[RESEARCH LABORATORIES, AMERICAN HOME FOODS, INC.]

# Glyoxal Hemimercaptals

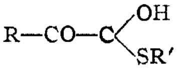
BY FRANK KIPNIS[1] AND JOHN ORNFELT

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 $\alpha,\beta$-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.

TABLE I

HEMIMERCAPTALS



$R{-}CO{-}C\begin{smallmatrix}\diagup OH \\ \diagdown SR'\end{smallmatrix}$

| R' | R | M.p., °C.[b] | Yield, % | Recrystallizing solvent | Formula | Analyses,[a] % Calculated Carbon | Calculated Hydrogen | Calculated Sulfur | Found Carbon | Found Hydrogen | Found 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 | $C\ H_4$ | 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 |  |
| $\beta$-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.

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.

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[1] Oxford Products, Inc., Cleveland 3, Ohio.

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

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[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 $\lambda_{max.}$ m$\mu$ | Primary band $\epsilon_{max.}$ | Secondary band $\lambda_{max.}$ m$\mu$ | Secondary band $\epsilon_{max.}$ |
|---|---|---|---|---|
| $C_6H_6$ | | | 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 m$\mu$ 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.

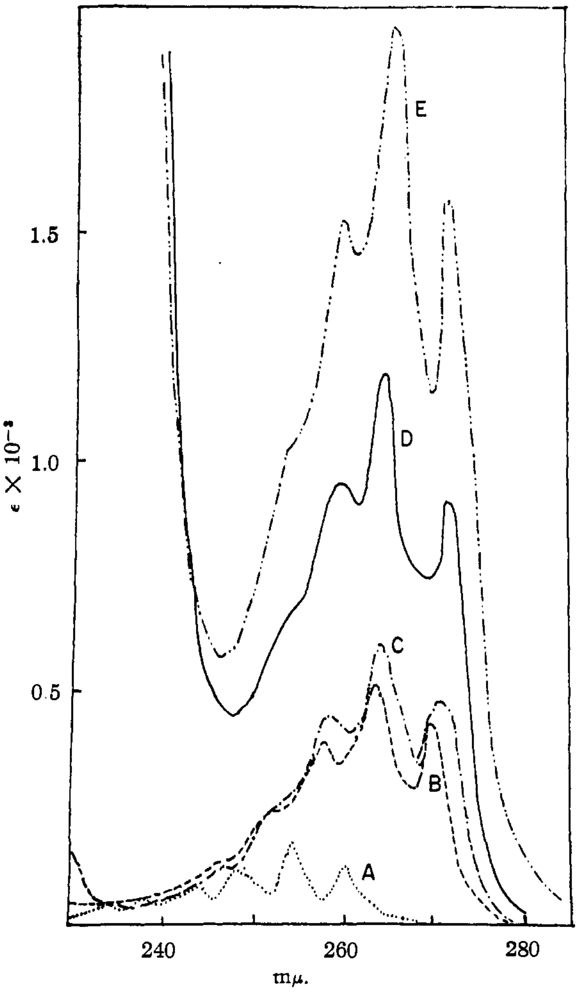

Fig. 1.—Absorption spectra: A, benzene; B, benzenephosphonic acid; C, benzenephosphonous acid; D, diphenylphosphinic acid; E, triphenylphosphine oxide.

## Experimental

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