[RESEARCH LABORATORIES, AMERICAN HOME FOODS, INC.]

Glyoxal Hemimercaptals

BY FRANK KIPNIS[1] AND JOHN ORNFELT

A series of crystalline hemimercaptals was prepared by the interaction of glyoxals with mercaptans. The products may be recrystallized from non-polar solvents and are stable over extended periods of time.

Hemimercaptals are rather unusual compounds whose methods of preparation have not been studied too extensively. A number have been prepared, derived from formaldehyde,[2] benzaldehyde,[3] methylglyoxal and phenylglyoxal with thioglycolic acid derivatives and with cysteine,[4] and hemimercaptols have been reported from alloxan,[5] polycyclic quinones[6] and from α,β-diketones.[7] It will be noted that of the hemimercaptals from glyoxals, only those have been prepared which contain carboxylic functions. It was desirable to prepare glyoxal hemimercaptals from alkyl, aryl and heterocyclic mercaptans containing no solubilizing groups. The results of this study are indicated in Table I.

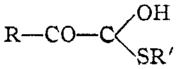
It has been found possible to prepare crystalline hemimercaptals in good yields by mixing the glyoxal with the mercaptan and recrystallizing from the appropriate solvent. From visual evidence, it would seem that the hemimercaptals dissociate on heating even in non-polar solvents, since the solutions have a rather strong yellow coloration, indicative of the presence of the glyoxal, whereas in solid form, the compounds are colorless crystals which seem perfectly stable, showing no dissociation or change in melting point after more than six months of storage.

Phenylglyoxal,[8] *p*-ethoxyphenylglyoxal,[9] thiophene-2-glyoxal[10] and furyl-2-glyoxal[11] were prepared by the oxidation of the corresponding methyl ketone with selenium dioxide.

Most of the mercaptans were available from commercial sources. 2-Thenylmercaptan was prepared from 2-thenyl chloride *via* the isothiouronium salt.[12] Furfuryl mercaptan has been prepared by several methods,[13–15] but that of Reichstein[14] gave the most consistent results.

TABLE I

HEMIMERCAPTALS



$R—CO—C{<}^{OH}_{SR'}$

R'	R	M.p., °C.[b]	Yield, %	Recrystallizing solvent	Formula	Analyses,[a] % Calculated Carbon	Hydrogen	Sulfur	Found Carbon	Hydrogen	Sulfur
Ethyl	C_6H_5	78–80	81.5	Ligroin	$C_{10}H_{12}O_2S$	61.19	6.17	16.34	61.26	6.50	16.49
n-Propyl	C_6H_5	84	84	Ligroin	$C_{11}H_{14}O_2S$	62.83	6.71	15.25	62.58	6.84	15.60
i-Propyl	C_6H_5	47–49	67	Ligroin	$C_{11}H_{14}O_2S$	62.83	6.71	15.25	62.86	6.96	15.65
n-Heptyl	$C\ H_5$	81	71	Ligroin	$C_{15}H_{22}O_2S$	67.63	8.32	12.04	67.24	8.36	12.29
n-Dodecyl	C_6H_5	80–81	83.5	Hexane	$C_{20}H_{32}O_2S$	71.38	9.58	9.53	71.23	9.76	9.78
n-Hexadecyl	C_6H_5	88	42.3	Heptane	$C_{24}H_{40}O_2S$	73.42	10.57	8.17	72.85	9.95	8.62
n-Octadecyl	C_6H_5	90.5–91	35.4	Hexane	$C_{26}H_{44}O_2S$	74.23	10.54	7.62	74.16	10.63	8.12
Benzyl	C_6H_5	72–74	77.5	Ligroin	$C_{15}H_{14}O_2S$	69.74	5.46	12.41	70.11	5.86	12.76
Phenyl	C_6H_5	97–98	80	Heptane	$C_{14}H_{12}O_2S$	68.83	4.95		68.73	4.67	
Furfuryl	C_6H_5	40	66	Pentane	$C_{13}H_{12}O_3S$	62.88	4.87		62.20	4.92	
p-Cresyl	C_6H_5	44–45	70	Pentane	$C_{15}H_{14}O_2S$	69.74	5.46		70.01	5.69	
Thiophene-2-methyl	*p*-C_2H_5–O–C_6H_4	37–38	89	Hexane	$C_{15}H_{16}O_3S_2$	58.42	5.23	20.79	58.60	5.50	20.65
n-Dodecyl	*p*-C_2H_5–O–C_6H_4	65–66	92	Hexane	$C_{22}H_{36}O_3S$	69.43	9.53	8.42	69.04	9.46	8.69
Benzyl	*p*-C_2H_5–O–C_6H_4	64–65	95	Hexane	$C_{17}H_{18}O_3S$	67.52	6.00		67.80	6.19	
n-Propyl	C_4H_3O	105–106	98	Heptane	$C_9H_{12}O_3S$	53.98	6.04		53.93	6.14	
n-Dodecyl	C_4H_3O	105–106	99	Heptane	$C_{18}H_{30}O_3S$	66.22	9.26	9.82	66.49	9.28	10.00
n-Hexyl	C_4H_3O	94.5–95.5	94	Heptane	$C_{12}H_{18}O_3S$	59.47	7.49	13.23	59.07	7.46	13.25
n-Heptyl	C_4H_3S	76–77	74	Heptane	$C_{13}H_{20}O_2S_2$	57.31	7.40		57.02	7.37	
Methyl	C_4H_3S	91–93	84	Hexane	$C_7H_8O_2S_2$	44.66	4.28		44.63	4.65	
Ethyl	C_4H_3S	58–59	71	Hexane	$C_8H_{10}O_2S_2$	47.50	4.48	31.70	47.42	5.08	31.71
n-Propyl	C_4H_3S	69	87	Hexane	$C_9H_{12}O_2S_2$	49.97	5.59	29.64	50.53	6.01	29.72
Benzyl	C_4H_3S	78–79	70	Hexane	$C_{13}H_{12}O_2S_2$	59.06	4.57		59.10	4.81	
β-Naphthyl	C_4H_3S	98–99	84	Hexane	$C_{16}H_{12}O_2S_2$	63.97	4.03	21.35	63.81	4.24	21.80
Thiophene-2-methyl	C_4H_3S	54–55	62	Hexane	$C_{11}H_{10}O_2S_3$	48.86	3.73	35.57	48.88	4.03	35.59
n-Dodecyl	C_4H_3S	80–81	95	Hexane	$C_{18}H_{30}O_2S_2$	63.11	8.83		63.21	8.97	
Phenyl	C_4H_3S	55–56	73	Hexane	$C_{12}H_{10}O_2S_2$	57.57	4.03	25.61	57.49	4.55	25.68
n-Octadecyl	C_4H_3S	91	89	Hexane	$C_{24}H_{42}O_2S_2$	67.55	9.92	15.03	67.17	9.70	15.70

[a] Analyses by Oakwold Laboratories, Alexandria, Virginia. [b] All melting points taken with Fisher–Johns apparatus.

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(1) Oxford Products, Inc., Cleveland 3, Ohio.

(2) T. G. Levi, *Gazz. chim. ital.*, **62**, 775 (1932).

(3) Fromm, *Ann.*, **235**, 135 (1889).

(4) M. P. Schubert, *J. Biol. Chem.*, **111**, 671 (1935).

(5) E. L. d'Ouville, F. J. Myers and R. Connor, THIS JOURNAL, **61**, 2033 (1939).

(6) A. Schonberg, O. Schütz, G. Arend and J. Peter, *Ber.*, **60**, 2344 (1927).

(7) (a) T. Reichstein and H. Staudinger, Swiss Patents 128,720, 130,605, 130,606, 130,607, 130,608; (b) British Patent 260,960; (c) German Patent 489,613; (d) U. S. Patent 1,696,419.

(8) H. A. Riley and A. R. Gray, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 509.

(9) F. Kipnis, H. Soloway and J. Ornfelt, THIS JOURNAL, **69**, 1231 (1947).

(10) F. Kipnis and J. Ornfelt, *ibid.*, **68**, 2734 (1946).

(11) F. Kipnis and J. Ornfelt, *ibid.*, **70**, 3948 (1948).

(12) F. Kipnis and J. Ornfelt, *ibid.*, **71**, 3571 (1949).

(13) W. R. Kirner and G. H. Richter, *ibid.*, **51**, 3134 (1929); W. R. Kirner, *ibid.*, **50**, 1958 (1928).

(14) H. Staudinger and T. Reichstein, U. S. Patent 1,715,795.

(15) J. Giral and A. Garciá Fernández, *Anales inst. invest. cient. Univ. Nuevo Leon*, **1**, 149 (1944).

Experimental

Thiophene-2-glyoxal *n*-Heptylhemimercaptal.—Fourteen grams (0.1 mole) of thiophene-2-glyoxal was mixed with 13.2 g. (0.1 mole) of *n*-heptyl mercaptan. A considerable amount of heat was generated, and on allowing the mixture to cool to room temperature, the entire mass crystallized. The product was purified by recrystallization from heptane, giving colorless crystals melting at 76–77° d.

The other hemimercaptals were prepared in a similar manner.

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[CONTRIBUTION FROM VENEREAL DISEASE EXPERIMENTAL LABORATORY, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

The Ultraviolet Absorption Spectra of Arylphosphonic and Diarylphosphinic Acids

BY H. H. JAFFÉ AND LEON D. FREEDMAN

The ultraviolet absorption spectra of a number of arylphosphonic and diarylphosphinic acids, and of a few related compounds have been determined. These spectra indicate that no resonance exists between a "pentavalent" phosphorus atom and an aromatic nucleus attached to it and that the P–O bond in the phosphoryl group has no appreciable double bond character. Evidence is also presented which confirms the "keto" structure usually assigned to benzenephosphonous acid.

In connection with a study of certain organic phosphorus compounds in this Laboratory, it appeared desirable to investigate the effect of the phosphono ($-PO_3H_2$) and phosphinico ($>PO_2H$) groups on the ultraviolet absorption spectra of benzene and its derivatives. The present paper describes the results obtained with arylphosphonic acids, diarylphosphinic acids and a few related compounds.

TABLE I

Compound	Primary band $\lambda_{max.}$ mμ	$\epsilon_{max.}$	Secondary band $\lambda_{max.}$ mμ	$\epsilon_{max.}$
C_6H_6			254.5	180
$C_6H_5PO_3H_2$			263.5	524
$C_6H_5PO_3H^-$			263.0	383
$C_6H_5PO_3^=$			258.0	239
$C_6H_5PO_2H_2$	216	7,100	264.5	616
$C_6H_5PO_2H^-$			263.5	477
$(C_6H_5)_2PO_2H$	224	13,100	265.0	1,200
$(C_6H_5)_2PO_2^-$	222	12,000	264.0	882
$(C_6H_5)_3PO$	224	21,300	265.5	2,420
$(C_6H_5)_3P$[a]			261[b]	11,000[b]
ClC_6H_5			264.0	206
o-$ClC_6H_4PO_3H_2$	217	12,300	270.5	798
m-$ClC_6H_4PO_3H_2$	215	8,130	271.0	649
p-$ClC_6H_4PO_3H_2$	224	14,400	264.0	292
(*o*-$ClC_6H_4)_2PO_2H$			273.5	1,738
(*m*-$ClC_6H_4)_2PO_2H$			273.0	1,390
(*p*-$ClC_6H_4)_2PO_2H$[c]	234	22,200	265.0	1,000
$NO_2C_6H_5$	260	7,100		
m-$NO_2C_6H_4PO_3H_2$	263	6,400		
p-$NO_2C_6H_4PO_3H_2$[d]	270	10,400		
p-$NO_2C_6H_4PO_3H^-$	272	10,800		
p-$NO_2C_6H_4PO_3^=$[e]	278	10,300		
(*m*-$NO_2C_6H_4)_2PO_2H$[f]	263	14,300		
(*p*-$NO_2C_6H_4)_2PO_2H$	274	21,100		
(*p*-$NO_2C_6H_4)_2PO_2^-$	272	21,400		
(*m*-$ClC_6H_4)C_6H_5PO_2H$			272.5	1,250
(*m*-$NO_2C_6H_4)C_6H_5PO_2H$[g]	263	7,570		
(*p*-$NO_2C_6H_4)C_6H_5PO_2H$	272	11,500		
(*p*-$NO_2C_6H_4)C_6H_5PO_2^-$	272	11,500		

[a] The spectrum of this compound has been previously determined by J. E. Purvis, *J. Chem. Soc.*, 105, 1372 (1914). [b] It is uncertain whether these values should be assigned to the primary or secondary band. [c] The purity of this compound was doubted at first when the spectrum was determined and the strong absorption band at 234 mμ was observed. Therefore, the compound was recrystallized two more times from dilute alcohol; no change in the spectrum was noted. [d] Secondary primary band; $\lambda_{max.}$ 213, $\epsilon_{max.}$ 5,950. [e] Second primary band: $\lambda_{max.}$ 216, $\epsilon_{max.}$ 5,580. [f] Second primary band: $\lambda_{max.}$ 218, $\epsilon_{max.}$ 26,100. [g] Second primary band: $\lambda_{max.}$ 220, $\epsilon_{max.}$ 19,600.

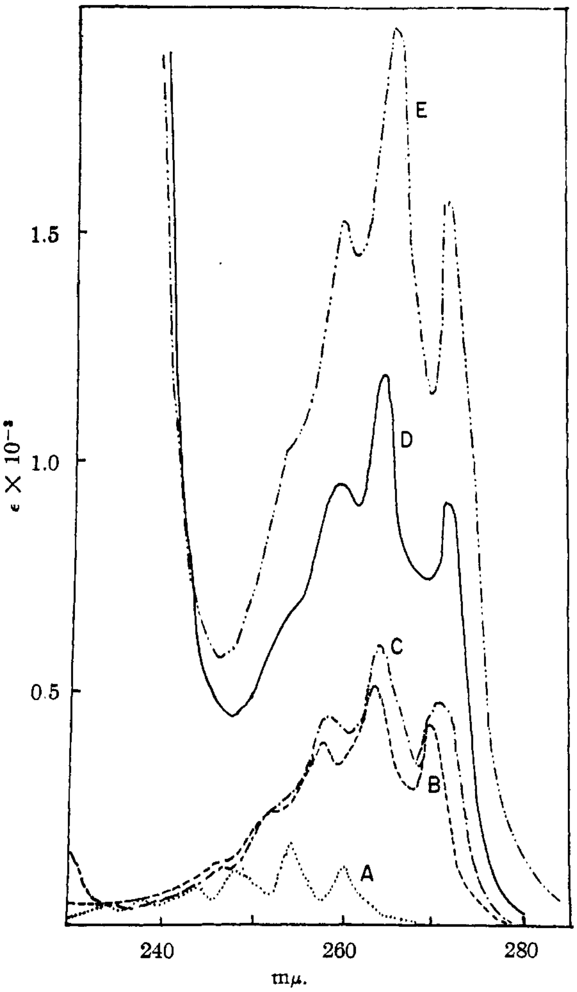

Fig. 1.—Absorption spectra: A, benzene; B, benzenephosphonic acid; C, benzenephosphonous acid; D, diphenylphosphinic acid; E, triphenylphosphine oxide.

Experimental

All compounds studied were prepared in this Laboratory. The synthesis of the arylphosphonic and the symmetrical