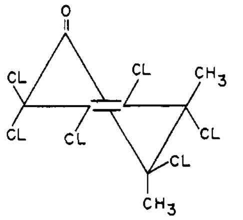
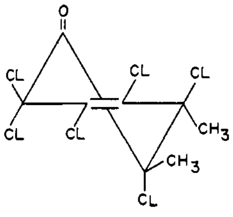
89°C, as the more soluble fraction. Although only a single $\delta CH_3 = 1.98$ ppm was observed for **24** in deuterochloroform, two separate peaks were observed in deuterobenzene. Two nonequivalent methyl groups were observed for **25** in deuterochloroform. The high-field chemical shifts of these methyl protons of **24** and **25** indicate that they are stereoisomers of 2,2,3,4,5,6-hexachloro-5,6-dimethyl-3-cyclohexen-1-one. The ir absorption frequencies of $\nu_{C-O} = 1768$ and $1752\ cm^{-1}$ for **24** and **25**, respectively, indicate that the methyl group at 6 C is axial in **24** and equatorial in **25**. The 5-methyl groups of **24** and **25** may probably be axial and equatorial, respectively.



24



25

Chlorination of **9** or dichloro-2,3,5-trimethylphenol gives liquids containing a 3-cyclohexenone (**26**) and a 2-cyclohexenone (**27**) as the major components. No coupling of the methyl protons is observed for either compound. Therefore, the two adjacent methyl groups are not bound to a common double bond as in **14**. The proton chemical shifts of **26** are assigned by reference to the chemical shifts of the 5-methyl and 6-methyl groups of **25** and the 3-methyl groups of **23**, **15**, or **16**. The alternate structure of pentachloro-2,3,5-trimethyl-3-cyclohexen-1-one for **26** may be ruled out because the proton chemical shift of the 3-methyl group should then be in the region of 2.11 ~ 2.14 ppm as in **21a** or **21b**.

2-Cyclohexen-1-ones. The ir carbonyl absorption of a 2-cyclohexenone is intermediate of the corresponding 3-cyclohexenone and 2,4-cyclohexadienone. The 2-cyclohexenone is normally found in the liquid fraction of the chlorination products. Table III contains the 2-cyclohexenones identified. The absence of methyl coupling in **27** limits its structure to pentachloro-3,5,6-trimethyl-2-cyclohexen-1-one. The $\delta CH_3 =$ 2.47 ppm is assigned to the 3-methyl group on the double bond conjugated to the carbonyl in agreement with those of **4**, **9**, **12**, and **13**.

The structures given for **28** and **29** are based on the relative proton chemical shifts and absence of proton coupling. Ketone **30** was obtained by repeated recrystallization of the solid fraction formed by chlorination of 3-chloroaniline. Ketones **31** and **32** were identified in the liquid fractions obtained by the chlorination of 3-chloro-6-methylaniline and 3-chloro-2-methylaniline, respectively (*4*). The elucidation of the steric configurations of these 2-cyclohexenones requires further investigation.

The identification of the numerous chlorination products indicates that the chlorination of the polymethyl phenols and anilines in acetic acid proceeds essentially in an analogous manner as in the chlorination of cresols and toluidines (*4*). However, the positions of the methyl groups and the conditions of the chlorination determine the composition of the products. In the case of 2,6-dimethyl phenols with different groups at the *m*-positions, the *o*-position adjacent to an unsubstituted or a methylated *m*-position is chlorinated preferentially than the *o*-position adjacent to a chlorinated *m*-position. Stereoisomers of 3-cyclohexenones are readily obtained by the chlorination of anilines rather than phenols. The relative chemical shifts of axial and equatorial α-methyl protons are influenced by the neighboring atomic groups.

REFERENCES

(1) Denivelle, L., Fort, R., *Compt. Rend.*, **235**, 1514 (1952).
(2) Kumamoto, J., Kato, T., *J. Ind. Chem.* (Japan), **60**, 1325 (1957).
(3) Morita, E., *Rubber Chem. Technol.*, **43**, 171 (1970).
(4) Morita E., Dietrich, M. W., *Can. J. Chem.*, **47**, 1943 (1969).
(5) Muller, H., Linde, H., *J. Prak. Chem.*, **4**, 69 (1956).
(6) Vollbracht, L., Huysmans, W. G. B., Mijs, W. J., Hageman, H. J., *Tetrahedron*, **24**, 6265 (1968).

Received for review June 24, 1971. Accepted October 18, 1971.

Synthesis of Bis-α-tetralones

JERRY HIGGINS,[1] C. S. MENON, and Z. JANOVIC
Department of Chemistry, Illinois State University, Normal, Ill. 61761

The synthesis of two bis-α-tetralones, 7,7′-oxydi-1-tetralone and 7,7′-ethylene-1-tetralone, are described.

In the course of studies aimed at producing photocondensation polymers (*2*) by the photolytic coupling of aromatic diketones, it was desirable to prepare some bis-α-tetralones as possible monomers. Although α-tetralone couples quite readily on exposure to uv light (*1*) to give the corresponding pinacol, we were unsuccessful in coupling the bis-α-tetralones under the same reaction conditions. However, since the bis-α-tetralones are important potential intermediates in the formation of binaphthalenes and fuse-ringed aromatic derivatives (*4*), we would like to report the synthesis of 7,7′-oxydi-1-tetralone (**3a**) and 7,7′-ethylenedi-1-tetralone (**3b**).

The formation of cyclic ketones by intermolecular acylation is a well-known method in organic chemistry (*3*). Such ring closures have been effected by a variety of methods generally involving either the direct cyclodehydration of the acids or the cyclodehydrohalogenation of the acid chlorides by intramolecular Friedel-Crafts reactions. The cyclization of γ-phenylbutyric acid in such a way gives α-tetralone in 70–80% yield. Using a similar procedure, we have been successful in the preparation of two bis-α-tetralones by the cyclization of the corresponding diacids (Figure 1).

---

[1] To whom correspondence should be addressed.

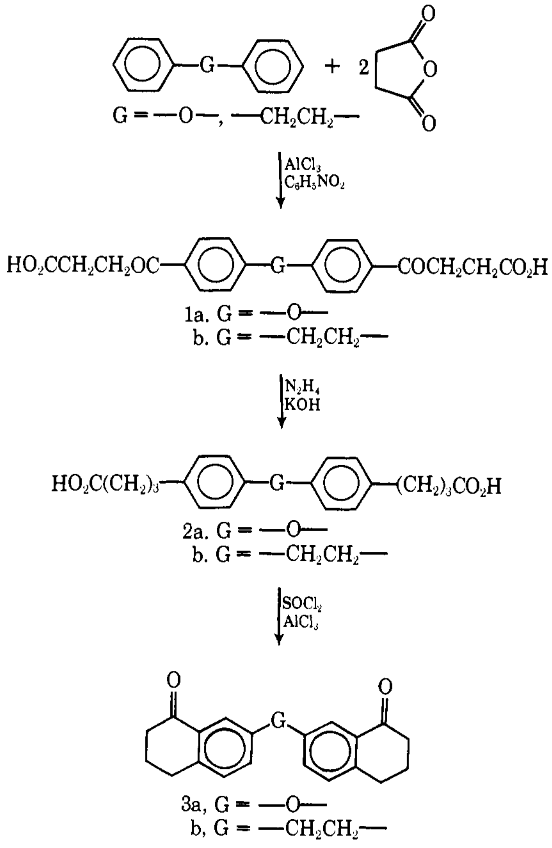


Figure 1

EXPERIMENTAL

All melting points are uncorrected. The microanalyses were performed by Micro-Analysis, Inc., Marshallton, Wilmington, Del. Infrared spectra were taken on a Beckman IR-8 and Perkin-Elmer Model 700 instruments. The nmr spectra were obtained with a Hitachi Perkin-Elmer R-20 instrument at ambient temperature.

p,p'-**Oxybis(*p*-benzoylpropionic Acid) (1a).** To 380 ml of nitrobenzene were added 85 grams (0.50 mole) of diphenyl ether and 125 grams (1.25 moles) of succinic anhydride. With stirring, 335 grams (2.52 moles) of aluminum chloride was added slowly. The reaction solution became very viscous and was allowed to stand overnight at room temperature. The reaction product was hydrolyzed with 10% hydrochloric acid, the solid filtered, redissolved in 10% aqueous sodium hydroxide, filtered again, and finally acidified to give 148 grams (80%) of product. The product was recrystallized from glacial acetic acid, mp 225°C.

Anal. Calcd. for $C_{20}H_{18}O_7$: C, 64.88%; H, 4.90%. Found: C, 65.15%; H, 4.98%.

p,p'-**Ethylenebis(β-benzoylpropionic Acid) (1b).** The same experimental procedure as that given for **1a,** using bibenzyl instead of diphenyl ether gave **1b** in 81% yield, mp 248–50°C.

Anal. Calcd. for $C_{22}H_{22}O_6$: C, 69.11%; H, 5.80%. Found: C, 68.86%; H, 5.72%.

p,p'-**Oxybis(γ-phenylbutyric Acid (2a).** To 250 ml of diethylene glycol were added 60 grams (0.16 mole) of compound **1a** and 35 grams of sodium hydroxide. After all of the compound had dissolved, 30 ml of hydrazine hydrate (64%) was added to the warm solution. After refluxing for 3.5 hr, the water was distilled until a head temperature reached 195°C, and then refluxing was continued at this temperature for an additional 4 hr. After the usual work-up, the product was recrystallized from benzene–tetrahydrofuran (1:1) to give 34.7 grams (61%) of white crystals, mp 168-9°C.

Anal. Calcd. for $C_{20}H_{22}O_5$: C, 70.17%; H, 6.48%. Found: C, 69.98%; H, 6.60%.

p,p'-**Ethylenebis(γ-phenylbutyric Acid) (2b).** The same procedure as that described for **2a** gave **2b** in 46% yield, mp, 180-2°C.

Anal. Calcd. for $C_{22}H_{26}O_5$: C, 74.54%; H, 7.39%. Found: C, 74.88%, H, 7.42%.

7,7'-Oxydi-1-tetralone (3a). To 150 ml of thionyl chloride was added 34.7 grams (0.098 mole) of compound **2a.** The solution was refluxed for 3 hr and the excess thionyl chloride removed by distillation. To the residue were added 150 ml of carbon disulfide and 60 grams of aluminum chloride in small portions. After the addition of the aluminum chloride, the dark solution was refluxed for 3 hr. The reaction solution was cooled, hydrolyzed with cold 10% hydrochloric acid, and the product was filtered and recrystallized from ethanol to give 23.2 grams (77%) of white crystalline product, mp 158-9°C.

Nmr ($CDCl_3$): quintet (4H) 7.92 τ, triplet (4H) 7.41 τ, triplet (4H) 7.07 τ, doublet (4H) 2.82 τ, singlet (2H) 2.44 τ.

Ir (KBr): 2940 m, 1675 s, 1595 m, 1481 s, 1262 m, 1235 s, 940 w, 908 m, 825 w.

Anal. Calcd. for $C_{20}H_{18}O_3$: C, 78.43%; H, 5.92%. Found: C, 78.12%; H, 5.84%.

7,7'-Ethylenedi-1-tetralone (3b). This compound was prepared by using the same procedure as that described for **3a** using **2b** as the starting material. White crystals were obtained in 50% yield, mp 170-1°C.

Nmr ($CDCl_3$): quintet (4H) 7.88 τ, triplet (4H) 7.38 τ, multiplet (8H) 7.04 τ, doublet (4H) 2.74 τ, single (2H) 2.08 τ.

Ir (KBr): 2920 s, 2855 m, 1660 s, 1602 s, 1485 m, 1408 s, 1285 s, 1030 m, 895 m, 820 s.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 82.96%; H, 6.97%. Found: C, 82.92%; H, 6.83%.

LITERATURE CITED

(1) Bergmann, F., Hirshberg, Y., *J. Amer. Chem. Soc.,* **65,** 1429 (1943).
(2) Higgins, Jerry, Johannes, Arland H., Jones, Joe F., Schultz, Ronald, McCombs, D. A., Menon, C. S., *J. Polymer Sci. Part A-1,* **8,** 1987 (1970).
(3) Jonson, W. S., "Organic Reactions," Vol. 11, R. Adams, Ed., p 114, Wiley, New York, N. Y., 1944.
(4) Yax, Emile, Ourisson, Guy, *Bull. Soc. Chem. Fr.,* **11,** 4153 (1967).

Received for review June 28, 1971. Accepted October 29, 1971. This work was supported by the Army Research Office-Durham, Durham, N. C.