[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

Spectroscopic and Other Properties of Large Ring Mono- and Dimeric Benzocyclanones Prepared by a High-dilution Friedel–Crafts Reaction[1]

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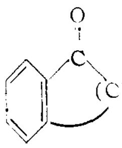
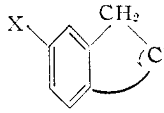
In the high-dilution Friedel–Crafts reaction: 6-phenylhexanoyl chloride gave I ($n = 5$) in 67% yield; 6-(3,5-dimethylphenyl)-hexanoyl chloride gave IV in 54% yield; 7-phenylheptanoyl chloride gave a 5% yield of dimeric ketone, V, and a 0.4% yield of trimer, VI; 8-phenyloctanoyl chloride gave a trace of unidentified crystalline product in addition to polymer; 10-phenyldecanoyl chloride gave a small yield of paracyclanone, VII, and the dimer, VIII. It was confirmed[5] from spectral data that the phenyl and carbonyl groups of I ($n = 5$) are not completely conjugated. Resonance is inhibited much more in the oxime of I ($n = 5$). There is nearly complete inhibition of phenyl–carbonyl interaction in IV, and a slight inhibition in VII. All the other ketones prepared appear to be completely conjugated. A shift in λ_{max} in the ultraviolet spectrum of V is interpreted in terms of a spatial interaction of the two conjugated systems such as could occur in configuration VA. Compound IV gives the deacylation reaction, whereas I ($n = 5$) does not. Attempts to obtain diastereoisomers of the *l*-menthydrazone of I ($n = 5$) led to inconclusive results.

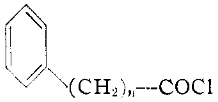
The synthesis of large ring benzocyclanones such as I ($n > 4$) was undertaken for four reasons: (1) to study the high-dilution Friedel–Crafts reaction; (2) to study the ultraviolet and infrared spectroscopic properties of the benzocyclanones as a function of structure and configuration; (3) to determine the effect of structure on the aromatic deacylation reaction[3]; and (4) to attempt a possible resolution of a ketone such as I. The buckling of a large ring ($n > 4$) may allow the separation of enantiomorphs, provided the system is rigid enough.



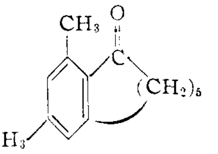
I



II



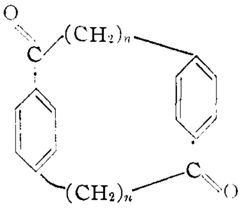
III



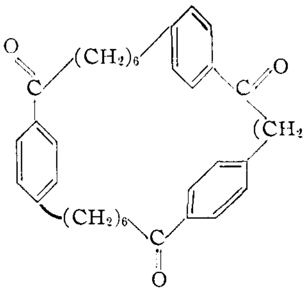
IV

Syntheses by the High-dilution Friedel–Crafts Reaction.—A high-dilution Friedel–Crafts reaction was tried on acid chlorides of type III (n = 5, 6, 7 and 9). During the course of this work there have appeared two papers, one by Huisgen and Rapp,[4] the other by Hedden and W. G. Brown,[5] in which have been described the high-dilution Friedel–Crafts synthesis of 1,2-benzocycloöctene-1-one-3 (I, $n = 5$). The method described herein is quite similar to that of the above authors, and the yield (67%) of I ($n = 5$) obtained from 6-phenylhexanoyl chloride (III, $n = 5$) is comparable to theirs. The high-dilution ring closure of 6-(3,5-dimethylphenyl)-hexanoyl chloride to 1,2-(1′,3′-dimethylbenzo)-cycloöctene-1-one-3 (IV) was accomplished in 54% yield. The structure of the latter was proved by its deacylation[3] in 70% sulfuric acid to yield ω-(3,5-dimethylphenyl)-caproic acid in 94% yield.

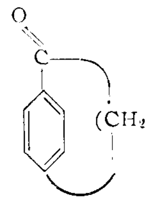
The high-dilution Friedel–Crafts procedure on 7-phenylheptanoyl chloride failed to yield benzocyclononanone (I, $n = 6$). Instead, there was isolated a 5% yield of the dimeric diketone V, and a 0.4% yield of trimer VI, together with a very small amount of another crystalline product, m.p. 160–161°, which was not identified. The main product was polymeric. Hedden and Brown report only unidentified polymeric products in this reaction.[5] The attempted ring closure of 7-phenylheptanoic acid in polyphosphoric acid also is reported as yielding only polymeric products.[6] Apparently, the ring closures to yield V and VI are subject to considerably less steric strain in the transition state than the ring closure to the monomeric ketone (I, $n = 6$). This is in line with other findings.[7] The structures of the neutral ketones V and VI were determined by their molecular weight and oxidation in good yield to terephthalic acid.



V, $n = 6$
VIII, $n = 9$



VI



VII

The general procedure as applied to 4.5 g. of 8-phenyloctanoyl chloride yielded, in addition to polymer, only a few mg. of a crystalline material which

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[1] Supported in part by the Office of Naval Research. Abstracted from the Ph.D. theses of H. K. Latourette (May, 1951) and W. A. Sweeney (March, 1954).

[2] Procter and Gamble Fellow, 1952–1953.

[3] W. M. Schubert and H. K. Latourette, THIS JOURNAL, **74**, 1829 (1952).

[4] R. Huisgen and W. Rapp, *Ber.*, **85**, 826 (1952).

[5] G. D. Hedden and W. G. Brown, THIS JOURNAL, **75**, 3744 (1953).

[6] P. D. Gardner, W. J. Horton, G. Thomson and R. R. Twelves, *ibid.*, **74**, 5527 (1952).

[7] V. Prelog, *J. Chem. Soc.*, 420 (1950).

was not identified. From 10-phenyldecanoyl chloride there was obtained a 3.1% yield of a monomeric *para*-bridged ketone, VII, and a 0.7% yield of dimeric ketone, VIII, as identified products. Compound VII, which formed a 2,4-dinitrophenylhydrazone and showed infrared and ultraviolet spectra typical of an aromatic ketone, gave the correct molecular weight for a monomer and was oxidized to terephthalic acid in 70% yield. The dimer VIII was identified by its molecular weight and oxidation to terephthalic acid.

Infrared and Ultraviolet Spectra.—Hedden and Brown[5] have shown from the decrease in the intensity of the ultraviolet absorption spectrum of 1,2-benzocycloöctene-1-one-3 (I, $n = 5$), that the carbonyl group in this compound is twisted out of the plane of the ring. They have calculated the angle of twist to be 45°. As expected, the introduction of an *ortho* methyl (*i.e.*, compound IV) has damped even more the resonance interaction of the carbonyl group with the ring, so that IV has a spectrum similar to acetomesitylene (see Table I). These same effects are reflected in the infrared, with an increase in frequency of the carbonyl band (*i.e.*, a shift toward the absorption frequency of an aliphatic carbonyl group) accompanying a decrease in carbonyl-ring conjugation (Table II, compare compounds I and IV).

TABLE I

ULTRAVIOLET SPECTRA,[a] VALUES OF λ_{max} AND ϵ_{max}

Compound	λ_{max} (mμ)	ϵ
p-Methylacetophenone	253	14,100
Acetomesitylene	247	2,500
I ($n = 5$)	248.5	6,950
IV	245[b]	2,100
V	250.5	30,400[c]
VI	254	30,600[c]
VIII	255	30,400[c]
VII	256	11,200
Tetralone oxime	255	11,500
XIV	255[b]	750

[a] All spectra in 95% ethanol. The curves are quite smooth, with no fine structure.[8] [b] No peak; plateau in this region. [c] ϵ per conjugated unit is half of this value.

TABLE II

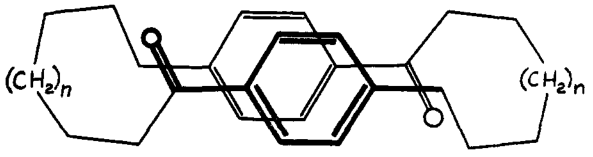
WAVE LENGTH OF THE CARBONYL BAND OF THE BENZOCYCLANONES IN CARBON TETRACHLORIDE SOLUTION

Compound	μ	Compound	μ
I ($n = 5$)	6.00[a]	VI	5.937
	5.97	VII	5.933
IV	5.95[a]	VIII	5.933
V	5.914		

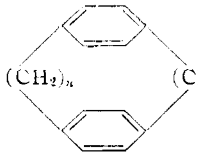
[a] Pure liquid.

The carbonyl group of the ketone VII apparently is twisted slightly out of the plane of the ring by the demands of the ten carbon *para* bridge, judging by the fact that the ultraviolet absorption intensity is about 70% that of the unhindered aromatic ketones (Table I).

The ultraviolet absorption spectra of the dimers V and VIII and of the trimer VI all show "normal" intensities, indicating there is little, if any, interference with the coplanarity of the carbonyl groups with the rings. In the Fischer–Taylor–Hirschfelder models of these compounds, the carbonyl groups and the ring can be made coplanar with no difficulty. Since the models are presumed "stiffer" than the actual molecules, the actual molecules should readily attain coplanarity of the rings and carbonyl groups. In the model of compound V the two benzene rings can easily be fitted next to each other in a head-to-tail manner (conformation VA). Electronic interaction between the two conjugated systems, having in VA the advantage of symmetry, could cause V to have the configuration VA. Such interaction may account for the shift toward shorter wave lengths (about 4 mμ) in λ_{max} in the ultraviolet for this compound as compared to compound VIII and VI (Table I). A shift toward lower wave lengths of 0.02 μ of the carbonyl band in the infrared for V as compared to VI, VIII and VII (Table II) is also observed. There were no other readily discernible unique features of the infrared spectrum.



VA, $n = 1$
VIIIA, $n = 4$



IX, $n = 2$, $m = 2$
X, $n = 2$, $m = 3$
XI, $n = 2$, $m = 4$
XII, $n = 3$, $m = 6$
XIII, $n = 5$, $m = 6$

Cram and Steinberg[9a] attribute certain abnormalities in the ultraviolet spectra of the paracyclophanes IX, X, XI and XII to two factors: (1) an enforced puckering of the benzene rings (more predominant in IX and X) and (2) a "*trans*-spatial overlap of the π-orbitals of the two benzene rings," presumed more pronounced in IX and X than in XI and XII. The ultraviolet spectrum of XIII showed no abnormalities, corresponding closely to the spectrum of the linear analog. Therefore, neither of the above factors was considered operative in XIII.[9b] A spatial overlap of the π-orbitals of the two unsaturated systems of the VA could account for the abnormalities found in the spectrum of this diketone, if it is presumed the effect of having longer *para* bridges than in XIII is offset by additional interaction of the π-bond systems of carbonyl groups.[10] On the other hand, the interaction between the two conjugated systems may be largely electrostatic, since in VA a region of low electron density on one conjugated system is adjacent to a region of high electron density on the other.

The trimer VI shows no abnormalities in its ul-

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[8] Complete curves have been deposited as document number 4298 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[9] (a) D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951); (b) *ibid.*, **74**, 5388 (1952).

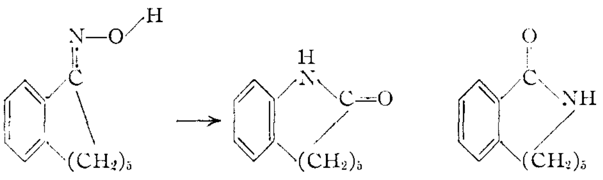
[10] If the coplanar carbonyl group is formally considered part of the benzene ring system, then the "*para*" bridges would contain only five carbon atoms.

traviolet or infrared spectrum and has presumably no interaction of the type postulated for V. The trimer has many more competitive conformations and would gain a proportionately smaller energy by association of two of its three conjugated systems. Association likewise appears absent in the dimeric ketone VIII, judging from its "normal" ultraviolet and infrared spectrum. This can be attributed to: (1) more competitive conformations than for V and (2) greater steric strain in a conformation such as VIIIA. In this arrangement the bridges can be considered as making up two pseudo rings, one at each end. Conformation VIIIA with its ten membered bridges would have pseudo medium sized rings which would be crowded. On the other hand, VA would have less crowded pseudo rings.

Chemical Behavior.—Compound I ($n = 5$) has an "unhindered" carbonyl group, readily forming carbonyl derivatives, whereas IV is completely inert to carbonyl reagents. The behavior of the latter in this respect corresponds to that found by Kadesch for 6,9-dimethylbenzosuberone.[11] All the other ketones prepared readily formed carbonyl derivatives.

The deacylation of IV to form 6-(3,5-dimethylphenyl)-hexanoic acid occurred easily in 70% sulfuric acid at 40°, whereas I ($n = 5$) could not be deacylated. The inertness of I ($n = 5$) to deacylation may be explained as due to either or both of the following factors: (1) absence of activating groups in the free *ortho* and *para* positions and (2) insufficient non-coplanarity of the carbonyl group, making resonance stabilization of the ketone too great and thus leading to a higher activation energy for the reaction.[12]

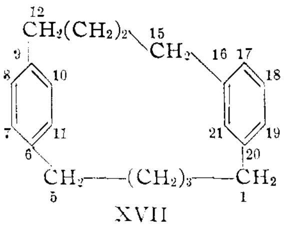
It was considered possible that the oxime, XIV, would undergo a deacylation type reaction provided that, under the acid conditions required, the Beckmann rearrangement did not take precedence. Conjugation between the ring and the C=NOH group should be damped more than that between the ring and carbonyl group of the corresponding ketone (I, $n = 5$). The expected decreased conjugation in XIV is reflected in the ultraviolet spectrum (Table I), in which absorption in the region of 250 mμ is very low as compared to tetralone oxime. When XIV was treated with 85% sulfuric acid, no "deacylation" could be detected. The Beckmann rearrangement occurred, giving, according to qualitative tests, the anilide XV rather than XVI. Thus the ring and the hydroxyl group of the oxime were evidently *trans*.[13]



XIV XV XVI

Attempts were made to separate diastereoisomers of the *l*-menthydrazone of I ($n = 5$), but the results were inconclusive. Such a separation should be possible if the substituted carbonyl group is held out of the plane with sufficient rigidity. It would perhaps be easier to resolve a compound such as II ($n = 5$ or 6) since there would be but small resonance interaction forces tending to cause easy interconversion of its enantiomorphs. The tendency of the carbonyl group of I ($n = 5$) to conjugate with the ring would probably overcome the strain energy in a coplanar configuration sufficiently for easy interconversion of its enantiomorphs.

A Proposed System of Naming.—Cram and Steinberg[9] have suggested the name paracyclophane be used as a family name for compounds containing two phenyl groups connected in the *para* positions by methylene chains. It is proposed the name cyclophane be the family name for all such ring compounds containing any number of benzene rings attached at *ortho, meta* or *para* positions by aliphatic chains. The number of carbon atoms in the aliphatic bridges would be designated together with the type of attachment (*p*, *m* or *o*). For example, compound XVII would be named (5-*p*-4-*m*)-cyclophane. In naming types of bridges *p* would take precedence over *m*, and *m* over *o*.



XVII

Numbering of the carbon atoms would start with the first designated bridge, continue around the positions of the benzene ring (numbering first around the longest side of the benzene ring), and then go on to the next bridge as shown for compound XVII. For example, in this way IV would be called 9,11-dimethyl-(6-*o*)-cyclophanone-1; V, (7-*p*-7-*p*)-cyclophandione-1,14; VI, (7-*p*-7-*p*-7-*p*)-cyclophantrione-1,14,27; and VII, (10-*p*)-cyclophanone-1. Some of these compounds would have extremely cumbersome names using the Ring Index system.

Experimental

1-(3,5-Dimethylphenyl)-cyclohexanol-1.—The method of Snyder, Adams and McIntosh[14] used to prepare 5-bromo-1,3-diethylbenzene was applied to the conversion of 6-bromo-2,4-dimethylaniline to 5-bromo-1,3-dimethylbenzene[15] (71% over-all yield), b.p. 96° (20 mm.) $n^{25}D$ 1.5462. To the Grignard reagent prepared from the bromoxylene (109 g.) and magnesium (14.2 g.) in 500 ml. of dry ether was added cyclohexanone (57.7 g.) at a rate to maintain reflux temperature. The addition complex was decomposed with dilute ammonium chloride and the organic layer separated and dried over potassium carbonate. Upon distillation at 117–118° (1.5 mm.) a heavy oil was obtained which solidified overnight. One recrystallization from nitromethane yielded 71 g. (59% yield), m.p. 45–50°. An analytical sample, prepared by several recrystallizations from hexane, melted at 55–55.5°.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 81.97; H, 10.05.

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[11] R. G. Kadesch, THIS JOURNAL, **66**, 1207 (1944).

[12] This factor plays a role in similar aromatic electrophilic substitutions by hydrogen; see *e.g.*, W. M. Schubert and Roland E. Zahler, *ibid.*, **76**, 1 (1954).

[13] G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., p. 338 ff.

[14] H. R. Snyder, R. R. Adams and A. V. McIntosh, THIS JOURNAL, **63**, 3282 (1941).

[15] E. Fischer and A. Windaus, *Ber.*, **33**, 1673 (1900).

Hey and Jackson[16] list this compound as a liquid, b.p. 150–160° (2 mm.). Their compound is apparently the corresponding olefin, obtained directly by decomposition of the Grignard product with dilute sulfuric acid. They subsequently treated the material with formic acid to dehydrate it but found no change in boiling point.

δ-(3,5-Dimethylbenzoyl)-valeric Acid.—Following the method of Fieser and Szmuszkovicz[17] as applied to 1-phenylcyclohexanol-1, 1-(3,5-dimethylphenyl)-cyclohexanol-1 (80 g.) on chromic acid oxidation yielded δ-(3,5-dimethylbenzoyl)-valeric acid (64.7 g., 70.5% yield), m.p. 63–67°. An analytical sample, recrystallized from hexane, melted at 73.8–74.2°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.44; H, 7.73.

6-(3,5-Dimethylphenyl)-hexanoic Acid.—By the Huang-Minlon modification[18] of the Wolff–Kishner reduction, 160 g. of δ-(3,5-dimethylbenzoyl)-valeric acid yielded crude 6-(3,5-dimethylphenyl)-hexanoic acid, which after recrystallization from petroleum ether gave 71.1 g. (45%), m.p. 44–48°. An analytical sample, further recrystallized from methanol–water, melted at 54–54.5° and gave a neutralization equivalent of 224 (calculated is 220).

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.36; H, 9.19.

By the general method of Shriner and Fuson,[19] 1 g. of the substituted hexanoic acid was oxidized with potassium permanganate to yield 250 mg. (26%) of trimesic acid, m.p. 360–366°.

Preparation of Acid Chlorides.—All the acid chlorides used in the high-dilution Friedel–Crafts reactions were prepared from the corresponding acids by refluxing with excess thionyl chloride and then distilling the reaction mixture. In Table III are listed the properties of the acid chlorides. References are given to the known acid chlorides and the known acids.

TABLE III

PROPERTIES OF ACID CHLORIDES USED IN HIGH-DILUTION FRIEDEL–CRAFTS REACTIONS

Acid chloride[a]	Yield, %	B.p. (obsd.)[b] °C.	Mm.
$C_6H_5(CH_2)_5COCl$[5]	83	151–152	11[20]
1,3,5-$C_6H_3(CH_2)_5COCl$	83	127	1.3
$C_6H_5(CH_2)_6COCl$[21]	94	118–120	1[22]
$C_6H_5(CH_2)_7COCl$[23]	69	129–130	1
$C_6H_5(CH_2)_9COCl$[24]	46	160–164	2.3

[a] References given after acid chlorides are those describing corresponding known acids. [b] References are to properties of known acid chloride.

1,2-Benzocycloöctene-1-one-3.—The following technique was typical of all the high-dilution ring closures reported. A 5-liter three-necked flask was fitted with a Hershberg stirrer, a modified Hershberg dropping funnel and a condenser to which was attached a calcium chloride drying tube. The apparatus was carefully dried with a flame. Granular aluminum chloride (41.9 g., 0.32 mole) and one liter of carbon disulfide (dried by distillation from phosphorus pentoxide) was placed in the flask. While the mixture was stirred at room temperature a solution of 6-phenylhexanoyl chloride (32 g., 0.15 mole) in three liters of dried carbon disulfide was added at such a rate that addition was complete in eight days. One liter of water then was added and the mixture stirred. The organic layer was removed and distilled. After the solvent was recovered, 1,2-benzocycloöctene-1-one-3 (17.8 g., 67%) was collected by distillation in a modified Claisen flask, b.p. 122.5° (5 mm.), $n^{25}D$ 1.5577. Brown and Hedden[5] report a b.p. of 142° (10 mm.), $n^{25}D$ 1.5618.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.56; H, 8.14.

The ketone (0.67 g.) when heated with potassium permanganate (10 g.) and 2 ml. of 10% sodium hydroxide in 200 ml. of water yielded *o*-phthalic acid. This was sublimed to give phthalic anhydride (0.21 g.), identical in m.p. and mixed m.p. with an authentic sample.

When the ketone was heated in 85% sulfuric acid at various temperatures from 80 to 150°, it gave no deacylation; none of the desired 6-phenylhexanoic acid was obtained.

The oxime was prepared by refluxing a mixture of ketone (0.58 g.), hydroxylamine hydrochloride (0.6 g.), pyridine (0.6 ml.) and alcohol (5 ml.) for two hours. Evaporation of part of the alcohol precipitated the oxime, which, after recrystallization from aqueous methanol, melted at 86.5–88°.

Anal. Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.99. Found: C, 75.93; H, 7.77.

1,2-(1′,3′-Dimethylbenzo)-cycloöctene-1-one-3.—By the above method, 31.3 g. of 6-(3,5-dimethylphenyl)-hexanoyl chloride in 2600 ml. of carbon disulfide was added in ten days to 36.7 g. of aluminum chloride and 700 ml. of carbon disulfide. Isolation gave 14.4 g. (54% yield) of slightly yellow liquid, b.p. 118° (1.6 mm., in modified Claisen flask), $n^{25}D$ 1.5412. This compound formed neither an oxime nor a 2,4-dinitrophenylhydrazone when subjected to the conditions given by Shriner and Fuson.[19]

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.82; H, 9.05.

The above ketone (0.182 g.) was warmed with 10 ml. of 70% sulfuric acid at 40° for four days. The mixture was diluted with water and extracted with ether. The ether solution was extracted with water and then dilute sodium hydroxide. Acidification of the basic solution yielded 0.186 g. (94.3%) of 6-(3,5-dimethylphenyl)-hexanoic acid, m.p. 52.5–53.5°, no depression in m.p. when mixed with an authentic sample.

High-dilution Friedel–Crafts Reaction of 7-Phenylheptanoyl Chloride.—By the above procedure, 28.9 g. of 7-phenylheptanoyl chloride in 2 liters of carbon disulfide was added in seven days to 38 g. of aluminum chloride and 600 ml. of carbon disulfide. After decomposition with water, the organic layer was separated from the water layer and from a considerable amount of brown powder. The residue, after distillation of the carbon disulfide, was a light orange solid (6 g.) which showed no tendency to distil at 240° (2 mm.). A series of recrystallizations from hexane yielded 1.2 g. (5% yield) of white solid, m.p. 146–147°. The melting point was raised to 147–148° by sublimation under 0.3 mm. pressure. The compound was insoluble in aqueous base and gave a precipitate with 2,4-dinitrophenylhydrazine reagent.[19] The mol. wt. determined by benzene freezing point lowering was 355. The theoretical value for the dimeric product, V, is 376.

Anal. Calcd. for $C_{26}H_{32}O_2$: C, 82.93; H, 8.57. Found: C, 83.13; H, 8.44.

About 40 mg. of the dimeric ketone was refluxed for three hours with a mixture of 10 ml. of pyridine, 10 ml. of 0.1 *N* sodium hydroxide and 1 g. of potassium permanganate. The mixture was acidified, then treated with sodium bisulfite to remove manganese dioxide. The remaining precipitate was filtered with suction, washed with water and dried; yield 17 mg. It melted at greater than 400° and had an infrared spectrum identical with that of authentic terephthalic acid.

The residue obtained from the mother liquors of the recrystallizations of the dimeric ketone, V, yielded 30 mg. of a compound which upon recrystallization from carbon tetrachloride had a m.p. of 160–161°. It was insoluble in aqueous base and showed a carbonyl band in the infrared corresponding to an aromatic ketone but differed in spectrum from the dimer, V. No further characterization was made.

The residue from the mother liquors of the previous recrystallization was extracted with methanol in the cold and the material from this extract was recrystallized several times from hexane in the deep freeze to yield 105 mg. (0.4%)

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[16] D. H. Hey and E. R. B. Jackson, *J. Chem. Soc.*, 645 (1934).

[17] L. F. Fieser and J. Szmuszkovicz, THIS JOURNAL, **70**, 3352 (1948).

[18] Huang-Minlon, *ibid.*, **68**, 2487 (1946).

[19] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[20] I. M. Heilbron, "Dictionary of Organic Compounds," Vol. III, Oxford University Press, New York, N. Y., 1943, p. 392.

[21] H. Stetter and W. Dierichs, *Ber.*, **85**, 1061 (1952).

[22] H. Staudinger and F. Müller, *ibid.*, **56**, 714 (1923).

[23] W. Borsche, *ibid.*, **52**, 2084 (1919).

[24] D. Papa, E. Schwenk and H. Hankin, THIS JOURNAL, **69**, 3018 (1947).

of white solid, m.p. 94.5–95.5°. It was insoluble in aqueous base and gave a precipitate with 2,4-dinitrophenylhydrazine reagent.[19] Oxidation by the method used on the above dimer gave terephthalic acid in 50% yield. The molecular weight by the benzene freezing point method was found to be 520; calculated for the trimer VI is 564.

Anal. Calcd. for $C_{39}H_{48}O_3$: C, 82.93; H, 8.57. Found: C, 82.78; H, 8.94.

A higher-dilution technique, similar to that of Hedden and Brown,[5] gave an extremely low yield of carbon disulfide soluble material. The main product was a paper-like material, which burned with a smoky flame and left a residue.

High-dilution Friedel–Crafts Reaction of 8-Phenyloctanoyl Chloride.—By the general procedure, 4.5 g. of 8-phenyloctanoyl chloride in 500 ml. of carbon disulfide was added in four days to 6 g. of aluminum chloride in 200 ml. of carbon disulfide. After decomposition of the reaction mixture, only a very small amount of a solid was recovered from the organic layer, m.p. 92–116°. After one recrystallization, a few mg., m.p. 125–130°, was obtained. No further characterization was made.

High-dilution Friedel–Crafts Reaction of 10-Phenyldecanoyl Chloride; VII and VIII.—The same general procedure was used, except that the acid chloride was not distilled because of extensive decomposition during distillation. A solution of crude 10-phenyldecanoyl chloride (made from the reaction of thionyl chloride with 49 g. of 10-phenyldecanoic acid) in 3 liters of carbon disulfide was added in 14 days to 50 g. of aluminum chloride in one liter of carbon disulfide. Three-fourths of the carbon disulfide was removed by distillation and the residual mixture decomposed with 2.5 liters of dilute hydrochloric acid. The organic layer, after separation from the water layer and from a large amount of light brown solid, was distilled to remove carbon disulfide. The liquid residue (6.4 g.) was distilled in a modified Claisen flask. The distillate, b.p. 158–163° (3 mm.), was a heavy oil which soon solidified in the receiver, yield 1.23 g. (3.1%). After several recrystallizations from methanol–hexanol, plates, m.p. 91–92°, were obtained. The compound was insoluble in base and gave an orange precipitate with 2,4-dinitrophenylhydrazine reagent.[19]

Using the procedure outlined for the oxidation of V, 100 mg. of the ketone yielded 50 mg. (70% yield) of terephthalic acid, identified by its infrared spectrum. The mol. wt. of VII by freezing point depression of benzene was 225; calculated for a monomeric ring closure product is 230.

Anal. Calcd. for $C_{16}H_{20}O$: C, 83.42; H, 9.63. Found: C, 83.27, 83.82; H, 9.22, 9.39.

The residue from the above distillation was extracted with methanol to give 290 mg. (0.7% yield) of a material which on repeated recrystallization from methanol melted at 83–83.5°. It was insoluble in aqueous sodium hydroxide and formed an orange precipitate with 2,4-dinitrophenylhydrazine reagent.[19] The mol. wt. by the benzene freezing point method was 491; calculated for dimeric diketone is 460. Oxidation with basic permanganate, as performed on compound V, gave a 50% yield of terephthalic acid, identified by its infrared spectrum.

Anal. Calcd. for $C_{32}H_{44}O_2$: C, 83.42; H, 9.63. Found: C, 83.72; H, 10.00.

Beckmann Rearrangement of 1,2-Benzocycloöctene-1-one-3.—A solution of the oxime (86 mg.) in 10 ml. of 85% sulfuric acid was kept at 40° for 12 days. The solution was diluted with water and extracted with ether. The ether extract yielded only a trace of acidic material and 48 mg. (55%) of neutral product, m.p. 116–120°. After two recrystallizations from aqueous alcohol it melted at 132–134°; yield 35 mg. The infrared spectrum corresponded to that of a lactam. The compound was hydrolyzed by refluxing in 20% hydrochloric acid (5 ml.) and alcohol (2 ml.). There was obtained an amphoteric product which was diazotized with hydrochloric acid and sodium nitrite at 0°. A portion of the clear solution obtained gave off a gas and deposited a precipitate when warmed to room temperature. Another portion gave an immediate red-orange precipitate with a solution of β-naphthol in 10% sodium hydroxide.

The *l*-Menthydrazone of 1,2-Benzocycloöctene-1-one-3.—By the general method of Woodward, Kohman and Harris,[25] 2,3-benzocycloöctene-2-one-1 (10.6 g.) and *l*-menthydrazide (13 g.) yielded an oil which solidified in two days, m.p. 60–90°. No definite separation of diastereoisomers could be discerned after several recrystallizations from ligroin (b.p. 70–90°) and 80% isopropyl alcohol. The melting points of crystals obtained varied from 75 to 125° with most melting between 115 and 117°. Several such fractions, which gave C and H analyses that checked approximately for the menthydrazone, varied in $[\alpha]^{25}_D$ from −31.5° for the lowest melting fraction (75–80°) to −38.7° for the highest melting fraction (120–125°).

In a mutarotation experiment, a sample of the 120–125° melting fraction (0.25 g.) was heated to reflux in 10 ml. of ligroin (b.p. 70–90°) for 48 hours. The product recovered by evaporation of the solvent was dried in a Fischer drying pistol over paraffin and phosphorus pentoxide. It was discolored (indicating possible decomposition) and melted at 110–112°, $[\alpha]^{25}_D$ −28.9°.

[25] R. B. Woodward, T. P. Kohman and G. C. Harris, THIS JOURNAL, **63**, 120 (1941).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reactions of Grignard Reagents with *p*-Duroylphenol

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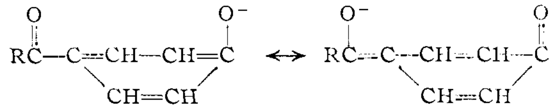
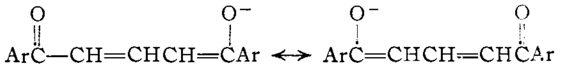
p-Duroylphenol condenses readily with *t*-butylmagnesium chloride to give a product which can be isolated in either of the two tautomeric forms IV and V (in text) by the correct choice of solvent for recrystallization. A similar product, isolated in the keto form, is obtained when the *t*-amyl reagent is employed. Under the influence of the *t*-alkyl reagents the methyl ethers of the enol forms of these compounds undergo displacement of the methoxyl group by the hydrocarbon radical of the reagent.

The phenoxide ions I derived from *p*-acylphenols are vinylogs of the corresponding carboxylate ions and, except that they involve aromatic rings, are closely analogous to the 1,5-diarylpentadienolonates (II).[3] The analogy implies that the phenoxide ions I are vulnerable to nucleophilic attack at a position *ortho* to the keto substituent. We have been able to verify this prediction experimentally by treating *p*-duroylphenol (III) with Grignard reagents.

I


II

$$\mathrm{Ar\overset{\overset{\large O}{\|}}{C}{-}CH{=}CHCH{=}\overset{\overset{\large O^-}{|}}{C}Ar \longleftrightarrow Ar\overset{\overset{\large O^-}{|}}{C}{=}CHCH{=}CH\overset{\overset{\large O}{\|}}{C}Ar}$$

This hydroxy ketone reacts with *t*-butylmagne-

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[3] R. C. Fuson and L. R. Melby, THIS JOURNAL, **75**, 5402 (1953).