones showed one hydroxyl group as determined by hydroxyl analysis and formed mono-3,5-dinitrobenzoates. These ketones gave negative tests for unsaturation, and were not affected by periodic acid. With 2,4-dinitrophenylhydrazine, three of the reduction products formed substituted pyrazolines.

Hydroxy ketones of type (II) could not be further reduced with lithium aluminum hydride. This was of special interest because it has been reported that a similar ketone obtained from ethylketene dimer was reduced by lithium aluminum hydride to the diol.[7] Also, it has been demonstrated in this Laboratory that catalytic hydrogenation of (I) gave the corresponding diol compounds.[5] Failure of lithium aluminum hydride to reduce the ketene dimers to the diol compounds might be due to the incapacity of the reagent to reduce the exocyclic carbon–carbon double bond. Hence, decomposition of the intermediate complex would be followed by isomerization to the keto form (II).



$$II + \xrightarrow{H_2NNHC_6H_3(NO_2)_2} C_6H_{11}-(CH_2)_{n+1}-C-CH-(CH_2)_nC_6H_{11}$$

III

Lithium aluminum hydride reduction of monosubstituted ketene dimers of this type has not been previously reported.

Acknowledgment.—The authors wish to express appreciation to the Research Corporation for several Frederick Gardner Cottrell grants which supported this study. Also, appreciation is extended Dr. C. R. Dillard for assaying the lithium aluminum hydride used in this investigation.

Experimental[8]

Reduction of Ketene Dimers.—Essentially the same procedure was followed in all reduction experiments. The reduction of cyclohexylketene dimer was carried out as follows: A suspension containing 3 g. of lithium aluminum hydride (0.047 mole, 60% assay) in 75 ml. of dry diethyl ether was placed in a three-necked flask equipped with a stirrer, condenser set for reflux, and a dropping funnel. Into the dropping funnel was placed 7 g. (0.027 mole) of cyclohexylketene dimer, b.p. 108–111° (2 mm.). The flask was placed over a hot-plate and the dimer was added at such a rate as to maintain a gentle reflux. After addition of the dimer, the reaction mixture was cooled in a water-bath and the excess lithium aluminum hydride cautiously decomposed with cold water. Hydrogen gas evolved and a white sludge formed. The entire mixture was transferred to a large beaker, cooled in an ice-water-bath and 100 ml. of 20% sulfuric acid added slowly with stirring. The ether layer was separated and the aqueous layer extracted with several portions of ether. The ether layer and extracts were combined, washed with a saturated solution of sodium bicarbonate, then with water and dried over anhydrous magnesium sulfate. A semi-solid residue formed upon removal of the ether *in vacuo*. Distillation of the residue under reduced pressure gave 1.5 g. of a white waxy solid, m.p. 58.5–60°, b.p. 145–148° (4 mm.).

Physical constants and analytical data of the reduction products are given in Table I.

Preparation of Benzoates.—A sample of each reduction product was converted to its 3,5-dinitrobenzoate. Analytical data for these derivatives are shown in Table II.

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[1] R. F. Nystrom and W. G. Brown, This Journal, **69**, 1197 (1947); *ibid.*, **69**, 2548 (1947); *ibid.*, **70**, 3738 (1948).

[2] A. E. Finholt, A. C. Bond and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

[3] R. E. Lutz and D. F. Hinkley, *ibid.*, **72**, 4091 (1950).

[4] L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

[5] C. M. Hill, M. E. Hill, H. I. Schofield and L. Haynes, *ibid.*, **74**, 166 (1952).

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

[7] R. L. Wear, *ibid.*, **73**, 2390 (1951).

[8] All melting points shown in this paper are corrected.

TABLE I

LITHIUM ALUMINUM HYDRIDE REDUCTION PRODUCTS OF ω-CYCLOHEXYLALKYLKETENE DIMERS OF TYPE: $[C_6H_{11}(CH_2)_n—CHCO]_2$

								Analyses, %			
								Carbon		Hydrogen	
n	Moles reagent per mole dimer	Formula	Yield, %	No. OH	B.p. °C.	Mm.	M.p., °C.	Calcd.	Found	Calcd.	Found
0	1.8	$C_{16}H_{28}O_2$	21	0.82	145–148	4	58.5–60	76.2	76.6	11.1	11.4
1	1.7	$C_{18}H_{32}O_2$	62	.77	168–172	3	52.5–53.5	77.1	76.9	11.4	11.8
2	1.8	$C_{20}H_{36}O_2$[a]	45	.90	94–96	10		77.9	78.3	11.8	12.2
4	2.0	$C_{24}H_{44}O_2$	71	.89			39.5–40	79.1	78.8	12.1	12.0

[a] Refractive index^{20}D 1.4771.

TABLE II

DERIVATIVES OF REDUCTION PRODUCTS OF TYPE (II)

	3,5-Dinitrobenzoate				Pyrazoline			
			Nitrogen, %				Nitrogen, %	
n	Formula	M.p., °C.	Calcd.	Found	Formula	M.p., °C.	Calcd.	Found
0	$C_{23}H_{30}O_7N_2$	104–104.4	6.28	6.42	$C_{22}H_{30}N_4O_4$	64–65	13.5	13.7
1	$C_{25}H_{34}O_7N_2$	58–58.5	5.91	6.01	$C_{24}H_{34}N_4O_4$	109	12.7	12.3
2	$C_{27}H_{38}O_7N_2$	55–56	5.58	5.70	[a]			
4	$C_{31}H_{46}O_7N_2$[b]	59	5.02	5.20	$C_{30}H_{46}N_4O_4$	112–113	10.6	10.9

[a] Attempts to isolate the pyrazoline were unsuccessful. [b] *Anal.* Calcd.: C, 66.7; H, 8.24. Found: C, 67.2; H, 8.40.

Preparation of Substituted Pyrazolines.—Treatment of samples of the reduction products with 2,4-dinitrophenylhydrazine, in the usual manner, gave deep orange colored pyrazolines. Several modifications of this procedure failed to produce a suitable derivative of the reduction product where n = 2.

Analytical data of these derivatives are described in Table II.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF SMITH COLLEGE AND WELLESLEY COLLEGE, AND THE DYSON PERRINS LABORATORY OF OXFORD UNIVERSITY]

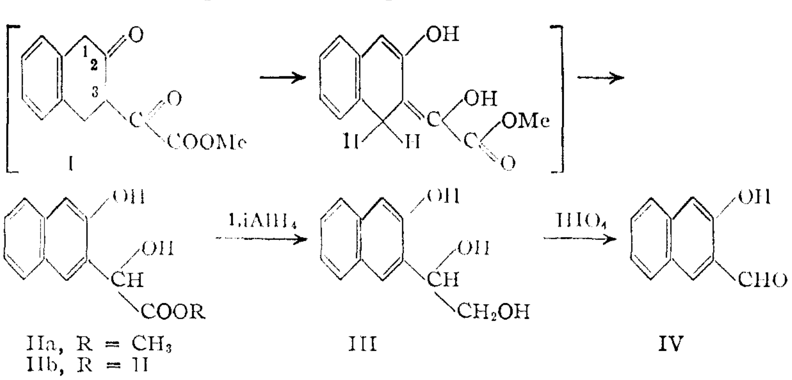
Some Unusual Reactions of 2-Tetralone

BY MILTON D. SOFFER, ROBERTA A. STEWART AND GRACE L. SMITH

Methoxide catalyzed condensation of dimethyl oxalate with 2-tetralone in non-polar media, results in substitution in the 3-position accompanied by dehydrogenation of the tetralone nucleus at the expense of the side chain. The structure of the product, methyl 3-hydroxy-2-naphthylglycolate, is shown by degradation. 2-Tetralone is smoothly converted to β-naphthol by the action of bromine.

Although the alkylation of 2-tetralone and its monocyclic analog, phenylacetone, proceeds exclusively[1,2] in the highly reactive position, C_1, ester condensation may take a different course. It has been shown recently that while formylation of phenyl acetone with ethyl formate occurs at C_3 in the presence of sodium alkoxide or sodamide in non-polar media (ether), the reaction in alcoholic sodium methoxide or ethoxide proceeds exclusively at C_1.[3] On the other hand, the only product reported from the condensation of phenylacetone with ethyl oxalate in the presence of ethanolic sodium ethoxide is the C_3-glyoxalate.[4]

In the present work it was shown that the glyoxalation of 2-tetralone, with methyl oxalate and dry sodium methoxide in benzene, occurs in the 3-position and takes a unique course. The crystalline product had the expected enolic properties, but failed to undergo elimination of carbon monoxide when heated with powdered soft glass.[5] The isolation of methanol from the latter treatment[5] precluded an initial lactone structure.



I

IIa, R = CH_3
IIb, R = H

III

IV

Inspection of the formula for the 3-glyoxalate (I) shows that it may be regarded as the fully ketonoid form of the phenolic hydroxy ester, IIa, which could arise from the glyoxalate by a series

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[1] M. D. Soffer, R. A. Stewart, J. C. Cavagnol, H. E. Gellerson and E. A. Bowler, THIS JOURNAL, **72**, 3704 (1950).

[2] C. M. Suter and A. W. Weston, *ibid.*, **64**, 533 (1942).

[3] M. Montagne, *Bol. inst. quim. Univ. Auton. Mex.*, **2**, No. 2, 57 (1946); *C. A.*, **44**, 130 (1950).

[4] H. Keskin, *Rev. faculté sci. univ. Istanbul*, Ser. A, **11**, No. 4, 143 (1946).

[5] W. E. Bachmann, W. Cole and A. L. Wilds, THIS JOURNAL, **62**, 824 (1940).