These derivatives were prepared as authentic reference samples in order to identify sugars being investigated in another research project.

EXPERIMENTAL

Acetylation of D-glucose. Finely powdered D-glucose (5.145 g.) was mixed with acetic anhydride (60.0 ml.) and Amberlite IR-120 cation exchange resin (0.100 g.). The mixture was heated to 98–99° with stirring and within 1.5 hr. dissolution of the sugar was complete. After stirring for 7 hr. at this temperature, the refractive index of the solution became constant. The solution was then decanted from the resin, and the resin was washed several times with small portions of acetic anhydride; the washings being then added to the main portion of the solution. This solution was then concentrated (*in vacuo*) at 85–90° to a thin sirup, cooled to room temperature and poured with stirring into 300 ml. of ice and water. While standing at 5° for 12 hr. a sirup separated from the aqueous phase. This liquid was removed from the sirup by decantation and extracted three times with ethyl ether. The extracts were combined, concentrated (*in vacuo*) at 50° and added to the sirup. Aqueous methanol (80 ml. of 75% w./w.) was used to dissolve the viscous product which crystallized at −10° within 24 hr. The pentaacetate, three times recrystallized from aqueous methanol, showed a melting point of 97° and a specific rotation of $[\alpha]^{25}D$ +148°, in chloroform (*c*, 1). Further recrystallization from aqueous methanol did not alter the melting point nor the specific rotation. The yield was 58.0%. The product is believed to be 2,3,4,6-tetraacetyl-α-acetyl-D-glucopyranoside.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: acetyl, 55.10. Found: acetyl, 54.84.

Acetylation of sucrose. Powdered sucrose (5.000 g.), acetic anhydride (100 ml.) and Amberlite IR-120 (0.200 g.), were stirred for 6 hr. at 55–60°. After cooling to room temperature, the solution was separated from the resin by decantation and poured slowly into 600 ml. of ice and water. The resin was washed several times with 10-ml. portions of acetic anhydride, and the washings were also added to the ice and water. The sirup which separated from the aqueous phase after severals hours was isolated by decantation of the aqueous solution. The aqueous phase was extracted three times with 30-ml. portions of chloroform, and the extracts were combined, concentrated (*in vacuo*) at 50° and added to the sirup. The sirup was dissolved in ethanol (30 ml.), and water was added (approx. 5 ml.) until the solution became slightly turbid. Crystallization at 5° began very slowly but was complete after approximately 7 days. The product was recrystallized twice from aqueous ethanol. Further recrystallization did not alter the melting point nor the specific rotation; m.p., 73.5°; $[\alpha]^{25}D$ +60.65°, in chloroform (*c*, 1). The yield of octaacetyl sucrose 44.2%.

Anal. Calcd. for $C_{28}H_{37}O_{19}$: acetyl, 50.74. Found: acetyl, 49.59.

Acetylation of D-fructose. Powdered D-fructose (5.000 g.), was added at room temperature to acetic anhydride (100 ml.) containing a suspension of Amberlite IR-120 (0.300 g.). The reactants were stirred and the temperature was raised to 50° and kept at that temperature for 2 hr. After cooling to room temperature (0.5 hr.), the solution was decanted from the resin and slowly stirred into a mixture of ice and water (500 ml.). The resin was washed several times with 20-ml. portions of acetic anhydride; the washings being also added slowly to the ice and water. While stirring was continuing for 12 hr. a sirup separated from the aqueous phase. This phase was removed and extracted three times with 20-ml. portions of ethyl ether. The extracts and sirup were combined in a separatory funnel and washed with saturated sodium bicarbonate solution until effervescence ceased. After washing twice with water, the product was concentrated (*in vacuo*) at 50° to a thin sirup. Seed crystals were obtained by dissolving a small amount of sirup in a small volume of ethyl ether and permitting the solvent to evaporate very slowly at 5°. The main portion of the product was then crystallized at 5° from chloroform. After recrystallizing three times from chloroform, the melting point, 128–129°, and the specific rotation, $[\alpha]^{25}D$ −80.1° in chloroform (*c*, 1.5), remained constant. The yield was 40.1%.

Anal. Calcd. for $C_{16}H_{22}O_{11}$: acetyl, 55.10 Found: acetyl, 54.90.

The product is believed to be the 2,3,4,5-tetraacetyl-β-acetyl derivative of D-fructose.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MINNESOTA, DULUTH
DULUTH 12, MINN.

A Chart of Ultraviolet Absorption Maxima of 2,4-Dinitrophenylhydrazones

J. P. PHILLIPS

Probably the largest single group of very similar compounds for which ultraviolet spectra in a single solvent have been determined is the 2,4-dinitrophenylhydrazones of aldehydes and ketones in chloroform. A survey of three volumes of "Organic Electronic Spectral Data" [1] supplemented by a few collections of data from earlier and later literature[2,3] readily yielded about 740 distinct compounds of this class plus a number of duplicates. Fortunately the reproducibility of duplicates was rarely worse than 2–3 mμ.

The size of this group suggested the possibility of making a useful Colthup-type chart of the range of wave lengths for the principal absorption maximum as a function of the carbonyl compound structure. Although the rather unspecific relations of structure and spectrum in the ultraviolet as compared to the infrared might make such a chart disappointingly vague, its utility as a speedy reference made the effort worth a trial. Because of classification problems and the desire to avoid too many separate categories only 459 compounds found their way into the final chart (Fig. 1). Since many steroids, most natural products, and most naphthalenones and

(1) M. J. Kamlet (ed.), "Organic Electronic Spectral Data," Vol. I, Interscience Publishers, New York, 1960; Vol. II, H. E. Ungnade (ed.), 1960; Vol. IV, J. Phillips and F. C. Nachod (ed.), *in press.*

(2) E. A. Braude and R. N. Jones, *J. Chem. Soc.*, 498 (1945).

(3) L. A. Jones *et al., J. Org. Chem.*, **25**, 226 (1960); *J. Am. Chem. Soc.*, **82**, 105 (1960); *Anal. Chem.*, **28**, 191 (1956).

Figure 1

Fig. 2. Number of 2,4-dinitrophenylhydrazones having given wave length of maximum absorption (740 compounds). Each interval is 5 mμ, except first and last
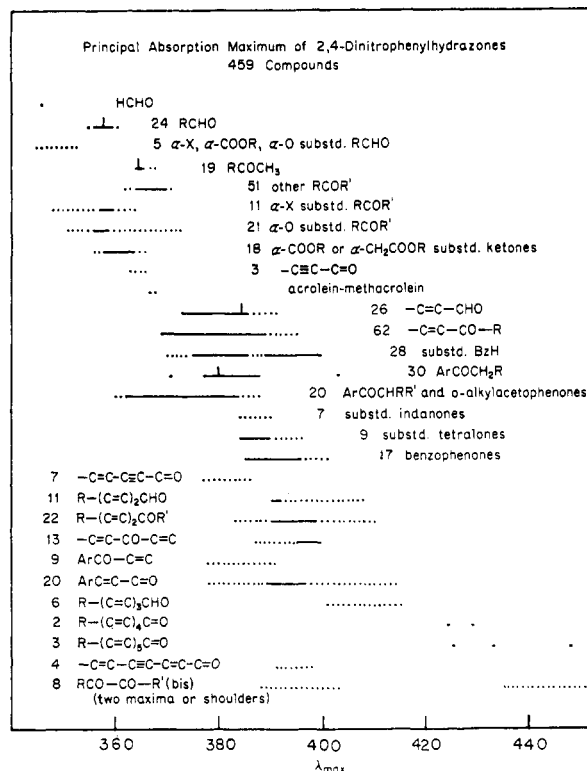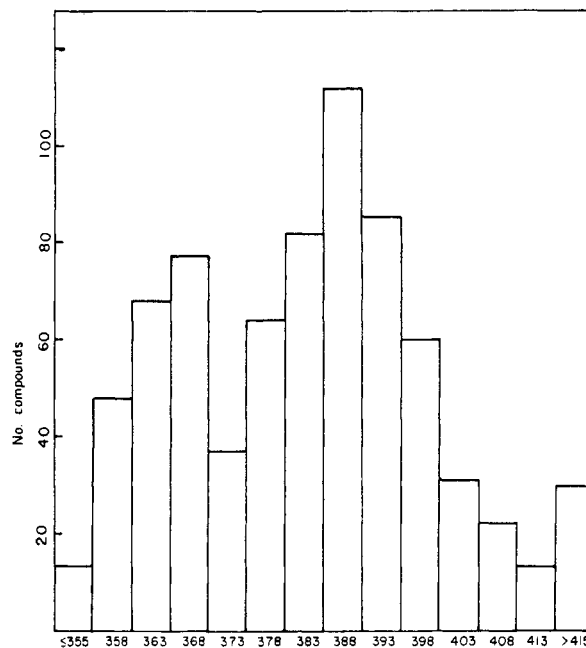
ketones from higher ring systems were left out, it is possible that the selection exhibits bias toward the simpler aldehydes and ketones. Those desiring subtle or elegant interpretations beyond the scope of such a chart have a voluminous literature to fall back on, especially if steroids[4] or problems of isomerism[5] need to be considered.

In the chart dotted lines represent wave length ranges that are sparsely populated (a density never greater than one compound per millimicron), and solid lines regions of higher population; an occasional vertical line represents an outstanding concentration of compounds at or close to that wave length.

It is well known that not only the wave length but also the molar absorbancy of the 2,4-dinitrophenylhydrazones tends to increase with increasing wave length. A frequency plot of the entire collection of 740 compounds (Fig. 2) shows that the most common wave lengths are 361–370 and 386–390 mμ, representing, respectively, saturated ketones (including those containing only isolated additional chromophores) and conjugated or aromatic systems. Of about 220 compounds having the wave length maximum at 370 mμ or less there were 130 having log ε in the 4.34–4.39 range. Of more than 500 having the wave length maximum above 370 mμ there were 275 with log ε in the 4.43–4.51 region.

(4) C. Djerassi and E. Ryan, J. Am. Chem. Soc., 71, 1000 (1949).

(5) F. Ramirez and A. F. Kirby, J. Am. Chem. Soc., 76, 1037 (1954).

A more detailed analysis of the log ε distribution could be expected to show a general but small additional rise with increasing length of the conjugated systems in the unsaturated and aromatic compounds. Very rarely, however, were log ε values below 4.3 or above 4.7 encountered.

Proposals of determining molecular weights of carbonyl compounds by measuring light absorbancy of the 2,4-dinitrophenylhydrazones, assuming a fixed molar absorbancy for the 2,4-dinitrophenylhydrazone, have been made. As long as the carbonyl compound is a saturated one, the procedure could be highly accurate, but in the light of the above findings would be rather dubious for any other variety of carbonyl.

The following notes help to explain Fig. 1:

1. Saturated aldehydes have λ_{max} 358 ± 1; log ε 4.35 ± 0.01.

2. Saturated methyl ketones have λ_{max} 365 ± 1; log ε 4.35 ± 0.01; all other saturated ketones have λ_{max} 367 ± 2; log ε 4.36 ± 0.02. (Under the heading "saturated" are included also compounds lacking a functional group substituent but possibly containing isolated multiple bonds or even aryl groups if insulated by one or more methylene groups.)

3. Substitution of halogen, hydroxy, acetoxy, methoxy, COOR, or CH₂COOR groups on the α-carbon of saturated aldehyde or ketone usually produces a hypsochromic shift, though this rule has some exceptions, notably α-methoxycyclohexanones.

4. Triple bonds in place of double bonds at any point in a conjugated system give a hypsochromic shift compared to the corresponding double bond system.

5. In the lower members of the α,β-unsaturated aldehydes the maximum is notably shorter than in the series as a whole. For this reason, acrolein and methacrolein were tabulated separately but crotonaldehyde and tiglaldehyde were included with the main series.

6. Substituted benzaldehydes and benzophenones show

wave length variations largely in accord with the well known chromophoric properties of their substituents. In the benzaldehyde section of the chart the solid segment at longer wave lengths is composed almost entirely of *o,p*-alkoxy or hydroxy derivatives. The *p*-dialkylamino derivatives absorb well above 400 mμ and do not appear on the chart. The number of aromatic aldehydes of heterocyclic or higher ring systems was too small to justify entry in the table.

7. Acetophenones (or higher homologs) lacking *o*-alkyl substituents or α-substituents resemble the benzaldehydes. (End compounds on the chart are the *p*-nitro and *p*-amino derivatives respectively at left and right.) Apparently *o*-substituents or two α-substituents exert a considerable steric hindrance. The problem is complicated by the fact that a number of α-substituted acetophenones have two isomeric 2,4-dinitrophenylhydrazones absorbing about 20 mμ apart. For a detailed discussion see papers by Ramirez.[5]

8. Tetralones and indanones are logically related to the acetophenones in spectra.

9. Bis-2,4-dinitrophenylhydrazones generally absorb at about the expected wave length for the corresponding mono compounds but with approximately doubled absorbancy. Notable exceptions are the vicinal dicarbonyl compounds, where the 2,4-dinitrophenylhydrazone groups are conjugated with each other, and the maxima included usually a band near 400 and also one around 430 mμ.

Preparation of Tropilidene Derivatives from Tropylium Bromide

NEDRA W. JORDAN AND I. W. ELLIOTT[1]

Tropylium bromide (1) has been shown to replace protons on reactive methylene, hydroxyl, amino and amido groups.[2-4] We report here an extension of these reactions in which tropylium bromide is allowed to react with 2-carbethoxycyclopentanone, potassium phthalimide, and 1,3-indandione to afford respectively II, III, and IV. The structures of the products are supported by analyses and infrared spectra. The latter is useful to show the presence of the intact cycloheptatriene ring.[3]

The substituted indandiones (IV) were prepared

IVa. $n = 1$
b. $n = 2$
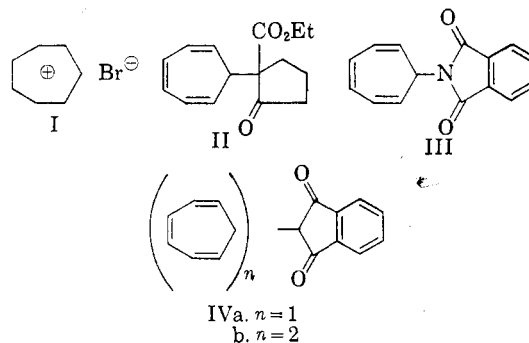
as potential blood anticoagulant drugs.[5] Both 2-tropyl-1,3-indandione (IVa) and 2,2-ditropyl-1,3-indandione (IVb) were isolated, depending on the method of preparation and purification. Compound IVa in dichloromethane solution undergoes a color change from yellow to red on the addition of base, but IVb does not. This change can be ascribed to an increase in the enol content in IVa.[6]

In 1939 Kohler[7] prepared an adduct of tropilidene with maleic anhydride in refluxing xylene. The structure of this compound was resolved in 1953 by Alder and Jacobs as *endo-cis*-3,6-*endo*-cyclopropyl-1,2,5,6-tetrahydrophthalic anhydride (V).[8] A reaction between tropilidene and maleic anhydride at room temperature in ether afforded the same adduct. The yield of the adduct formed under the milder reaction conditions was about half that from refluxing xylene, but no attempts were made to determine optimum conditions for the reaction in ether or to obtain quantitative recovery of the products. In an extension of the Diels-Alder reactions of cycloheptatriene, new adducts (VI) have

V

VIa. R = H
b. R = –CH(COCH$_3$)$_2$
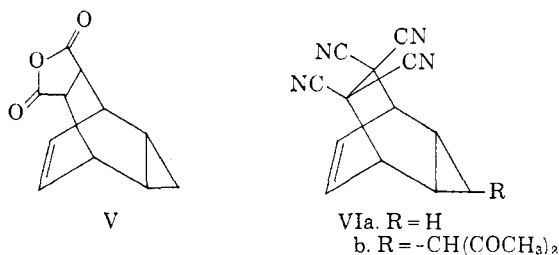
been synthesized from the dienophile tetracyanoethylene with tropilidene and tropylacetylacetone, and the structures of these products are assigned by analogy with the adduct from maleic anhydride (V) and from similar infrared spectra.

Weiss and Lalande have discussed the spectra of a series of maleic anhydride adducts with tropilidene derivatives, but they did not explicitly

(1) To whom correspondence concerning this note should be addressed.

(2) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 353 (1957).

(3) K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

(4) M. E. Volpin, I. S. Akrem, and D. N. Kursanov, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 1501 (1957); *Chem. Abstr.*, **52**, 7175c (1958).

(5) See S. L. Shapiro, K. Geiger, and L. Freedman, *J. Org. Chem.*, **25**, 1860 (1960) for a discussion and references on these compounds.

(6) *Cf.* A. Schönberg and F. Singer, *Chem. Ber.*, **94**, 241 (1961); A. Schönberg and G. Schutz, *Chem. Ber.*, **94**, 667 (1961).

(7) W. Kohler, M. Tishler, H. Potter, and H. T. Thomsen, *J. Am. Chem. Soc.*, **61**, 1057 (1939).

(8) K. Alder and G. Jacobs, *Chem. Ber.*, **86**, 1528 (1953).