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# Physical and Spectral Properties of 2-Aryl-1,3-Dioxolanes and Heteroatomic Analogs

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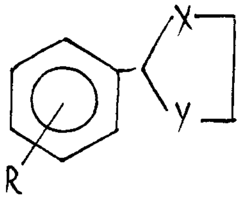
**Physical properties of 2-aryl-1,3-dioxolanes, 1,3-dithiolanes, 1,3-oxathiolines, and 1,3-N,N-dimethyl imidazolidines are reported. A very convenient pair of bands of medium to strong intensity is invariably found in the IR between 10.0 and 11.1 microns (1000 to 901 cm.$^{-1}$) characteristic of the heterocyclic five-membered ring and useful for analysis in the presence of the usual starting materials for the preparation of these compounds. The benzylic hydrogens of the four different heterocyclic systems show markedly different chemical shifts in their NMR spectra. Substituents on the phenyl rings have almost no effect on the chemical shift.**

FOR THE PURPOSES of careful kinetic investigations (autoxidations, hydrolyses, hydrogen abstraction reactions), the authors desired pure samples of compounds of the form



I $X = Y =$ oxygen
II $X = Y =$ sulfur
III $X =$ oxygen, $Y =$ sulfur
IV $X = Y = >NCH_3$

These compounds were obtained by standard procedures described in the experimental section.

Table I shows densities, refractive indexes, melting and boiling points, and infrared spectra bands between 10.0 and 11.1 microns (1000 to 901 cm.$^{-1}$), which were invariably found in the compounds studied. Spectra of alkyl analogs (Nos. 8, 15, and 20) also gave these bands, indicating that these absorptions do not arise from the aromatic moiety. All starting materials showed complete absence of absorptions in these regions. Assignments have been made in an earlier work for compounds related to the types reported here.

Bergman and Pinchas (*4*) have assigned bands to noncyclic acetals in the 8.7- to 10.0-micron (1200 to 1000 cm.$^{-1}$) region as characteristic of the C—O—C—O—C grouping. The bands reported do not invariably appear in IR spectra of cyclic acetals (*4, 17*), such as compounds of Type I. Other workers (*2, 23*) have studied cyclic acetals and ketals in detail and report bands at or near those reported here. These absorptions are attributed to ring breathing and ring stretching.

Compounds of Type II have been studied in detail (*11*). Bands in the far infrared region (900 to 300 cm.$^{-1}$) from 11.1 to 33.3 microns have been assigned to the ring system. All compounds reported were cyclic dithioacetals or ketals in the aliphatic series. Bands at 970 to 975 cm.$^{-1}$ (10.30 to 10.25 microns) were attributed to —$CH_2$— twisting. Absorption at 955 cm.$^{-1}$ (10.48 microns) was not reported.

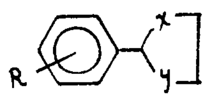
Compounds of Type III have been studied in somewhat less detail. 2-Alkyl-1,3-oxathiolanes are reported to have a strong absorption at ~9.3 microns (*3, 6*). This absorption is also found in spectra of aromatic aldehydes. Therefore, the choice for characterizing the heterocyclic system would avoid that absorption.

The imidazolidine system, IV, has been studied for *N,N*-dibenzyl analogs (*5*). Absorption at 9.1 and 9.8 microns (1099 to 1020 cm.$^{-1}$) have been attributed to the heterocyclic ring. 2-Phenyl-1,3-*N,N*-dimethyl imidazolidine gave no absorption at 9.1 microns and a medium band at 9.73 microns (1028 cm.$^{-1}$). Other members of our series absorbed at or near 9.1 and 9.8 microns. The bands observed at 10.24 and 11.06 microns (977, 904 cm.$^{-1}$) are considered more reliable in this system for the purposes of analysis, since starting materials show absorption between 9.1 and 9.8 microns.

Table I also describes the NMR spectra of the systems. Midpoints of the chemical shifts for the indicated groupings are tabulated. Integration of the spectra gave excellent agreement with indicated structures. Compounds of Type I, II, and IV gave $A_2B_2$ patterns for the ethylene hydrogen resonances. Compounds of Type III gave complex patterns for the ethylene hydrogens consisting of three groups of multiplets in the ratio 1:1:2. The phenyl absorptions were all normal for the substituents involved. The benzylic hydrogens were observed as a sharp singlet characteristic for the heterocyclic system but insensitive to substituents on the phenyl ring.

Detailed analysis of NMR spectra for systems of Type I (*1*) and III (*19*) have been carried out for the sake of describing conformation of the cyclic systems. Our chemi-

Table I. Data on 2-Aryl-1,3-Dioxolanes and Heteroatomic Analogs



| | | | | Physical Constants | | | | IR Bands | | | NMR Data Chemical Shifts, τ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| No. | R | $x$ | $y$ | $d^{25}$ g./cm.$^3$ | $n_D^{20}$ | B.P., ° C./mm. (m.p., ° C.) | Lit. | Band I μ(cm.$^{-1}$) | Band II μ(cm.$^{-1}$) | Solvent | Benzylic H | —CH$_2$ CH$_2$— | Phenyl H | Phenyl Subs. |
| 1 | H | O | O | 1.1127 | 1.5270 | 61–62/1.0 | (*13*) | 10.35<br>(966) | 10.58<br>(945) | neat | 5.68 | 3.75$^a$ | 7.32$^b$ | . . . |
| 2 | $p$-$CH_3$ | O | O | 1.0801 | 1.5246 | 88/2.4 | (*21*) | 10.25<br>(976) | 10.53<br>(950) | neat | 5.65 | 3.77$^a$ | 7.18$^a$ | 2.22 |
| 3 | $p$-$OCH_3$ | O | O | 1.1589 | 1.5350 | 91/0.25<br>(25–26) | (*21, 22*) | 10.30<br>(971) | 10.55<br>(948) | neat | 5.62 | 3.80$^a$ | 7.08$^a$ | 3.57 |
| 4 | $p$-$NO_2$ | O | O | . . . | . . . | (90) | (*12, 21*) | 10.25<br>(976) | 10.60<br>(943) | neat | 5.85 | 4.06$^a$ | 7.90$^a$ | . . . |
| 5 | $m$-$NO_2$ | O | O | . . . | . . . | (55–56) | (*10, 21*) | 10.30<br>(971) | 10.63<br>(941) | neat | 5.87 | 4.08$^b$ | 7.85$^b$ | . . . |
| 6 | $p$-$i$Pr | O | O | 1.0392 | 1.5153 | 75/.20 | | 10.35<br>(966) | 10.60<br>(943) | neat | . . . | . . . | . . . | . . . |
| 7 | $p$-Cl | O | O | 1.2459 | 1.5406 | 80/1.0 | (*20*) | 10.30<br>(971) | 10.60<br>(943) | neat | 5.63 | 3.83$^a$ | 7.32$^a$ | . . . |
| 8 | $^c$ | O | O | 0.8993 | 1.4306 | 42/.60 | (*22*) | 10.30<br>(971) | 10.62<br>(942) | neat | . . . | . . . | . . . | . . . |
| 9 | H | S | S | . . . | . . . | 78/.50<br>(27) | (*7*) | 10.25<br>(976) | 10.49<br>(953) | neat | 5.58 | 3.22$^a$ | 7.33$^b$ | . . . |
| 10 | $p$-$CH_3$ | S | S | . . . | . . . | (60.5–62.5) | (*14*) | 10.28 | 10.47 | $CCl_4$ | 5.60 | 3.33$^a$ | 7.23$^a$ | 2.27 |
| 11 | $p$-$OCH_3$ | S | S | . . . | . . . | (62.5–63.5) | (*8, 14*) | 10.30<br>(971) | 10.49<br>(953) | $CCl_4$ | 5.60 | 3.35$^a$ | 7.13$^a$ | 3.75 |
| 12 | $m$-$NO_2$ | S | S | . . . | . . . | (66–67) | | 10.10<br>(990) | 10.48<br>(954) | melt | 5.67 | 3.45$^a$ | 7.88$^b$ | . . . |
| 13 | $p$-iPr | S | S | . . . | . . . | (60–61) | | 10.30<br>(971) | 10.48<br>(954) | $CCl_4$ | . . . | . . . | . . . | . . . |
| 14 | $p$-Cl | S | S | . . . | . . . | (60–61) | (*14*) | 10.28<br>(973) | 10.47<br>(955) | $CCl_4$ | 5.50 | 3.30$^a$ | 7.30$^a$ | . . . |
| 15 | $^d$ | S | S | 1.0449 | 1.5315 | 41/.10 | | 10.25<br>(976) | 10.47<br>(955) | neat | . . . | . . . | . . . | . . . |
| 16 | H | S | O | 1.1618 | 1.5851 | 72/.45 | (*16*) | 10.30<br>(971) | 10.67<br>(937) | neat | 5.97 | 4.25$^e$<br>3.68$^e$<br>2.93$^e$ | 8.22$^b$ | . . . |
| 17 | $p$-$CH_3$ | S | O | 1.1208 | 1.5765 | 81/.55 | | . . . | . . . | . . . | 5.93 | 4.28$^e$<br>3.72$^e$<br>2.97$^e$ | 7.18$^a$ | 2.22 |
| 18 | $p$-$OCH_3$ | S | O | . . . | . . . | 110/.45 | (*18*) | 10.35<br>(966) | 10.68<br>(936) | neat | 5.95 | 4.40$^e$<br>3.70$^e$<br>3.10$^e$ | 7.10$^a$ | 3.70 |
| 19 | $p$-$i$Pr | S | O | 1.0389 | 1.5151 | 87/2.0 | | 10.35<br>(966) | 10.60<br>(943) | neat | 5.97$^f$ | 4.30$^{e,f}$<br>3.72$^f$<br>2.98$^f$ | 7.02$^{e,f}$ | 3.63$^f$ |
| 20 | $^g$ | S | O | 0.9860 | 1.4789 | 33/.30 | | 10.34<br>(967) | 10.65<br>(939) | neat | . . . | . . . | . . . | . . . |
| 21 | H | $>NCH_3$ | $>NCH_3$ | 0.9682 | 1.5271 | 65/.60 | | 10.25<br>(976) | 11.05<br>(905) | neat | 3.22 | 2.83$^a$ | 7.37$^f$ | $^h$ |
| 22 | $p$-$CH_3$ | $>NCH_3$ | $>NCH_3$ | 0.9573 | 1.5248 | 68/.20 | | 10.26<br>(975) | 11.15<br>(897) | neat | 3.22 | 2.88$^a$ | 7.23$^a$ | 2.28$^h$ |
| 23 | $p$-$OCH_3$ | $>NCH_3$ | $>NCH_3$ | 1.0227 | 1.5326 | 83/.20 | | 10.24<br>(977) | 11.03<br>(903) | neat | 3.17 | 2.85$^a$ | 7.12$^a$ | 3.65$^h$ |
| 24 | $p$-Cl | $>NCH_3$ | $>NCH_3$ | 1.0807 | 1.5404 | 74/.23 | | 10.24<br>(977) | 11.08<br>(903) | neat | 3.20 | 2.87$^a$ | 7.35$^a$ | $^h$ |

[a] Center of $A_2B_2$ pattern. [b] Center of multiplet. [c] 2-$n$-Hexyl-1,3-dioxolane. [d] 2-$n$-Butyl-1,3 dithiolane. [e] Centers of 3 groups of multiplets in ratio 1:1:2 from top to bottom. [f] 2-($m$-Methoxyphenyl)-1,3-oxothiolane. [g] 2-$n$-Butyl-1,3-oxothiolane. [h] N-methyl groups appear as singlets at 2.08–2.13τ.

cal shift data and general spectral characteristics are in agreement with literature values. Under present conditions, the heterocyclic system was probably conformationally stable (*19*).

Table II summarizes the significant spectral data observed in this study.

## EXPERIMENTAL

**Preparations.** Compounds of Type I, II, and IV were made by the method of Sulzbacher *et al.* (*22*). Equimolar portions of aldehyde and glycol (or heteroanalog) in 400 ml. of benzene or toluene (for 0.5 mole preparation) were refluxed with ~100 mg. of $p$-toluene sulfonic acid catalyst.

Table II. Summary of Spectral Data

| | IR | | NMR, τ | |
|---|---|---|---|---|
| Type | μ | cm.$^{-1}$ | Benzylic H | —$CH_2CH_2$— |
| I | 10.27 ± 0.03<br>10.58 ± 0.05 | 974<br>945 | 5.73 ± 0.12 | 5.58 ± 0.17 |
| II | 10.07 ± 0.07<br>10.47 ± 0.01 | 993<br>955 | 5.58 ± 0.08 | 3.33 ± 0.12 |
| III | 10.32 ± 0.03<br>10.64 ± 0.04 | 969<br>940 | 5.95 ± 0.02 | 4.33 ± 0.07<br>3.68 ± 0.03<br>3.02 ± 0.08 |
| IV | 10.24 ± 0.01<br>11.06 ± 0.03 | 977<br>904 | 3.20 ± 0.03 | 2.87 + 0.03 |

Water was removed through a Dean-Stark trap. Crude material was washed with ~ 1*M* NaOH, dried with anhydrous $K_2CO_3$, and distilled at reduced pressure under a nitrogen atmosphere. Middle cuts free of carbonyl and hydroxyl absorption in the IR were used for analyses. Crude yields were nearly quantitative. Purified material was obtained in 60 to 90% yield and stored under nitrogen.

Compounds of Type III were usually made according to a modified procedure of Fieser (*9*). One-half mole each of aldehyde and 1,2-ethanedithiol were mixed in 300 ml. of glacial acetic acid. Five milliliters of $BF_3$ in ether (Eastman Organic Purified) was added with stirring. An exothermic reaction occurred. After cooling, methanol was added. A small piece of dry ice induced crystallization if the product was a solid. The product was recrystallized from methanol or sublimed in vacuo. Yields of purified product were 60 to 80%. Melting points are uncorrected. Compounds of Type III were not prepared by this procedure owing to polymer formation.

**Density and Refractive Index.** Density measurements were made in new water-calibrated, 1-ml. volumetric flasks. Refractive index was measured on a Bausch & Lomb refractometer, Type 33-45-58, with prisms thermostated at 20° C.

**Spectra.** All IR spectra reported were taken on a Perkin-Elmer Model 21. Bands reported in Table II are medium to strong intensity and broad. Complete spectra were taken between 2 and 15.5 microns (5000 to 645 $cm.^{-1}$), and characteristic absorptions where appropriate were noted at expected wavelengths (phenyl, nitro, etc.). The absence of carbonyl absorption at 5.6 to 6.0 microns (1788 to 1667 $cm.^{-1}$) was used as an indication of sample purity.

NMR spectra were taken with a Varian A60 operating at 60 mc. per second. Chemical shifts are recorded on the scale relative to an internal tetramethylsilane reference. The sweep width used was 500 c.p.s.

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# Low Pressure Adsorption of Helium on Microporous Solids

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**The adsorption of helium on five different microporous solids was measured by a gravimetric technique over a temperature range from boiling nitrogen to room temperature, at pressures at and below 1 atm. (absolute). The procedure is detailed, and the results are presented. The results compare favorably with some other published findings.**

THIS WORK was undertaken in an attempt to establish the existence or absence of measurable amounts of helium adsorption on various representative microporous solids. Helium adsorption is negligibly small, and an assumption to this effect has an important utility in the measuring of adsorption of other gases. A similar assumption also has a use in establishing mechanisms of flow through microporous materials. The error accompanying this assumption in the latter determination may be significant (*5*), and principally for this reason, the work was undertaken.

Since zero helium adsorption could not be assumed in the present case and since gravimetric measurements were to be made, an alternate method of evaluating the volume occupied by the solid material had to be used to assess the value of buoyancy. Buoyancy determinations were of extreme importance in this work since the magnitude of the buoyant force was several times that of the weight of gas adsorbed in the usual case. Thus, the otherwise minor uncertainties in solid volume could lead to major uncertainties in the amount of gas adsorbed. Although several methods of determining the solid volumes were considered, the one used in this investigation was that of measuring the apparent weight change upon immersion of the sample (including its container) in liquid nitrogen.

Adsorption isotherms of nitrogen and argon were measured for purposes of comparison, and surface areas of the adsorbents were determined from nitrogen adsorption at the temperature of its normal boiling point.

## EXPERIMENTAL

**Adsorbents.** There were five different adsorbents used in this work.

GRADE KH-1 ACTIVATED CHARCOAL, approximately

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