

of *o*-acetylbenzoic acid¹¹ in 25 ml. of benzene and 3 ml. of concentrated sulfuric acid at 60–70°, 4.02 g. (0.025 mole) of γ -phenylpropyl azide is added dropwise with stirring. The reaction mixture upon dilution with 25 ml. of water is separated. From the benzene layer a colorless amorphous solid, 3.9 g., m.p. 221–223° after recrystallization from ethanol, is obtained.

Anal. Calcd. for (C₉H₆O₂)_n: C, 73.95; H, 4.11; O, 21.91. Found: C, 73.82; H, 4.28; O, 21.90.

(11) H. L. Vale, *THIS JOURNAL*, **69**, 1547 (1947).

This product, no depression in mixture m.p., is obtained when *n*-butyl azide is substituted for γ -phenylpropyl azide. Under similar experimental conditions in which no azide is present *o*-acetylbenzoic acid is nearly quantitatively recovered.¹²

(12) S. Gabriel, *Ber.*, **17**, 2665 (1884), reports that concentrated sulfuric acid transforms *o*-acetylbenzoic acid into an unidentified compound, C₁₅H₁₂O₄, m.p. 213–215°.

NEW ORLEANS 18, I.A.

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, TENNESSEE A. AND I. STATE UNIVERSITY]

Reduction with Lithium Aluminum Hydride. II. Lithium Aluminum Hydride Reduction of Aryloxyalkylketene Monomers and Dimers

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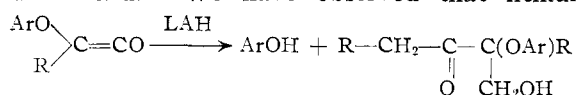
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Lithium aluminum hydride reduction of aryloxyalkylketene monomers and dimers of the type, Ar—C=C=O, where Ar

is *p*-*t*-butylphenoxy and 2,4-dichlorophenoxy, and R is H, C₂H₅, *n*-C₃H₇ and *n*-C₄H₉, has been investigated. Lithium aluminum hydride converted the *p*-*t*-butylphenoxyalkylketene monomers to β -ketocarbinols and *t*-butylphenol; the dimers to glycols. 2,4-Dichlorophenoxyketene monomer was reduced to 2,4-dichlorophenoxyethanol and 2,4-dichlorophenoxyethylketene dimer to the corresponding glycol. The infrared spectra of the ketenes and their reduction products have been studied.

An earlier investigation in this Laboratory established that lithium aluminum hydride reduces (ω -cyclohexylalkyl)-ketene dimers to β -ketocarbinols. We have shown also that high pressure catalytic reduction of monomeric and dimeric aryloxyketenes produces glycols and the corresponding phenol.² The present investigation was undertaken with the object of exploring the reductive action of lithium aluminum hydride on aryloxyalkylketene monomers and dimers.

An ethereal solution of lithium aluminum hydride reacted with the *p*-*t*-butylphenoxyalkylketene monomers to give substituted β -ketocarbinols and the corresponding phenol. The constitution of the β -ketocarbinols indicated that lithium aluminum hydride cleaved the ketene monomers at the ether bond.³ We have observed that lithium



aluminum hydride reacts with *p*-*t*-butylphenoxyethyl-, *p*-*t*-butylphenoxypropyl- and *p*-*t*-butylphenoxybutylketene monomers to give 2-ethyl-2-(*p*-*t*-butylphenoxy)-3-keto-1-hexanol (67%), 2-*n*-propyl-2-(*p*-*t*-butylphenoxy)-3-keto-1-heptanol (30%) and 2-*n*-butyl-2-(*p*-*t*-butylphenoxy)-3-keto-1-octanol (32%), respectively. *t*-Butylphenol was isolated from each experiment. These reduction products were similar to those isolated in our study of lithium aluminum hydride reduction of ω -cyclohexylalkyl-ketene dimers.¹ However, catalytic hydrogenation of aryloxyalkylketene monomers gave substituted 1,3-glycols.²

(1) A. S. Spriggs, C. M. Hill and G. W. Senter, *THIS JOURNAL*, **74**, 1555 (1952).

(2) C. M. Hill, M. E. Hill, A. O. Williams and E. M. Shelton, *ibid.*, **75**, 1084 (1953).

(3) V. L. Tweedie and M. Cuscurida, *ibid.*, **79**, 5463 (1957).

Lithium aluminum hydride reduced 2,4-dichlorophenoxyketene monomer to 2,4-dichlorophenoxyethanol (85%).

Glycols were formed when lithium aluminum hydride reacted with *p*-*t*-butylphenoxyalkylketene and 2,4-dichlorophenoxyethylketene dimers. In these experiments, lithium aluminum hydride reduced *p*-*t*-butylphenoxy-, *p*-*t*-butylphenoxyethyl-, *p*-*t*-butylphenoxy-*n*-propyl-, *p*-*t*-butylphenoxy-*n*-butyl- and 2,4-dichlorophenoxyethylketene dimers to 2,4-di-(*p*-*t*-butylphenoxy)-, (72%), 2,4-(*p*-*t*-butylphenoxy)-2,4-diethyl-(30%), 2,4-di-(*p*-*t*-butylphenoxy)-2,4-di-*n*-propyl-(25%), 2,4-di-(*p*-*t*-butylphenoxy)-2,4-di-*n*-butyl-(31%) and 2,4-di-(2,4-dichlorophenoxy)-2,4-diethyl-1,3-cyclobutanediol (77%), respectively.²

The ketene monomers were characterized by molecular weight determinations, infrared spectra, comparison of observed physical constants with those reported (in some cases) and preparation of solid derivatives. The monomers formed substituted hydrazides when treated with 2,4-dinitrophenylhydrazine. The infrared spectra of the ketene monomers showed four bands in the double bond region, 5.7, 5.8, 5.9 and 6.02 μ ; the band at 6.02 μ is characteristic of the C=C bond. Infrared spectra of the ketene monomers were analogous.

The ketene dimers reacted with 2,4-dinitrophenylhydrazine to produce the dihydrazones. The infrared spectra of the dimers were similar, showing two bands in the double bond region at 5.7 and 5.8 μ .

Reduction products of *p*-*t*-butylphenoxyethyl- and *p*-*t*-butylphenoxy-*n*-butylketene monomers formed substituted pyrazolines when treated with 2,4-dinitrophenylhydrazine; the reduction product from 2,4-dichlorophenoxyketene monomer gave the 3,5-dinitrobenzoate. Attempts were made to pre-

TABLE I
 ARYLOXYALKYLKETENES, $p-t\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}=\text{CO}$

Ketene, R		M.p. or b.p. ^c		d_{20}^4	n_D^{20}	Yield, ^a %	Carbon, %		Hydrogen, %	
		°C.	Mm.				Calcd.	Found	Calcd.	Found
C ₂ H ₅	Monomer ^b	151-154	4	1.0000	1.5092	10	77.50	77.46	8.25	8.47
	Dimer ^c	172-174	5	1.0110	1.5142	35	77.50	78.10	8.25	8.50
<i>n</i> -C ₃ H ₇	Monomer ^d	131-134	1	0.9724	1.5082	25	77.60	77.15	8.62	8.60
	Dimer	167-170	1	1.0270	1.5115	20	77.60	77.50	8.62	8.15
<i>n</i> -C ₄ H ₉	Monomer ^c	113-115	4	0.9923	1.5090	23	78.04	78.21	8.95	9.25
	Dimer ^c	165-167	4	1.0410	1.5174	28	78.04	78.91	8.95	9.30
		179-181	4			9	75.79	75.61	7.37	7.50
H	Monomer ^c	M. 84-85								
H	Monomer	107-108	5			20	47.29	47.60	1.97	2.05
		M. 137-138		2,4-Cl ₂ C ₆ H ₃ OC=CO						
		182-184	10			25	51.95	51.68	3.46	3.51
C ₂ H ₅	Dimer ^e	M. 94-95								

^a Based on grams of acid chlorides. ^b Molecular weight determined cryoscopically; calcd. 218, found 250. ^c C. M. Hill, M. E. Hill, A. O. Williams and E. M. Shelton, THIS JOURNAL, 75, 1085 (1953), reported molecular weights. ^d Molecular weight calcd. 232, found 287. ^e C. M. Hill, H. I. Schofield, A. S. Spriggs and M. E. Hill, THIS JOURNAL, 73, 1660 (1951), reported molecular weight.

 TABLE II
 2,4-DINITROPHENYLHYDRAZIDES AND 2,4-DINITROPHENYLHYDRAZONES OF KETENES $p-t\text{-C}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}=\text{CO}$

Ketene, R		Hydrazide				Hydrazone			
		Formula	M.p., °C.	Nitrogen, % Calcd.	Found	Formula	M.p., °C.	Nitrogen, % Calcd.	Found
C ₂ H ₅	Monomer	C ₂₀ H ₂₄ N ₄ O ₆	221-222	13.42	13.60				
	Dimer					C ₄₀ H ₄₄ N ₈ O ₁₀	196-197	14.12	13.98
<i>n</i> -C ₃ H ₇	Monomer	C ₂₁ H ₂₆ N ₄ O ₆ ^a	202-203	13.02	13.16				
	Dimer					C ₄₂ H ₄₈ N ₈ O ₁₀	196-197	13.57	13.73
<i>n</i> -C ₄ H ₉	Monomer	C ₂₂ H ₂₈ N ₄ O ₆ ^b	223-224	12.80	13.10				
	Dimer					C ₄₄ H ₅₂ N ₈ O ₁₀	127-128	13.14	13.00

^a Molecular weight determined by the Rast method; calcd. 340, found 366. ^b Molecular weight calcd. 444, found 443.

 TABLE III
 LITHIUM ALUMINUM HYDRIDE REDUCTION PRODUCTS OF KETENES
 $p-t\text{-Butylphenoxy: C}_6\text{H}_4\text{C}_6\text{H}_4\text{OC}=\text{CO}$

Ketene, R	Products	β-Keto-carbinol, formula	Glycol, formula	B.p.		d_{20}^4	n_D^{20}	Yield, ^b %	Carbon, %		Hydrogen, %	
				°C.	Mm.				Calcd.	Found	Calcd.	Found
C ₂ H ₅	Monomer	C ₁₈ H ₂₈ O ₃ ^{c,d}		100-103	3	0.9853	1.5080	67	74.00	74.29	9.57	9.33
	Dimer		C ₂₈ H ₄₀ O ₄ ^e	129-132	3	.9408	1.5148	30	76.34	76.53	9.09	9.45
<i>n</i> -C ₃ H ₇	Monomer	C ₂₀ H ₃₂ O ₃ ^{e,f}		120-122	10	.9901	1.5038	30	75.00	75.48	10.00	10.35
	Dimer		C ₃₀ H ₄₄ O ₄ ^g	156-159	9	.9982	1.5041	25	76.92	76.30	9.40	9.15
<i>n</i> -C ₄ H ₉	Monomer	C ₂₂ H ₃₆ O ₃ ^{e,h}		130-133	9	1.0061	1.5075	32	75.86	76.56	10.34	10.45
	Dimer		C ₃₂ H ₄₈ O ₄ ^e	160-161	15	0.9974	1.5037	31	77.41	77.96	9.68	9.55
H	Dimer		C ₂₄ H ₃₂ O ₄ ⁱ	143-144	3	1.0496	1.5202	72	75.00	74.82	8.33	8.68

^a Other ketenes reduced: (1) 2,4-dichlorophenoxyketene monomer gave 2,4-dichlorophenoxyethanol (85%), b.p. 139-140° (7 mm.), m.p. 46.5-47.5°, 3,5-dinitrobenzoate m.p. 140.5°. Anal. Calcd. for C₁₆H₁₀Cl₂N₂O₇: N, 6.98. Found: N, 6.97. (2) 2,4-Dichlorophenoxyethylketene dimer gave the corresponding glycol (77%), b.p. 142-143° (4 mm.), d_{20}^4 1.3292, n_D^{20} 1.5483, 3,5-dinitrobenzoate m.p. 110-111°. Anal. Calcd. for C₂₄H₂₄Cl₂N₄O₁₄: N, 6.56. Found: N, 6.62. ^b Based on grams of ketene. ^c Formed substituted pyrazoline with 2,4-dinitrophenylhydrazine reagent, m.p. 127-128.5°. Anal. Calcd. for C₂₄H₃₀N₄O₅: N, 12.33; mol. wt., 454. Found: N, 12.46; mol. wt., 430. A. S. Spriggs, C. M. Hill and G. W. Senter, THIS JOURNAL, 74, 1555 (1952), reported similar reaction. ^d Second reduction product, *p-t*-butylphenol (20%), m.p. 95-96°. R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 326, and C. M. Hill, M. E. Hill, A. O. Williams and E. M. Shelton, THIS JOURNAL, 75, 1086 (1953), reported 95° and 94-95°, respectively. ^e Infrared spectra described in the text. ^f *p-t*-Butylphenol (17%) isolated, m.p. 95-96°. ^g 3,5-Dinitrobenzoate melted at 85-85.5°. Anal. Calcd. for C₄₄H₄₈N₄O₁₄: N, 6.55. Found: N, 6.82. ^h *p-t*-Butylphenol (51%) isolated as second product, m.p. 94-95°. ⁱ 3,5-Dinitrobenzoate melted at 130.5-131.5°, light green crystals. Anal. Calcd. for C₃₈H₃₆N₄O₁₄: N, 7.30. Found: N, 7.38.

pare solid derivatives of all reduction products; in some cases our efforts were unsuccessful. Products isolated from reduction of the dimers showed the presence of hydroxyl groups. The glycols

obtained from *p-t*-butylphenoxy-, *p-t*-butylphenoxy-*n*-propyl- and 2,4-dichlorophenoxyethylketene dimers formed 3,5-dinitrobenzoates. The infrared spectra of reduction products from the monomers

indicated two OH bands at 3.03 and 9.5 μ and the C=O band at 5.8 μ .

Infrared spectra of the products isolated from reduction of the dimers showed OH bands at 3.0 and 9.5 μ . The C=O band was absent in the spectra of these products.

Experimental⁴

Synthesis of Ketenes.—The ketenes employed in this study were synthesized by slight modification of the method reported previously.² Physical constants and analyses of the ketenes are shown in Table I.

Preparation of Derivatives of Ketenes.—Substituted hydrazides were prepared by treating samples of the ketene monomers with 2,4-dinitrophenylhydrazine reagent¹; dihydrazones of the dimers were prepared similarly.

Physical constants and nitrogen analyses of the 2,4-dinitrophenylhydrazides of the ketene monomers and the 2,4-dinitrophenylhydrazones of the dimers are given in Table II.

Lithium Aluminum Hydride Reduction of Ketenes.—The procedure followed for reduction of the ketenes was essentially the same as that reported in an earlier study.¹ To a suspension of 2 g. (0.05 mole) lithium aluminum hydride in 800 ml. of dry diethyl ether was added *p-t*-butylphenoxy-*n*-butylketene monomer (17.4 g.). The reaction mixture was heated for 21 hours, cooled, hydrolyzed, and extracted with ether. Distillation of the dried extract gave two re-

action products: *p-t*-butylphenol, b.p. 149–152° (9 mm.) (m.p. 95–96°); and 2-*n*-butyl-2-(*p-t*-butylphenoxy)-3-keto-1-octanol, b.p. 160–161° (9 mm.). Physical constants of the reduction products of the ketene monomers and dimers are described in Table III.

Preparation of Derivatives of Reduction Products.—A 1- to 2-g. sample of each reduction product obtained from the ketene monomers was treated, in the usual manner, with 2,4-dinitrophenylhydrazine reagent. Two of the reduction products formed substituted pyrazolines. Treatment of 1-g. samples of reduction products from the ketene dimers with 3,5-dinitrobenzoyl chloride gave, in three cases, the corresponding 3,5-dinitrobenzoates. Description of the physical constants of derivatives is shown in the footnotes to Table III.

Determination of Number of Hydroxyl Groups.—The number of hydroxyl groups in the several reduction products was determined by the procedure of Siggia.⁵ By this procedure the reduction products from *p-t*-butylphenoxy-alkyl- and 2,4-dichlorophenoxyethylketene dimers showed 1.9 to 2.4 hydroxyl groups; the product from 2,4-dichlorophenoxyketene monomer indicated 0.9 hydroxyl group.

Acknowledgment.—The authors express appreciation to Professor David C. Gandy for assistance in the microanalysis work.

(5) S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 4.

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(4) All melting points are corrected.

[CONTRIBUTION FROM THE CENTRAL RESEARCH LABORATORY, ALLIED CHEMICAL CORP.]

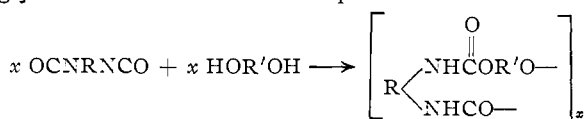
Terminal Unsaturation in Polypropylene Glycol

BY G. J. DEGE, R. L. HARRIS AND J. S. MACKENZIE

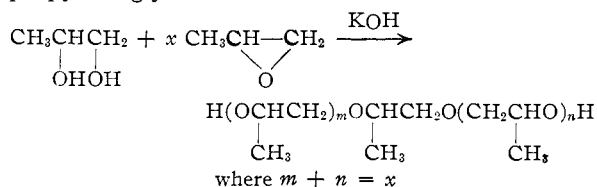
RECEIVED DECEMBER 4, 1958

Both allyl and *cis*-propenyl end groups are present in polypropylene glycol synthesized by the base-catalyzed addition of propylene oxide to propylene glycol initiator. The *cis*-propenyl group is readily identifiable from the characteristic 5.98 and 13.83 μ absorption bands in the infrared spectrum. Evidence for allyl unsaturation is provided by the periodate scission of the double bond and recovery of the released formaldehyde. The presence of terminal unsaturation in polypropylene glycol can seriously limit the length of the polymer chain in the reaction with diisocyanates to form polyurethans. The amount of *cis*-propenyl unsaturation formed in the synthesis of polypropylene glycol increases with increasing reaction temperature, catalyst concentration and extent of certain metallic surfaces. There is no simple relationship between any of the known reaction variables and the amount of allyl unsaturation produced.

There has been increasing interest in the synthesis of polyurethan flexible foams by the reaction of aromatic diisocyanates with polymeric glycols. Of considerable importance in this con-



nection are the polypropylene glycols derived from the base-catalyzed addition of propylene oxide to propylene glycol initiator. Evidence that the base-



catalyzed scission of the oxide ring yields primarily secondary hydroxyl groups has been obtained by a number of investigators;¹ although it should be

noted that recent nuclear magnetic resonance measurements² on polypropylene glycol have indicated the proportion of primary hydroxyl groups to be higher than previously suspected. Polypropylene glycol in the 2000 molecular weight range is particularly well adapted to the synthesis of polyurethane foams. Of necessity this material must have a fairly high degree of bifunctionality in order not to seriously limit the polyurethan molecular weight. One of the important factors contributing to the generation of shortened polyurethan chains is the presence of terminal unsaturation in the polymeric glycol. Commercially available polypropylene glycol in the 2000 molecular weight range may contain anywhere from 4 to 20 terminal olefinic linkages per 100 polymer molecules. While it has not been possible to directly relate the properties of polyurethan foams to the polypropylene glycol

(1) A. A. Petrov, *J. Gen. Chem. (U.S.S.R.)*, **14**, 1038 (1944); C. A., **40**, 7153 (1946); H. C. Chitwood and B. T. Freure, *THIS JOURNAL*, **68**, 680 (1946); P. D. Bartlett and S. D. Ross, *ibid.*, **70**, 926 (1948);

A. R. Sexton and E. C. Britton, *ibid.*, **70**, 3606 (1948); W. Reeve and A. Sadle, *ibid.*, **72**, 1251 (1950); R. C. Elderfield, ed., "Heterocyclic Compounds," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 32; H. A. Pecorini, Doctoral Thesis, University of Michigan, 1954; Univ. Microfilms, Ann Arbor, Mich., Publ. No. 11337.

(2) A. J. Havlik and A. F. Hildebrandt, Abstracts of Papers, 134th Meeting, American Chemical Society, Chicago, Ill., September, 1958, p. 14-T.