specific activity 404 c.p.m. The specific activity of the benzoic acid obtained from another portion of the same sample of hydro-isomerate from experiment 5 was 393 c.p.m. Therefore, the two values agree to within 3%. If all or part of the radioactivity of the benzoic acid had been derived from the toluene produced by the demethanation of 1,1-dimethylcyclohexane, its radioactivity would have been markedly lowered by the addition of non-radioactive 1,1-dimethylcyclohexane.

The saturated hydrocarbons, 5.11 g., $n^{20}_{D}$ 1.4320, obtained from the preceding chromatographic separation were combined with 12.06 g. of non-radioactive ethylcyclohexane, $n^{20}_{D}$ 1.4325. The material was analyzed as illustrated in Diagram 2. Since the specific activity of the benzoic acid was increased substantially by this procedure, a new species of this acid probably arose by way of the aromatization of 1,1-dimethylcyclohexane, which would lead to toluene and, upon oxidation, to benzoic acid.

The benzoic acid containing the new isotopic species was decarboxylated as before. The carbon dioxide evolved was absorbed in aqueous sodium hydroxide, precipitated as barium carbonate and assayed; specific activity 447 c.p.m.

The benzene obtained from the decarboxylation reaction was purified, burned and assayed; specific activity 114 c.p.m.

**Validity of the Analytical Scheme.**—The dehydrogenation step was conventional, utilizing platinized-alumina catalyst which had been tested for "acidity" with 1,1,3-trimethylcyclohexane and found to cause no noticeable amount of isomerization.[19]

The oxidation product of *o*-xylene was examined in order to determine whether benzoic acid was produced from this hydrocarbon under conditions of potassium permanganate oxidation.[38] *o*-Xylene, 4.2 ml. (Eastman Kodak Co., White label, $n^{20}_{D}$ 1.5024) was oxidized with potassium permanganate as described previously. After removing the manganese dioxide by filtration, the filtrate was combined with 0.366 g. of radioactive benzoic acid having a specific activity of 2456 c.p.m. The solution was alkaline and, therefore, the mixture of acids was homogenized. The benzoic acid was re-isolated and purified as before and assayed; specific activity 2401 c.p.m. Therefore only a negligible quantity of benzoic acid was produced in this oxidation.

In order to determine the purity of the benzoic acid obtained by repeated recrystallization from water, the following experiment was performed. Radioactive benzoic acid, 0.1188 g., derived from the hydro-isomerate of experiment 4 having a specific activity of 363 c.p.m. was sublimed twice at 100° and atmospheric pressure. A portion of the sublimate was burned and assayed, specific activity 362 c.p.m. Therefore, benzoic acid purified by repeated recrystallization was not contaminated with traces of isophthalic acid (or any toluic acid) because extensive fractionation of the radioactivity would have occurred upon sublimation at 100° and atmospheric pressure.

The radioactivity assays reported in this paper were performed with a Nuclear Instruments Co.[39] No. 162 Scaling Unit and a Tracerlab-TGC-2 Geiger–Müller tube.[40] For convenience, each counting rate reported in this work is referred to as "Specific Activity," which is defined as the number of counts per minute above background, corrected for coincidence losses, of an "infinitely thick" layer of barium carbonate, 4.52 cm.$^2$ in area. Each value reported is the average of at least two determinations. The individual counting rates were known to an accuracy of 3%. In order to permit a ready comparison of the radioactivities of different compounds, the specific activities reported in the tables were multiplied by the number of carbon atoms in the compound to correct for dilution by non-tagged carbon atoms.

**Acknowledgment.**—The authors are indebted to Dr. H. M. Neumann for his assistance in the work with $C^{14}$-labeled compounds.

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[39] Nuclear Instrument and Chemical Corporation, 223 W. Erie St., Chicago, Ill.

[40] Tracerlab, Inc., 130 High St., Boston, Mass.

EVANSTON, ILLINOIS

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

# The Synthesis of 2,7-Disubstituted Tropones *via* Aromatization

BY NELSON J. LEONARD, LEE A. MILLER[1,2] AND JAMES W. BERRY

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A new method is here reported for the synthesis of tropones, specifically those substituted with similar aralkyl groups in the 2- and 7-positions. The general method involves the isomerization and dehydrogenation of substituted 2,7-dibenzylidenecycloheptanones to the correspondingly substituted 2,7-dibenzyltropones in boiling triethylene glycol solution using palladium-on-charcoal.

The successful employment of palladium-on-charcoal in a refluxing glycol solvent for the synthesis of substituted γ-pyrones,[3] γ-pyridones[4] and tropolones[5] by isoaromatization suggested that a similar method might produce substituted tropones. In the isoaromatization conversions realized previously, the number of multiple linkages in precursor and product was identical. For the conversion of type I to type II to be effected, it would obviously be necessary to introduce one double bond in addition to those isomerized. We were led to expect that the process might be feasible because of the dehydrogenations and the disproportionations known to take place using palladium catalyst and heat[6] and because of the recognized aromatic nature of the tropone nucleus.[7,8]

2,7-Dibenzylidenecycloheptanone (Ia) and similar compounds in the series (Ib-l) were made by the method of Cornubert, Joly and Strébel,[9] with modifications in the purification procedure depending upon the particular 2,7-disubstituted cy-

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[1] Eli Lilly and Company Fellow, 1953–1954.

[2] Monsanto Chemical Company Fellow, 1954–1955.

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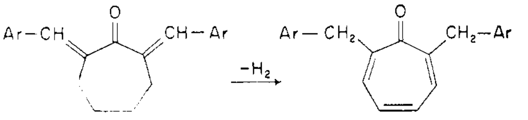
cloheptanone. Condensation of cycloheptanone with a series of aromatic aldehydes by means of sodium ethoxide in ethanol solution produced compounds which were logically assigned structures of type I on the basis of analysis, yellow color, infrared absorption spectra (see Table I) and the deep red color each gave with sulfuric acid.[10]



I II

Ar
a, $C_6H_5$
b, *p*-$CH_3C_6H_4$
*c*, *p*-$(CH_3)_2CHC_6H_4$
d, *p*-$CH_3OC_6H_4$

Ar
e, 3′,4′-$(CH_3O)_2C_6H_3$
f, 3′,4′-$CH_2O_2C_6H_3$
g, *p*-$(CH_3)_2NC_6H_4$
h, 1′-$C_{10}H_7$

Ar
i, 2′,3′-$(CH_3O)_2C_6H_3$
j, *o*-$ClC_6H_4$
k, 2′-$C_4H_3O$
l, $C_6H_5CH{=}CH$

Using the conditions which had been successful for the isoaromatization of 3,7-dibenzylidene-1,2-cycloheptanedione to 3,7-dibenzyltropolone,[5] 2,7-dibenzylidenecycloheptanone (Ia) was heated in triethylene glycol at 280° with 10% palladium-on-charcoal. The viscous yellow oil which was obtained resisted attempts at crystallization and purification by fractional distillation; however, chromatography on alumina and elution of the column with hexane–benzene (3:1) yielded a colorless solid, m.p. 64–65°. Microanalysis indicated a composition of $C_{21}H_{18}O$, which can be accommodated by the expression IIa, 2,7-dibenzyltropone. The infrared spectrum of the product was markedly different from that of 2,7-dibenzylidenecycloheptanone. Specifically, *inter alia*, the conjugated carbonyl maximum of Ia at 1672 $cm.^{-1}$ had disappeared, and a new maximum had appeared at 1627 $cm.^{-1}$ (in chloroform). This maximum lies in the 1620–1640 $cm.^{-1}$ region usually assigned to carbonyl stretching in tropones.[11,12] The infrared absorption maxima in the 1600–1500 $cm.^{-1}$ region were consistent with the presence of tropone and benzenoid aromatic[13] moieties, as in IIa. There was no spectral evidence for the presence of a cyclopropane ring[14] in the $C_{21}H_{18}O$ product. The aromatic structure IIa was favored over other possibilities by the colorless nature of the product and by the fact that treatment with concentrated sulfuric acid gave only a very pale yellow color, in marked contrast to the color reaction of its precursor Ia. The catalytic conversion of $C_{21}H_{20}O$ (Ia) to $C_{21}H_{18}O$ was accompanied by a striking change in the ultraviolet absorption observed for the two compounds, reminiscent of the ultraviolet spectral comparison of 3,7-dibenzylidene-1,2-cycloheptanedione with 3,7-dibenzyltropolone.[15] In 95% ethanol solution, 2,7-dibenzylidenecycloheptanone exhibited absorption maxima at 299 mμ, log ε 4.29; ~254 mμ, log ε 4.01; and 230 mμ, log ε 4.09. The $C_{21}H_{18}O$ compound showed maxima at 312 mμ, log ε 4.04, and 233 mμ, log ε 4.44, bearing some resemblance to those of 4-hydroxytropone (in methanol): 337 mμ, log ε 4.11; 288 mμ, log ε 4.27[16]; and tropone (in isoöctane): 310 mμ, log ε 3.67; 297 mμ, log ε 3.74; 225 mμ, log ε 4.33.[8] Final evidence of the correctness of the 2,7-dibenzyltropone structure IIa for the compound in question was obtained in a quantitative catalytic hydrogenation study. 2,7-Dibenzylidenecycloheptanone (Ia) absorbed two mole equivalents of hydrogen at 25° using 10% palladium-on-charcoal in ethanol[9]; the $C_{21}H_{18}O$ compound absorbed three mole equivalents of hydrogen during a longer period of time. The product of both reductions was 2,7-dibenzylcycloheptanone, isolated as the oxime. The reduction of a tropone to a cycloheptanone under these conditions is consistent with experience.[7]

Since the conversion of 2,7-dibenzylidenecycloheptanone to 2,7-dibenzyltropone constitutes a novel tropone synthesis, an effort was made to improve the yield of IIa by variation of the reaction conditions. Shortening the time of heating Ia in triethylene glycol with palladium-on-charcoal to 15 minutes produced the best results, but even under these conditions, the low yield of 16% reflected the critical thermal instability of the 2,7-dibenzyltropone, which was also ascertained in blank runs. Lower boiling glycols[3,4] were ineffective in promoting the isomerization–dehydrogenation of Ia to IIa and the use of chloranil[17] or chloranil with palladium was not helpful. Attempts to prepare 2,7-dibenzyltropone by other synthetic routes have been unsuccessful.

The method of synthesis of tropones, represented by the conversion of Ia to IIa, was tested for generality, and it was found that the substituted 2,7-dibenzylidenecycloheptanones Ib-g underwent isomerization and dehydrogenation to give the correspondingly substituted 2,7-dibenzyltropones (IIb-g). The structures of the products in this series were assigned on the basis of analogy with IIa; the analyses, which indicate the loss of two hydrogen atoms from the precursor in each case; the relative lack of color; the failure to give a distinct color reaction with sulfuric acid; and the infrared absorption spectra (see Table II). The course of the conversion has not been established, although the over-all result is one of double-bond isomerization and dehydrogenation and/or disproportionation. The reported yield of each tropone (Table II) was approximately reproducible in this Laboratory, and the magnitude of each yield is regarded more as a function of the thermal stability of the product and the relative ease of isolation than as an indication of the efficiency of the aromatization process. The method provides a route to 2,7-disubstituted tropones not hitherto available.

**Acknowledgment.**—The authors are particularly grateful for the assistance of Mr. John C. Little in this investigation.

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TABLE I

2,7-DISUBSTITUTED CYCLOHEPTANONES

| Cycloheptanone | I | Yield, % | M.p., °C. | Crystal form$^{a,b}$ | Infrared absorption maxima, cm.$^{-1}$ Conj. C=O | Conj. C=C and aromatic | | | Misc. | | | | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,7-Dibenzylidene- | a | | 106.5–108 | Ndls. | 1672$^e$ | 1612 | | | | | | | $C_{21}H_{20}O$[9,10] | | | | |
| 2,7-Di-(*p*-methylbenzylidene)- | b | | 129.5–130.5 | Ndls. | 1671$^f$ | ~1625$^g$ | 1612 | 1516 | 1199 | 1185 | 1146 | | $C_{23}H_{24}O$[19] | | | | |
| 2,7-Di-(*p*-isopropylbenzylidene)- | c | 43 | 116–117 | Plates | 1672$^f$ | ~1626 | 1614 | 1516 | 1202 | 1188 | 1147 | | $C_{27}H_{32}O$ | 87.05 | 87.05 | 8.66 | 8.75 |
| 2,7-Di-(*p*-methoxybenzylidene)- | d | 53 | 119–120 | Prisms | 1668$^f$ | 1609 | 1580 | 1516 | 1256 | 1041 | | | $C_{23}H_{24}O_3$ | 79.28 | 79.22 | 6.94 | 6.99 |
| 2,7-Di-(3',4'-dimethoxybenzylidene)- | e | 44 | 163.5–164 | Plates | 1668$^f$ | ~1623 | 1603 | 1516 | 1167 | 1145 | 1035 | | $C_{25}H_{28}O_5$ | 73.51 | 73.40 | 6.91 | 6.92 |
| 2,7-Di-(3',4'-methylenedioxybenzylidene)- | f | 47 | 137.5–138 | Ndls. | 1670$^f$ | ~1623 | 1606 | 1510 | 1225 | 1147 | 1047 | | $C_{23}H_{20}O_5$ | 73.39 | 73.28 | 5.36 | 5.44 |
| 2,7-Di-(*p*-dimethylaminobenzylidene)- | g | 25 | 200–201 | Ndls. | 1664$^f$ | 1604 | 1520 | | 1361 | 1189 | 1170 | 1145 | $C_{25}H_{30}N_2O$ | 80.17 | 79.98 | 8.07 | 7.85$^h$ |
| 2,7-Di-(1'-naphthylidene)- | h | 40 | 136–136.5 | Ndls. | 1678$^f$ | 1615 | 1517 | 1405 | | | | | $C_{29}H_{24}O$ | 89.65 | 89.45 | 6.23 | 6.30 |
| 2,7-Di-(2',3'-dimethoxybenzylidene)- | i | 53 | 98.5–99.5 | Ndls. | 1673$^f$ | ~1610 | 1600 | 1581 | 1177 | 1146 | 1014 | | $C_{25}H_{28}O_5$ | 73.51 | 73.60 | 6.91 | 6.80 |
| 2,7-Di-(*o*-chlorobenzylidene)- | j | 53 | 104–105 | Ndls.$^c$ | | | | | | | | | $C_{21}H_{18}Cl_2O$ | 70.60 | 70.70 | 5.08 | 5.24 |
| 2,7-Di-(2'-furfurylidene)- | k | 75 | 147–148 | Prisms$^d$ | 1672$^e$ | 1621 | | | Multiple bands, 1300–1100 | | | | $C_{17}H_{16}O_3$[20] | | | | |
| 2,7-Dicinnamylidene- | l | 26 | 207–208 | Ndls.$^c$ | 1663$^e$ | 1620 | | | 1214 | 1194 | 1144 | | $C_{25}H_{24}O$ | 88.19 | 87.92 | 7.11 | 7.34 |

[a] Yellow, except Ig, which is orange. [b] From ethanol except otherwise indicated. [c] Ethyl acetate. [d] Methanol. [e] Carbon disulfide. [f] Carbon tetrachloride. [g] ~ Denotes shoulder. [h] Calcd.: N, 7.48. Found: N, 7.77.

TABLE II

2,7-DISUBSTITUTED TROPONES

| Tropone | II | Yield, % | M.p., °C.$^{a,b}$ | Infrared absorption maxima, cm.$^{-1}$ Tropone C=O | Tropone and aromatic | | | | Misc. | Formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,7-Dibenzyl- | a | 16 | 64–65$^c$ | 1627$^e$ | 1606 | 1580 | 1523 | 1504 | | $C_{21}H_{18}O$ | 88.08 | 88.11 | 6.34 | 6.48 |
| 2,7-Di-(*p*-methylbenzyl)- | b | 57 | 139–140$^d$ | 1625$^f$ | 1586 | 1519 | | | | $C_{23}H_{22}O$ | 87.86 | 87.85 | 7.05 | 7.10 |
| 2,7-Di-(*p*-isopropylbenzyl)-$^g$ | c | 12 | 117–118 | ~1625$^{f,h}$ | 1594 | 1522 | | | | $C_{27}H_{30}O$ | 87.52 | 86.98 | 8.16 | 8.21 |
| 2,7-Di-(*p*-methoxybenzyl)- | d | 22 | 122–122.5 | 1617$^e$ | ~1590 | 1575 | 1518 | | 1040 | $C_{23}H_{22}O_3$ | 79.74 | 79.45 | 6.40 | 6.36 |
| 2,7-Di-(3',4'-dimethoxybenzyl)- | e | 25 | 148.5–149 | ~1625$^e$ | ~1610 | ~1598 | ~1576 | 1520 | 1034 | $C_{25}H_{26}O_5$ | 73.86 | 73.86 | 6.45 | 6.34 |
| 2,7-Di-(3',4'-methylenedioxybenzyl)- | f | 28 | 127–128 | 1627$^f$ | 1590 | 1515 | 1500 | | 1051 | $C_{23}H_{18}O_5$ | 73.79 | 73.79 | 4.85 | 5.20 |
| 2,7-Di-(*p*-dimethylaminobenzyl)- | g | 6 | 162–163 | 1616$^f$ | 1576$^i$ | 1516 | | | 1167 | $C_{25}H_{28}N_2O$ | 80.61 | 80.57 | 7.58 | 7.76$^j$ |

[a] Colorless needles, except IIg, which is orange, and IIe, which is buff-white. [b] From ethanol except otherwise indicated. [c] Pentane. [d] Ether. [e] Chloroform. [f] Carbon tetrachloride. [g] Not obtained analytically pure. [h] ~ Denotes shoulder. [i] Broad band. [j] Calcd.: N, 7.52. Found: N, 7.33.

TABLE III

2,7-DISUBSTITUTED CYCLOHEPTANONES: ULTRAVIOLET ABSORPTION MAXIMA[a]

| Cycloheptanone | I | λ, mμ | log ε | λ, mμ | log ε | λ, mμ | log ε |
|---|---|---|---|---|---|---|---|
| 2,7-Dibenzylidene- | a | 290 | 4.50[26] | | | 226 | 4.23 |
| | | (299 | 4.29$^b$ | ~254$^c$ | 4.01 | 230 | 4.09) |
| 2,7-Di-(*p*-methoxybenzylidene)- | d | 317 | 4.51 | ~254 | 4.12 | 230 | 4.26 |
| 2,7-Di-(*o*-chlorobenzylidene)- | j | 276 | 4.24 | ~228 | 4.22 | 211 | 4.49 |
| 2,7-Di-(2'-furfurylidene)- | k | 330 | 4.61 | 261 | 4.18 | | |
| 2,7-Di-(cinnamylidene)- | l | 337 | 4.84 | ~243 | 4.10 | 236 | 4.18 |
| | | | | | | ~231 | 4.15 |

[a] Determined in cyclohexane unless otherwise indicated. [b] In 95% ethanol. [c] ~ Denotes inflection point.

## Experimental[18]

**2,7-Disubstituted Cycloheptanones (I).**—The method of Cornubert, Joly and Strébel[9] for the preparation of 2,7-dibenzylidenecycloheptanone and similar compounds was used with minor modifications. The general method can be illustrated with specific directions for 2,7-di-(*p*-methoxybenzylidene)-cycloheptanone (Id). A mixture of 5.6 g. (0.05 mole) of cycloheptanone and 20.42 g. (0.15 mole) of freshly distilled anisaldehyde was added to a solution of 3.5 g. (0.15 gram atom) of sodium in 200 ml. of absolute ethanol under nitrogen at 25°. The mixture was brought to the boiling point on the steam-bath and then allowed to cool to room temperature. After 1 hr., 200 ml. of water was added and the resulting mixture was extracted several times with ether. The combined ether extracts were washed thoroughly with water, dried and evaporated. The resulting oily solid was recrystallized three times from ethanol. The properties of Id and the other 2,7-disubstituted cycloheptanones made in this way are included in Table I.

**2,7-Dibenzylidenecycloheptanone 2,4-Dinitrophenylhydrazone.**—A sample prepared from Ia and 2,4-dinitrophenylhydrazine was recrystallized from ethyl acetate, maroon prisms, m.p. 205–206°.

*Anal.* Calcd. for $C_{27}H_{24}N_4O_4$: C, 69.22; H, 5.16; N, 11.96. Found: C, 69.07; H, 5.15; N, 12.24.

**2,7-Disubstituted Tropones (II).**—The general method of isomerization–aromatization can be illustrated by the conversion of Id to 2,7-di-(*p*-methoxybenzyl)-tropone (IId). A mixture of 976 mg. (2.8 mmoles) of 2,7-di-(*p*-methoxybenzylidene)-cycloheptanone, 500 mg. of 10% palladium-on-charcoal and 25 ml. of redistilled triethylene glycol was heated at the reflux temperature for 30 minutes. The reaction mixture was filtered hot, and the residue on the filter was washed successively with 25 ml. of water, five 20-ml. portions of ether and 100 ml. of water. The filtrate and washings were combined, and the ether layer was separated. Further ether extraction was followed by combination of the ether extracts, drying and evaporation. The residue consisted of a pale yellow oil of approximately the same weight as the starting material. It was purified by chromatography on alumina. 2,7-Di-(*p*-methoxybenzyl)-tropone was obtained from the column by elution with hexane–benzene (1:1). The solvent was evaporated, and the residue was recrystallized twice from absolute ethanol. The properties of IId and the other 2,7-disubstituted tropones are given in Table II. Products other than tropones obtained by this treatment were not identified. Infrared analysis of crude products indicated that some aromatization had occurred with 2,7-di-(1′-naphthylidene)-cycloheptanone (Ih) and 2,7-di-(2′,3′-dimethoxybenzylidene)-cycloheptanone (Ii), but the corresponding tropones (IIh, i) were not obtained pure.

**Reaction of 2,7-Dibenzylidenecycloheptanone with Hydrogen Bromide in Acetic Acid.**—To 150 ml. of glacial acetic acid saturated with hydrogen bromide at 30° was added 5.0 g. (17 mmoles) of 2,7-dibenzylidenecycloheptanone. The red reaction mixture was heated at 55° for 21 hr., during which time a colorless solid separated. Recrystallization gave 6.2 g. (76%) of colorless fluffy needles, m.p. 163.5–164.5° with decomposition. The same product in equivalent yield was obtained when 1% of benzoyl peroxide was present in the reaction mixture.

*Anal.* Calcd. for $C_{21}H_{22}Br_2O$: C, 56.02; H, 4.93; Br, 35.50. Found: C, 56.06; H, 5.07; Br, 34.94.

Dehydrobromination was accomplished by heating the $C_{21}H_{22}Br_2O$ product with γ-collidine under reflux for 11 hr. 2,7-Dibenzylidenecycloheptanone, m.p. 107–108°, was obtained in 96% yield. The available information suggested that the bromine-containing compound could be 2,7-di-(α-bromobenzyl)-cycloheptanone, but no structural assignment is made at the present time.

**Quantitative Hydrogenation of 2,7-Dibenzylidenecycloheptanone and 2,7-Dibenzyltropone.**—A solution of 1.00 g. (3.5 mmoles) of 2,7-dibenzylidenecycloheptanone in 60 ml. of absolute ethanol was hydrogenated at 25° in the presence of 0.1 g. of 10% palladium-on-charcoal. Within 5 minutes the uptake of hydrogen ceased. The volume of hydrogen consumed was 187 ml. (117% of theoretical for 2 mole equivalents). The catalyst and solvent were removed and the residue was converted to the oxime, which was recrystallized twice from 80% ethanol, m.p. 110–111° (reported for 2,7-dibenzylcycloheptanone oxime[9] 112°).

A similar hydrogenation, during 18 hr. at 25°, of 44.3 mg. (0.16 mmole) of 2,7-dibenzyltropone in 40 ml. of absolute ethanol using 0.1 g. of 10% palladium-on-carbon resulted in an uptake of 10.4 ml. of hydrogen (100% of theoretical for 3 mole equivalents). The product was converted to the oxime, m.p. 109–110° (Kofler hot stage), which was identical with the 2,7-dibenzylcycloheptanone oxime described above. The melting point of mixtures of the two samples was 109–111°.

**Ethylene Glycol Ketal of Diethyl γ-Oxopimelate.**—The ketal was made from diethyl γ-oxopimelate[21] by the method which Lukes, Poos and Sarett[22] had used for the ethylene glycol ketal of the dimethyl ester. The product was collected at 115–116° (0.3 mm.), $n^{19}$D 1.4480, yield 72%, identifying infrared maxima at 1737, 1186 and 1040 cm.$^{-1}$.

*Anal.* Calcd. for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 57.09; H, 8.08.

Attempted acyloin ring closure using sodium and xylene apparently yielded no 8-oxo-9-oxy-1,4-dioxaspiro[4.6]hendecane. The only pure product isolated from this procedure was identified as 8-oxo-1,4-dioxaspiro[4.5]decane, infrared maxima at 1714, 1134, 1090, 1035 cm.$^{-1}$, m.p. 73.5–74.5°, undepressed on admixture with an authentic sample.[23]

**Ethylene Glycol Ketal of Diethyl γ-Oxosuberate.**—The ethylene glycol ketal of diethyl γ-oxosuberate[24] was obtained[22] in 56% yield, b.p. 121–125° (0.15 mm.), $n^{20}$D 1.4502, identifying infrared maxima at 1725, 1188 and 1032 cm.$^{-1}$.

*Anal.* Calcd. for $C_{14}H_{24}O_6$: C, 58.31; H, 8.39. Found: C, 58.53; H, 8.18.

**8-Oxo-1,4-dioxaspiro[4.6]hendecane.**—The ring closure of the ethylene glycol ketal of diethyl γ-oxosuberate was effected with sodium hydride in xylene, according to the directions of Blicke, Azuara, Doorenbos and Hotelling[25] for the conversion of dimethyl azelate to cyclooctanone. The yield of 8-oxo-1,4-dioxaspiro[4.6]hendecane was 39%, b.p. 102° (1.5 mm.), $n^{20}$D 1.4828, identifying infrared maxima at 1696 and 1106 cm.$^{-1}$.

*Anal.* Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.63; H, 8.36.

**Ultraviolet Absorption Spectra of 2,7-Disubstituted Cycloheptanones.**—The absorption maxima of selected 2,7-disubstituted cycloheptanones are given in Table III. A comparison of the longest wave length absorption maxima of these compounds with those of the corresponding 3,7-disubstituted 1,2-cycloheptanediones,[5] with application of a suitable correction for change of solvent, shows the general bathochromic shift caused by introduction of the second carbonyl and indicates that the chromophoric system is extended by this change in structure.

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[18] All melting points are corrected. The authors are indebted to Miss Helen Miklas, Mrs. Louise Griffing and Mr. James Brader for determination of the infrared absorption spectra, using a Perkin–Elmer automatic recording spectrometer, model 21, and to Miss Gerardine Meerman for determination of the ultraviolet absorption spectra, using a Cary recording spectrophotometer, model 11. We wish to thank Mrs. Esther Fett, Mrs. Lucy Chang, Mrs. R. Maria Benassi, Mr. Joseph Nemeth and Mr. R. J. Nesset for the microanalyses.

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