liters of water. The partial solution was saturated with hydrogen sulfide with frequent vigorous shaking. Filtering gave a colorless solution. Addition of concd. ammonium hydroxide yielded a white solid, which was purified by dissolving in the minimum amount of ethanol at room temperature and adding water to reprecipitate the product, m.p. 64–66°. There was obtained 14.4 g. (26.6% yield). This compound gradually decomposed in boiling ethanol.

Anal. Calcd. for $C_{10}H_{13}Cl_3N_2$: N, 10.47. Found: N, 10.68.

1,1,1-Trichloro-2-methylanilino-3-acetaminopropane.—A solution of 2.0 g. (0.0075 mole) of 1,1,1-trichloro-2-methylanilino-3-aminopropane in 10 g. (0.1 mole) of acetic anhydride was heated on the steam-bath for a few minutes. Chilling overnight in the refrigerator, followed by recrystallizing from ethanol–water, yielded 2.0 g. (83.3% yield) of product, m.p. 118–119°.

Anal. Calcd. for $C_{12}H_{15}Cl_3N_2O$: N, 9.05. Found: N, 9.07.

Greencastle, Indiana

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

The Synthesis, Properties and Catalytic Hydrogenation of Several Aryloxy Substituted Ketene Monomers and Dimers

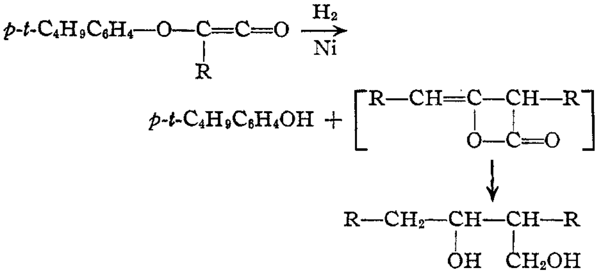
By Carl M. Hill, Mary E. Hill, Albert O. Williams and Essie M. Shelton

Received October 23, 1952

Three monomeric and two dimeric aryloxy ketenes of the type [p-t-C_4H_9-$C_6H_4OC(R)CO$], where R = H, CH_3, C_2H_5, n-C_4H_9 and n-C_5H_{11}, have been prepared by dehydrohalogenation of the corresponding acid chlorides. Properties of the acids and acid chlorides have been studied. Catalytic reduction of the p-t-butylphenoxyketenes and the isomers of three 2,4-dichlorophenoxyketene dimers of the type $[Cl_2C_6H_3OC(R)CO]_2$, where R = C_2H_5, n-C_3H_7 and n-C_4H_9, gave glycols and the corresponding phenol. p-t-Butylphenoxyketene dimer formed the glycol only.

In earlier papers[1,2] it was demonstrated that catalytic hydrogenation of alkyl and (ω-cyclohexylalkyl) ketene dimers led to the formation of aliphatic glycols only. It was of special interest, therefore, to synthesize and to investigate the behavior of aryloxyalkyl ketene monomers and dimers toward hydrogen at high pressures and temperatures, and in the presence of Raney nickel catalyst. It was postulated that the introduction of an oxygen atom between the β-olefinic carbon of the ketene functional group and the side chain would have a pronounced effect upon the reactivity of the ketene molecule during catalytic reduction. Also, it was believed that catalytic reduction of the two forms of each of three 2,4-dichlorophenoxyketene dimers[3] would give further experimental evidence of the existence of isomers.

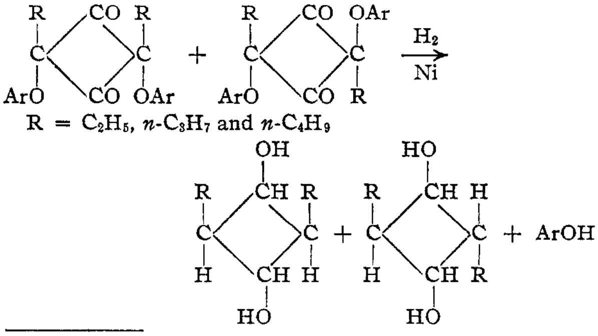
The results of this investigation indicate that, when the p-t-butylphenoxyketene monomers and one dimer are treated with hydrogen under pressures of 1500–3500 p.s.i., at temperatures of 200–350° and over Raney nickel, hydrogenation of the olefinic bond and cleavage of the ether bond take place. Such an attack of hydrogen upon the ketene molecule would lead to the formation of p-t-butylphenol and an alkyl ketene monomer.



However, the reduction products isolated from experiments using p-t-butylphenoxymethylketene dimer and p-t-butylphenoxyethyl-, p-t-butylphenoxy-n-butyl- and p-t-butylphenoxy-n-pentylketene monomers were p-t-butylphenol and glycols of the corresponding alkyl ketene dimers. This suggests dimerization of the transitory alkyl ketene monomers, followed by reduction of the dimers to glycols. Catalytic hydrogenolysis of ethers has been observed by Van Duzee and Adkins,[4] and Emerson and Heider.[5]

From p-t-butylphenoxyketene dimer, only one reduction product, 2,4-di-(p-t-butylphenoxy)-1,3-butanediol, was obtained. This is in agreement with our previous studies of cyclohexyl substituted alkyl[1] and alkyl ketene dimers.[2]

It has been observed in this Laboratory that dehydrohalogenation of 2,4-dichlorophenoxybutyryl, -valeryl and -caproyl chlorides produced, in each case, two forms of the ketene dimer.[3] It was tacitly assumed on basis of their solubility and boiling point differences that the two forms represented the *cis* and *trans* isomers. In the present study, it was observed that catalytic hydrogenation of each pair of dimers gave two different hydroxy compounds and 2,4-dichlorophenol.



---

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

[2] C. M. Hill, L. Haynes and M. E. Hill, *ibid.*, **74**, 3423 (1952).

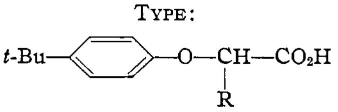
[3] C. M. Hill, H. I. Schofield, A. A. Spriggs and M. E. Hill, *ibid.*, **73**, 1660 (1951).

[4] E. M. Van Duzee and H. Adkins, *ibid.*, **57**, 147 (1935).

[5] W. S. Emerson, R. L. Heider, R. I. Longley, Jr., and T. C. Shafer, *ibid.*, **72**, 5314 (1950).

TABLE I

PHYSICAL CONSTANTS OF ARYLOXY SUBSTITUTED ACIDS OF TYPE:



$t\text{-Bu}-C_6H_4-O-\underset{R}{\underset{|}{CH}}-CO_2H$

R	M.p., °C.	Neutral equivalent[a] Calcd.	Neutral equivalent[a] Found	Yield, %
H	88–89	208	209	
CH_3[b]	86–87	222	225	
C_2H_5[c]	87–88.5	236	237	63
n-C_4H_9	89–90	264	263	69
n-C_5H_{11}	72–73	278	278	63

[a] Determined by titration in non-aqueous solution, using benzene–methanol and sodium methoxide: J. S. Fritz and N. M. Lisicki, *Anal. Chem.*, **23**, 589 (1951). [b,c] Reported m.p. 89–90.5° and 89–90.5°, respectively: L. F. Berhenke, L. E. Begin, B. M. Williams and F. L. Beman, THIS JOURNAL, **73**, 4458 (1951).

Determination of the number of OH groups in the hydroxy compounds indicated the presence of two such groups. The glycols from each pair of dimers had different properties and formed isomeric p-nitrobenzoates. The results of these reduction experiments give indication that the two forms of each ketene dimer represent the *cis* and *trans* geometric isomers.

The p-t-butylphenoxy acid chlorides were identified by chlorine analysis and preparation of the solid amides and two anilides.

The two p-t-butylphenoxyketene dimers were white crystalline solids; the three monomers were slightly yellow colored liquids which reacted positively to potassium permanganate and bromine in carbon tetrachloride. The monomers showed little tendency to polymerize upon standing.

Experimental[6]

Aryloxy Acids.—The first two acids of this series were purchased from Matheson Company, Inc. Other acids were synthesized by condensation of sodium p-t-butylphenolate with the appropriate ethyl α-bromoester, in methanol. The acids were purified by recrystallization from petroleum ether–benzene mixed solvent. Physical constants of the acids are described in Table I.

Acid Chlorides.—The acid chlorides were prepared by treatment of the acids with thionyl chloride. Description of the physical constants and analytical data of the chlorides is given in Table II.

TABLE II

PHYSICAL CONSTANTS AND ANALYTICAL DATA OF ACID CHLORIDES

R	Formula	B.p. °C.	Mm.	Yield, %	d^{20}_4	$n^{20}D$	Chlorine,[a] % Calcd.	Chlorine,[a] % Found
H	$C_{12}H_{15}O_2Cl$	130–132	5	90	1.1128	1.5162	15.68	15.67
CH_3	$C_{13}H_{17}O_2Cl$	143–145	26	60	1.0775	1.5092	14.76	14.76
C_2H_5	$C_{14}H_{19}O_2Cl$	131–132	3	94	1.0651	1.5055	13.95	14.12
n-C_4H_9	$C_{16}H_{23}O_2Cl$	143–144	3	95	1.0641	1.5018	12.57	12.22
n-C_5H_{11}	$C_{17}H_{25}O_2Cl$	149–150	6	97	0.9984	1.5003	11.97	11.86

[a] Analyzed by potentiometric titration method, using silver and silver–silver chloride electrodes.

TABLE III

ANALYTICAL DATA OF DERIVATIVES OF ACID CHLORIDES

	Amide				
R	Formula	M.p., °C.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found
H[a]	$C_{12}H_{17}O_2N$	131–132	86	6.77	6.87
CH_3[b]	$C_{13}H_{19}O_2N$	116–117	91	6.34	6.25
C_2H_5	$C_{14}H_{21}O_2N$	97–99	87	5.96	6.12
n-C_4H_9	$C_{16}H_{25}O_2N$	145–146	71	5.32	5.66
n-C_5H_{11}	$C_{17}H_{27}O_2N$	86–87	76	5.10	5.15

[a] M.p. of anilide 91–92°. *Anal.* Calcd. for $C_{18}H_{21}O_2N$: C, 76.32; H, 7.42; N, 4.95. Found: C, 76.48; H, 7.40; N, 5.20; yield 68%. [b] M.p. of anilide 83–84°. *Anal.* Calcd. for $C_{19}H_{23}O_2N$: C, 76.77; H, 7.74; N, 4.71. Found: C, 76.46; H, 7.58; N, 4.81.

Amides.—To a 0.5-g. sample of each acid chloride dissolved in 10 ml. of anhydrous ether was added dry ammonia, until precipitation of the amide was complete. The crude amide was filtered and recrystallized from methanol. Analytical data for the amides are described in Table III.

Anilides.—A 1.0-g. sample of the chloride was dissolved in 20 ml. of anhydrous benzene and an equivalent amount of aniline added. The mixture was warmed on a water-bath. The crude anilide was recrystallized from dilute methanol. Analytical data for the anilides are shown in Table III.

Synthesis of Ketenes.—The p-t-butylphenoxy and 2,4-dichlorophenoxy substituted ketenes used in this investigation were synthesized according to the procedure previously reported.[3] Physical constants and analytical data for the p-t-butylphenoxy ketenes are given in Table IV.

Catalytic Reduction of Ketenes.—Weighed samples (5–15 g.) of the ketenes were dissolved in 25 ml. of petroleum ether to which was added 2–4 g. of Raney nickel. The mixture was placed into the reaction bomb of the Parr high pressure apparatus (serial number 136) and treated at hydrogen pressure of 1500–3500 p.s.i. for 4–6 hours. Temperatures of 200–350° were employed. The reduction mixture was filtered free of catalyst and the solvent removed by distillation. Distillation of the residue, under reduced pressure, gave two fractions. The glycol fractions were washed with small portions of 15% sodium carbonate solu-

TABLE IV

PHYSICAL CONSTANTS AND ANALYTICAL DATA OF p-t-BUTYLPHENOXY KETENES

							Analyses					
R	Formula	B.p. or m.p. °C.	Mm.	Yield, %	d^{20}_4	$n^{20}D$	Mol. wt.[a] Calcd.	Mol. wt.[a] Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H dimer	$C_{24}H_{28}O_4$	180–183 M.p. 85–86	5	37			380	352	75.79	75.30	7.37	7.45
CH_3 dimer	$C_{26}H_{32}O_4$	147–150 M.p. 78–79	6	55			408	436	76.47	76.35	7.84	7.90
C_2H_5 monomer	$C_{14}H_{18}O_2$	175–176	12	66	1.0132	1.5178	218	222	77.06	77.50	8.26	8.36
n-C_4H_9 monomer	$C_{16}H_{22}O_2$	169–171	10	54	1.0157	1.5044	246	246	78.05	78.43	8.94	8.92
n-C_5H_{11} monomer	$C_{17}H_{24}O_2$	132–133	5	73	0.9771	1.5056	260	268	78.46	78.07	9.23	9.20

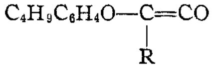
[a] Determined by cryoscopic method, using dry benzene as solvent.

---

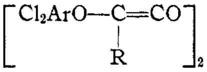
(6) All melting points are corrected.

TABLE V

PHYSICAL CONSTANTS AND ANALYTICAL DATA OF REDUCTION PRODUCTS OF KETENES

A. *p-t*-Butylphenoxy: 
$C_4H_9C_6H_4O—\underset{R}{C}=CO$

R, Ketene	Glycol Formula	Yield, %	B.p. or m.p. °C.	Mm.	d^{20}_4	$n^{20}D$	3,5-Dinitrobenzoate Formula	M.p., °C.	*p-t*-Bu-phenol[a] yield, %
H dimer	$C_{24}H_{34}O_4$	55	M.p. 88–89				$C_{38}H_{38}O_{14}N_4$[b]	140–141	
CH_3 dimer	$C_6H_{12}O_2$	50	83–84	20	1.0570	1.5328	$C_{20}H_{16}O_{12}N_4$[c]	126–127	40
C_2H_5 monomer	$C_8H_{18}O_2$[d,2]	65	75–77	10	0.9165	1.4458	$C_{22}H_{22}O_{12}N_4$[e]	165–166	37
n-C_4H_9 monomer	$C_{12}H_{26}O_2$[f]	40	125–126	3	0.9108	1.4343	$C_{26}H_{30}O_{12}N_4$[g]	162–163	35
n-C_5H_{11} monomer	$C_{14}H_{30}O_2$[h]	35	127–128	5	0.8957	1.4388	$C_{28}H_{34}O_{12}N_4$[i]	163–164	50

B. 2,4-Dichlorophenoxy: 
$\left[Cl_2ArO—\underset{R}{C}=CO\right]_2$

R, Ketene	Glycol[j] Formula	B.p. or m.p. °C.	Mm.	Yield, %	d^{20}_4	$n^{20}D$	No. OH	*p*-Nitrobenzoate Formula	Yield, %	M.p., °C.	Nitrogen, % Calcd.	Found
C_2H_5	$C_8H_{16}O_2$											
Liquid		60–63	3	55	1.0018	1.5228[k]	1.8	$C_{22}H_{22}O_8N_2$	48	118–119	6.33	6.34
Solid		59–61	3	20	1.0784	1.5362[l]	2.1		54	85–86	6.33	6.38
n-C_3H_7	$C_{10}H_{20}O_2$											
Liquid		63–65	3	20	1.0757	1.5362[m]	1.9	$C_{24}H_{26}O_8N_2$	56	88–90	5.96	5.98
		M.p. 21–23										
Solid		102–104	3	67	1.0612	1.5261[n]	2.2		68	114–115	5.96	5.82
n-C_4H_9	$C_{12}H_{24}O_2$											
Liquid		62	4	27	1.0688	1.5183[o]	2.3	$C_{26}H_{30}O_8N_2$	45	115–116	5.62	5.48
Solid		65–68	2	56	1.0378	1.5299[p]	1.9		61	119–120	4.62	5.52

[a] Identified by: m.p. 94–95° (lit. m.p. 95°: R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 1948, p. 272), mixed m.p. 94–95°. *Anal.* Calcd. for $C_{10}H_{14}O$: C, 80.00; H, 9.33. Found: C, 79.45–80.68; H, 9.02–9.60. [b] *Anal.* Calcd.: N, 7.23. Found: N, 7.24. [c] *Anal.* Calcd.: N, 11.11. Found: N, 11.32. [d] Ref. 2 reported b.p. 82–85° (16 mm.), d^{20}_4 0.9130, $n^{20}D$ 1.4230. [e] Reported m.p. 164–166°, footnote *d*,2; mixed m.p. with the 3,5-dinitrobenzoate prepared from authentic sample of 2-ethyl-1,3-hexanediol was 164–165°. [f] Reported b.p. 128–129° (1 mm.), d^{25} 0.9184 by M. S. Kulpinski and F. F. Nord, *J. Org. Chem.*, **8**, 256 (1943). [g] Literature m.p. 164–165°: footnote *d*,2; mixed m.p. with the 3,5-dinitrobenzoate prepared from authentic 2-*n*-butyl-1,3-octanediol was 163–164°. [h] Reported b.p. 125–127° (0.5 mm.), d^{23} 0.8984, footnote *f*. [i] Literature m.p. 163–164°: footnote *d*,2; mixed m.p. with 3,5-dinitrobenzoate prepared from authentic 2-*n*-pentyl-1,3-nonanediol was 163–164°. [j] The second reduction product isolated from each experiment was identified as 2,4-dichlorophenol, m.p. 42–43° (lit. m.p. 43°, footnote *a*, p. 271); m.p. of 3,5-dinitrobenzoate prepared from authentic 2,4-dichlorophenol was 143–144°; from isolated sample, 142–143°; mixed m.p. 143–144°. Yields were: 40, 35, 65, 28, 45 and 38%, respectively. [k] Refractive index taken at 21°. [l] *MR*D (calcd.) 40.47; (found) 41.64. [m] Refractive index taken at 25°. [n,o,p] *MR*D (calcd.) 49.71, 58.95, 58.95; (found) 49.76, 56.73 and 59.53, respectively.

tion and water, dried over anhydrous magnesium sulfate and redistilled. The phenol fractions were recrystallized from petroleum ether–benzene mixed solvent.

Physical constants and analytical data for the reduction products are shown in Table V.

NASHVILLE 8, TENNESSEE