double bonds. The peak at 6.00 p.p.m. was partly attributed to the axial ring hydrogens. These would be expected to appear about 0.4 p.p.m. upfield from the equatorial hydrogens. The ring was assumed to have either slow inversion or no inversion at all due to the mass and steric effects of the hydrazine substituent. Dissection of this peak into an upper triplet having the correct 1:2:1 ratio and a lower segment, indicates that a peak equivalent to four hydrogens is buried beneath the methyl peak. The hydrogen distribution by NMR is as follows:

	Theory	Found
OCH_2 and *t*-H	5	5.5
CH_3 and ring CH_2	16	15.3
N—H	1	1.2

Anal. Calcd. for $C_{12}H_{22}N_2O_4$: C, 55.79; H, 8.59; N, 10.85; mol. wt., 258; MR_D, 65.48. Found: C, 55.67; H, 8.22; N, 10.95 mol. wt., 251, 246; MR_D, 65.51.

Reaction of Lithium Aluminum Hydride with XIII.—The method and apparatus used was the same as in the reaction of lithium aluminum hydride with X. To a tetrahydrofuran solution of 401.4 mg. (1.40 mmoles) of XIII containing 10% impurity by vapor phase chromatographic[15] analysis was added 1.0 ml. of a 1.5 *M* lithium aluminum hydride solution in tetrahydrofuran. The hydrogen evolved equaled 36.4 ml., corrected for the volume of solution injected, a blank for the tetrahydrofuran and STP. Assuming XIII to have one active hydrogen and the 10% impurity to be the dimer of XIII and therefore two active hydrogens the amount of hydrogen evolution should have been 35.1 ml.

Hydrogenation of XI.—Using an apparatus and method identical to that used in the hydrogenation of X, 580 mg. (2.16 mmoles) of XI, 95% pure by vapor phase chromatographic analysis,[15] took up 54.8 ml. of hydrogen or 1.13 mmoles H_2/mmole XI. The ultraviolet spectrum of the filtered hydrogenated solution showed 0.189 mmole of benzene to have been formed during the hydrogenation. Vapor phase chromatographic analysis[15] of the solution stripped of solvent showed it to contain 12% ethyl hydrazodicarboxylate, 73% of a compound corresponding in retention time (6.3 min.) to XIII and 15% of a compound with 26.0-min. retention time. The peak corresponding to XIII was isolated on an alumina chromatographic column and had infrared and NMR spectra identical to XIII.

Anal. Calcd. for $C_{12}H_{22}N_2O_4$: C, 55.79; H, 8.59. Found: C, 55.94; H, 8.53.

A hydrogenation of X was carried out in an identical manner to the hydrogenations of X and XI described above with the exception that 2.0 mmoles of X dissolved in 4.0 ml. of ethanol was placed in the flask with the catalyst before saturating the latter with hydrogen. The hydrogen uptake was 61.0 ml. or 1.4 mmoles H_2/mmole X. Benzene was found by ultraviolet analysis to the extent of 1.24 mmoles, and again ethyl hydrazodicarboxylate was formed, although the major product was still XIII.

In order to determine the reason for the formation of benzene and ethyl hydrazodicarboxylate, 1.22 mmoles of X was dissolved in 5.0 ml. of ethanol and stirred under nitrogen with 0.14 g. of 10% palladium-on-charcoal for 23 hr. The work-up of the solution was the same as for the hydrogenations. Ultraviolet analysis showed that 1.00 mmoles of benzene was formed; 83% of the possible amount. Vapor phase chromatographic[15] analysis showed that 91% of the original amount of X had disappeared, and that the amount of ethyl hydrazodicarboxylate had increased. The same experiment was repeated using *p*-dioxane as the solvent. Stirring under nitrogen was continued for 48 hr.; but ultraviolet spectrum showed no formation of benzene, and vapor phase chromatographic analysis[15] showed no change in amount of ethyl hydrazodicarboxylate present. Again using *p*-dioxane as solvent, 0.55 g. of 10% palladium on charcoal was placed in 4.0 ml. of the *p*-dioxane, the mixture then being saturated with 15.1 ml. of hydrogen. Compound X, 5.83 mmoles, was diluted up to 5.0 ml. with *p*-dioxane and was added to the saturated catalyst. The mixture was stirred for 49 hr. at room temperature under nitrogen. The mixture was filtered, and the filtrate was stripped of volatile material, which contained 4.59 mmoles of benzene. Ethyl hydrazodicarboxylate, 4.25 mmoles, was precipitated from the residue by mixing with carbon tetrachloride.

Acknowledgment.—The authors wish to express their appreciation to Mr. George Rodgers and to Dr. Boyd E. Hudson for the determination and interpretation of the NMR spectra.

Double Bond Migration in 1,2-Diaroyl-1-cycloalkenes[1]

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Received January 16, 1962

A number of 1,2-diaroyl-1-cycloalkenes have been found to undergo isomerization to the corresponding 1,6-diaroyl-1-cycloalkenes. The rearrangement is catalyzed by hydrochloric acid and by sodium hydroxide.

An attempt to prepare 1,2-dimesitoyl-1-cyclohexene (II) by the action of iodine on the enol salt of *trans*-1,2-dimesitoylcyclohexane (I) produced instead the unsymmetrical olefin, 1,6-dimesitoyl-1-cyclohexene (III).[2] It has now been found that a shorter reaction time gives the symmetrical olefin in 74% yield.

It seemed likely that the symmetrical olefin had rearranged to the unsymmetrical isomer when the reaction time was prolonged. Confirmation of this speculation was obtained by treating the symmetrical olefin with sodium hydroxide; when the solution was allowed to stand for seventy two hours, the unsymmetrical olefin was obtained in 93% yield.

It is possible that the rearrangement is due to purely steric factors. To explore this idea, the corresponding diduroyl compound, containing larger groups, was studied. Under the same conditions

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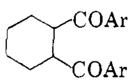
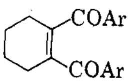
(1) This investigation was supported in part by Grant No. DA-ARO(D)-31-124-G137 from the Army Research Office, U. S. Army, Durham, N. C.

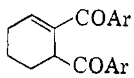
(2) R. C. Fuson, W. R. Hatchard, R. H. Kottke, and J. L. Fedrick, *J. Am. Chem. Soc.*, **82**, 4330 (1960).



I. Ar = Mes
Ia. Ar = Dur
Ib. Ar = C_6H_5
Ic. Ar = $C_6H_3(CH_3)_2$



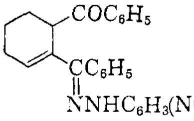
II. Ar = Mes
IIa. Ar = Dur
IIb. Ar = C_6H_5
IIc. Ar = $C_6H_3(CH_3)_2$



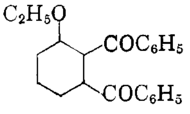
III. Ar = Mes
IIIa. Ar = Dur
IIIb. Ar = C_6H_5
IIIc. Ar = $C_6H_3(CH_3)_2$

used for the dimesitoyl olefin, 1,2-diduroyl-1-cyclohexene (IIa) was isomerized to 1,6-diduroyl-1-cyclohexene (IIIa), also in 93% yield.

Migration of the double bond occurred with smaller aroyl groups as well. The symmetrical dibenzoyl olefin, IIb, gave the corresponding unsymmetrical olefin, IIIb, in the form of an oil. Two solid derivatives were prepared: the mono-2,4-dinitrophenylhydrazone, IV, and the ethanol addition product, V.



IV

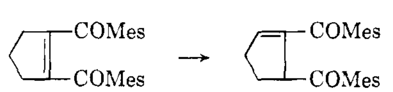


V

The structures of all three of these compounds (IIIb, IV, V) are consistent with spectral data.

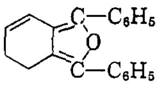
When the benzoyl groups were replaced by 3,4-dimethylbenzoyl groups, both of the expected olefinic compounds were obtained as crystalline solids; rearrangement of the symmetrical isomer, IIc, to the unsymmetrical derivative IIIc, occurred in 42% yield.

A similar rearrangement was observed in the cyclopentene series; 1,2-dimesitoyl-1-cyclopentene, VI, yielded 1,5-dimesitoyl-1-cyclopentene, VII.

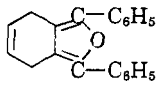


VI VII

That the unsymmetrical olefins are more stable than the symmetrical isomers is supported by the fact that the rearrangements are catalyzed by hydrochloric acid also. A complication arose with the unhindered diketones, which were converted into isobenzofurans. The structure assigned to the isobenzofuran from the dibenzoyl compound is 1,3-diphenyl-4,5-dihydroisobenzofuran, VIII, since the other possibility—the 4,7-dihydro compound, IX—is known.[3]



VIII

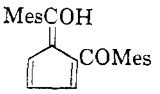


IX

Catalytic hydrogenation converted the dihydro compound, VIII, into the known tetrahydro derivative. This compound had proved to be helpful in another way. After many failures with other methods it was found that the symmetrical dibenzoylcyclohexene could be made from the tetrahydroisobenzofuran by oxidation with chromium trioxide. This procedure served also to convert 1,3-bis(3,4-dimethylphenyl)-4,5,6,7-tetrahydroisobenzofuran into 1,2-bis(3,4-dimethylbenzoyl)-1-cyclohexene and appears to be a general synthesis of unsaturated diketones of this type.

When the rearrangement was effected with alkali, it was necessary to exclude oxygen, which served as an aromatizing agent and led to the formation of the corresponding diaroylbenzenes. Thus an easy route is provided for aromatization of 1,2-diaroylcyclohexanes.[4]

Oxygen and sodium hydroxide had a similar dehydrogenating effect on 1,2-dimesitoyl-1-cyclopentene; the product was the fulvenol, X.[5]



X

Similar rearrangements in the presence of alkali have been reported for Δ^1-tetrahydrophthalic acid[6] and for Δ^1-cyclopentene-1,2-dicarboxylic acid.[7] In these cases the two carboxylate groups would repel each other because they carry like charges.

Experimental[8]

Formation of the Hindered, Symmetrical Olefins. 1,2-Dimesitoyl-1-cyclohexene.[9]—A solution of 11.3 g. (0.0300 mole) of *trans*-1,2-dimesitoylcyclohexane in 650 ml. of toluene was added dropwise to a Grignard reagent made from 8.16 g. (0.336 g.-atom) of magnesium and 31 ml. (0.407 mole) of ethyl bromide in 300 ml. of anhydrous ether. The reaction mixture was stirred at room temperature for 10 hr., heated under gentle reflux for another 2 hr., then poured slowly with stirring into an ice cold solution of 22.5 g. of iodine in 900 ml. of 95% ethanol. After 10 min. the iodine color was discharged by addition of sodium bisulfite solution, and the product isolated by conventional means. After two recrystallizations from 85% aqueous ethanol, the 1,2-dimesitoyl-1-cyclohexene formed slightly yellow crystals melting at 122.5–124.5°, yield 8.24 g. (74%). Recrystallization from hexane and 70% ethanol gave an analytical sample, m.p. 126.5–127°.

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[3] R. Adams and M. H. Gold, *J. Am. Chem. Soc.*, **62**, 56, 2038 (1940).

[4] R. C. Fuson, S. B. Speck, and W. R. Hatchard, *J. Org. Chem.*, **10**, 55 (1945).

[5] R. C. Fuson, C. L. Fleming, P. F. Warfield, and D. E. Wolf, *ibid.*, **10**, 121 (1945).

[6] A. von Baeyer, *Ann.*, **258**, 145 (1890).

[7] B. L. Nandi, *J. Indian Chem. Soc.*, **11**, 213 (1934).

[8] All melting points are corrected.

[9] This experiment was first performed by Dr. Roger H. Kottke.

Anal.[10] Calcd for $C_{26}H_{30}O_2$: C, 83.38; H, 8.07. Found: C, 83.43; H, 8.29.

The infrared spectrum[11] has a broad absorption band at 1645 cm.$^{-1}$ (conjugated carbonyl group). The NMR spectrum[12] (30%, deuterochloroform) shows no vinyl or tertiary proton peaks between the aromatic proton peak at 3.24 τ and the allylic and methyl proton peak at 7.70 τ.

***cis*-1,2-Diduroyl-1-cyclohexene Oxide.**[13] The procedure was similar to that used for the corresponding dimesityl compound.[2] From 3.6 g. (8.89 mmoles) of *trans*-1,2-diduroylcyclohexane[4] was obtained 1.98 g. (53%) of crude *cis*-1,2-diduroyl-1-cyclohexene oxide. After one recrystallization from acetone, it melted at 153–154.5°.

Anal. Calcd. for $C_{28}H_{34}O_3$: C, 80.34; H, 8.19. Found: C, 80.26; H, 8.15.

The infrared spectrum has carbonyl bands at 1710 and 1675 cm.$^{-1}$ and bands at 1240, 1170, and 835 cm.$^{-1}$, which are characteristic of a symmetrical epoxide.

1,2-Diduroyl-1-cyclohexene.—When applied to *trans*-1,2-diduroylcyclohexane (4.05 g.) the dehydrogenation procedure gave 4.0 g. of solid product which was purified by repeated washing with cold carbon disulfide, yield 2.06 g. (51%) of white powdery crystals, m.p. 201–202°. The compound decolorizes bromine in carbon tetrachloride. An analytical sample, m.p. 201.5–202.5°, was prepared by recrystallization from high-boiling petroleum ether.

Anal. Calcd. for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51. Found: C, 83.70; H, 8.49.

The infrared spectrum in chloroform shows a single, broad conjugated carbonyl band with maximum absorption at 1645 cm.$^{-1}$; in Nujol two carbonyl bands appear (1685–1690 and 1665 cm.$^{-1}$). No peaks are found between 3.10 τ (duryl, aromatic protons) and 7.74 τ (allylic protons) in the NMR spectrum (30%, deuterochloroform).

1,2-Dimesitoyl-1-cyclopentene.—By use of the procedure just described 3.55 g. (45%) of the cyclopentene was prepared from 8.01 g. of *trans*-1,2-dimesitoylcyclopentane.[5] Recrystallization from ethanol-water gave a pure sample, m.p. 120–120.5°.

Anal. Calcd. for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. Found: C, 83.12; H, 7.90.

The infrared spectrum has a broad carbonyl band with a maximum at 1638 cm.$^{-1}$; the NMR spectrum (15%, carbon disulfide) shows no peaks between 3.41 τ (singlet), assigned to the aromatic hydrogen atoms, and 7.38 τ (triplet), assigned to the allylic hydrogen atoms on the cyclopentene ring.

Aromatization of the Olefins.—Treatment of the symmetrical diketo olefins with base in the presence of air brought about aromatization. ***o*-Dimesitoylbenzene** was produced by allowing a solution of 1,2-dimesitoyl-1-cyclohexene (938 mg., 2.50 mmoles) in 450 ml. of ethanol to stand at room temperature in contact with the air after 1.65 ml. of 10% sodium hydroxide (4.13 mmoles) had been added. The solution soon developed a yellow color which slowly turned to orange and at the end of 24 hr. was orange-red. At the end of 72 hr. the crystalline precipitate that had formed was collected on a filter. An additional quantity of the solid precipitated when 450 ml. of water was added to the filtrate and the solution was cooled to 0°; total yield 712 mg. (77%), m.p. 236.5–237°. Determination of a mixture melting point and comparison of infrared spectra showed the product to be 1,2-dimesitoylbenzene.[4]

***o*-Diduroylbenzene.**—When the dehydrogenation procedure was applied to 1,2-diduroyl-1-cyclohexene (1.01 g., 2.50 mmoles), the reaction mixture slowly acquired a red color; after 72 hr. 0.5 g. of crystals melting at 274–275° and a less pure sample (0.23 g., m.p. 269–272°) were collected. The infrared spectrum was identical with that of *o*-diduroylbenzene,[4] and a mixture melting point with an authentic sample showed no depression.

***o*-Dibenzoylbenzene.**—A solution of 0.29 g. (1.00 mmole) of 1,2-dibenzoyl-1-cyclohexene in 120 ml. of absolute ethanol, to which 0.66 ml. of a 10% sodium hydroxide solution had been added, was allowed to stand in the usual way. Addition of water to the red solution did not precipitate the product, so the volume was reduced to 100 ml. by distillation under reduced pressure, and the solution extracted with ether. Evaporation of the ether left an oil, which was chromatographed on acid-washed alumina. Elution with cyclohexane-ether gave 97 mg. (34%) of *o*-dibenzoylbenzene, m.p. 144–146°. The product was identified by comparison of infrared spectra and a mixture melting point determination.

Isomerization of the Symmetrical Olefins with Base.—The procedure was the same as that for aromatization except that oxygen was excluded by operating under nitrogen. From 1.40 g. (3.74 mmoles) of 1,2-dimesitoyl-1-cyclohexene was obtained 1.30 g. (93%) of **1,6-dimesitoyl-1-cyclohexene,** m.p. 202–205°. Purification was effected by recrystallization from ethanol-water, m.p. 203.5–205°. The product, colorless crystals, was identified by comparison of its infrared spectrum with that of an authentic specimen.[2] Also, a mixture melting point determination showed no depression. The NMR spectrum (30%, deuterochloroform) has a tertiary hydrogen atom peak at 5.70 τ (multiplet), and an olefinic proton absorption peak at 3.25 τ (partially masked).

In a similar way 1.50 g. (3.73 mmoles) of 1,2-diduroyl-1-cyclohexene gave 1.40 g. (93%) of **1,6-diduroyl-1-cyclohexene** as colorless crystals, m.p. 178–181°. After three recrystallizations of the compound from ethanol–water, the melting point was 181–182°.

Anal. Calcd. for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51. Found: C, 83.84; H, 8.58.

The identity of the compound was confirmed by its properties. It decolorizes a solution of bromine in carbon tetrachloride. The infrared spectrum contains an olefinic peak at 1635 cm.$^{-1}$ and two carbonyl bands—one at 1645–1650 cm.$^{-1}$, assignable to a conjugated carbonyl group, and the other, at 1685–1690 cm.$^{-1}$, assignable to an unconjugated carbonyl group. Peaks at 3.27 τ (triplet) and 5.78 τ (multiplet) in the NMR spectrum (30%, deuterochloroform) show the presence of olefinic and tertiary hydrogen atoms, respectively. There is a 1:1 ratio of the areas under the peaks.

1,5-Dimesitoyl-1-cyclopentene, m.p. 136–140° (31%) was obtained from 1,2-dimesitoyl-1-cyclopentene (1.34 g.) in a similar way. It was purified by chromatography on acid-washed alumina followed by five recrystallizations from methanol, m.p. 149–150°.

Anal. Calcd. for $C_{25}H_{28}O_2$: C, 83.29; H, 7.83. Found: 83.09; H, 7.89.

The infrared spectrum has two carbonyl peaks (1650–1655 and 1692 cm.$^{-1}$) and a carbon-hydrogen deformation band at 800 cm.$^{-1}$, characteristic of a trisubstituted double bond. The NMR spectrum (15%, carbon disulfide) has an olefinic proton absorption peak at 3.70 τ (triplet) and a tertiary proton absorption peak at 5.65 τ (triplet) in a 1:1 area ratio.

The ethanol–water filtrate, after being allowed to stand open to the air for 12 hr., was reduced to one-half its original volume by distillation under reduced pressure and filtered. An orange-yellow solid was collected, yield 0.260 g. (20%), m.p. 223–236°. A pure sample (m.p. 248–248.5°) was obtained by recrystallization successively from ethanol, ethanol–chloroform, *n*-hexane, and acetone. The product was shown by a mixture melting point determination and by comparison of infrared spectra to be 1-mesitoyl-6-hydroxy-6-mesitylfulvene.[5] It gives a gelatinous, orange precipitate with ferric chloride solution. The infrared spectrum has a hydrogen-bonded carbonyl absorption band at 1620 cm.$^{-1}$. The ultraviolet spectrum[14] (ethanol) has a maximum at 254 mμ (log ϵ 4.19) and one at 335 mμ (log ϵ 3.98).

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[10] Microanalyses were performed by Mr. G. D. Callahan, Miss M. A. Weatherford, Mrs. A. S. Bay, and Miss J. Liu.

[11] The infrared spectra were determined by Mr. P. E. McMahon, Mr. W. Dalton, Mr. D. Fugii, Mr. D. H. Johnson, Miss D. Wood, Mrs. M. Verkade, and Miss C. Leubke.

[12] The NMR spectra were determined by R. O. W. Norton.

[13] This compound was first prepared by Dr. James L. Fedrick.

[14] The ultraviolet spectra were obtained by Ping-Kay Hon.

1,2-Dibenzoyl-1-cyclohexene yielded an oil which appeared to contain the expected unsymmetrical olefin. Evidence for its presence was obtained from the NMR spectrum (15%, carbon disulfide) which showed peaks at 3.44 τ (triplet, relative area 1) and at 5.38 τ (triplet, relative area 1). These peaks are assignable, respectively, to olefinic and tertiary hydrogen atoms.

A mono-2,4-dinitrophenylhydrazone, prepared from the oil, separated from absolute ethanol as red crystals melting at 208–209°.

Anal. Calcd. for $C_{26}H_{22}N_4O_5$: C, 66.37; H, 4.71; N, 11.91. Found: C, 66.29; H, 4.86; N, 12.02.

The infrared spectrum has one carbonyl band at 1678 cm.$^{-1}$. The peak for a conjugated carbonyl group (1643 cm.$^{-1}$) of the parent diketone is absent. The ultraviolet spectrum (ethanol) has a maximum at 379 mμ (log ϵ 4.44).

For purposes of comparison the mono-2,4-dinitrophenylhydrazone of *trans*-1,2-dibenzoylcyclohexane was prepared; it separated from ethanol as orange crystals, m.p. 138.5–140.5°.

Anal. Calcd. for $C_{26}H_{24}N_4O_5$: C, 66.09; H, 5.12; N, 11.86. Found: C, 66.37; H, 5.34; N, 11.88.

The ultraviolet spectrum (ethanol) shows a maximum at 364 mμ (log ϵ 4.35).

1,2-Dibenzoyl-3-ethoxycyclohexane.—This derivative was made in an attempt to prepare 1,6-dibenzoyl-1-cyclohexene oxide. To a solution of 0.570 g. of the oil from the previous section in 150 ml. of absolute ethanol was added 4 ml. of 30% hydrogen peroxide and 4.5 ml. of 10% sodium hydroxide solution. The reaction mixture was stirred 48 hr., 2 ml. of 30% hydrogen peroxide being added every 12 hr. The product crystallized from ethanol, m.p. 120–123°, yield 90 mg. (14%). After three additional recrystallizations from ethanol and one from acetone–water, the compound melted at 124–125.5°.

Anal. Calcd. for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19; mol. wt., 336.4. Found: C, 78.66; H, 7.24; mol. wt., 332.6.

The infrared spectrum has a carbonyl band at 1682 cm.$^{-1}$ and bands at 1255, 1110, 1095, and 838 cm.$^{-1}$ which are characteristic of an ether. The NMR spectrum (7%, carbon disulfide) shows the presence of an ethyl group (6.94 and 9.11 τ) and of three methinyl hydrogen atoms (6.09 τ).

1,2-Bis(3,4-dimethylbenzoyl)-1-cyclohexene was isomerized to the corresponding unsymmetrical olefin under the usual conditions. **1,6-Bis(3,4-dimethylbenzoyl)-1-cyclohexene** was crystallized from absolute ethanol, m.p. 91–93°, yield 42%. After another recrystallization from ethanol followed by two from high-boiling petroleum ether, the compound melted at 92.5–93.5°.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.28; H, 7.76.

Peaks for two carbonyl groups (1670–1675 and 1640 cm.$^{-1}$) are present in the infrared spectrum. An olefinic proton peak occurs at 3.44 τ (triplet, relative area 1) in the NMR spectrum (15%, carbon disulfide) along with a tertiary proton resonance peak at 5.36 τ (triplet, relative area 1).

Isomerization of the Symmetrical Olefins with Acid.—To a solution of 0.915 g. (2.18 mmoles) of 1,2-dimesitoyl-1-cyclohexene in 15 ml. of chloroform was added 2 ml. of concentrated hydrochloric acid. After the mixture had been kept under nitrogen for 72 hr., the chloroform layer was removed and to it was added 10 ml. of fresh chloroform. The solution was washed with four 10-ml. portions of water, and the chloroform was evaporated. The solid residue, when recrystallized from ethanol, gave 0.620 g. (76%) of 1,6-dimesitoyl-1-cyclohexene, m.p. 200.5–202°. After another recrystallization it melted at 201–203°. A mixture with an authentic sample showed no lowering of the melting point, and the infrared spectra of the two samples are superimposable. When this olefin was subjected to the treatment described for the symmetrical isomer, no change was observed.

Application of this procedure to 0.439 g. (1.09 mmoles) of 1,2-diduroyl-1-cyclohexene produced 0.406 g. (92%) of the unsymmetrical isomer, m.p. 176–178°. After recrystallization from ethanol it melted at 179–181°. It was identified by a mixture melting point determination with an authentic specimen and by a comparison of the infrared spectra.

In a similar way 0.786 g. (2.18 mmoles) of 1,2-dimesitoyl-1-cyclopentene was changed to the 1,5-isomer. The product was crystallized from methanol, yield 0.598 g. (76%), m.p. 146–148°. It was identified by its infrared spectrum and by a mixture melting point.

1,3-Diphenyl-4,5-dihydroisobenzofuran.—A solution of 1.90 g. (6.55 mmoles) of 1,2-dibenzoyl-1-cyclohexene in 45 ml. of chloroform was treated with 6 ml. of concentrated hydrochloric acid in the manner used for the isomerization experiments. The oil obtained was subjected to chromatography on 75 g. of acid-washed alumina. Elution with cyclohexane gave a fluorescent oil which was taken up in hot ethanol. When the solution was cooled to room temperature, a small amount of oil separated. The ethanol solution was decanted from this oil and cooled in a refrigerator; it gave 0.620 g. of 1,3-diphenyl-4,5-dihydroisobenzofuran, m.p. 67.5–69°, yield 35%. After repeated recrystallization from methanol, the compound melted at 71–72°.

Anal. Calcd. for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 87.94; H, 5.91.

The ultraviolet spectrum (ethanol) shows maxima at 233 mμ (log ϵ 4.20), 239 mμ (log ϵ 4.20), 264 mμ (log ϵ 4.29), and 326 mμ (log ϵ 4.44).

When treated with hydrogen in the presence of Adams' catalyst, the compound absorbed 1 mole of hydrogen to form **1,3-diphenyl-4,5,6,7-tetrahydroisobenzofuran**; it was recrystallized from ethanol, m.p. 93.5–95°. Its infrared spectrum is superimposable on that of the known compound. A mixture melting point showed no depression.

1,3-Bis(3,4-dimethylphenyl)-4,5,6,7-tetrahydroisobenzofuran was made from *trans*-1,2-bis(3,4-dimethylbenzoyl)-cyclohexane (6.97 g., 0.020 mole).[4] The product was recrystallized from absolute ethanol–chloroform, m.p. 144–146.5°, yield 4.37 g. (66%). After another recrystallization the compound melted at 146.5–147.5°.

Anal. Calcd. for $C_{24}H_{26}O$: C, 87.23; H, 7.93. Found: C, 86.89; C, 8.07.

Oxidation of the Tetrahydroisobenzofurans. 1,2-Dibenzoyl-1-cyclohexene.—The procedure is similar to that of Clar, John, and Hawran.[15] A solution of 1.54 g. (0.0154 mole) of chromium trioxide in 30 ml. of water and 30 ml. of glacial acetic acid was poured slowly into a solution of 6.33 g. (0.0234 mole) of 1,3-diphenyl-4,5,6,7-tetrahydroisobenzofuran[4] in 200 ml. of glacial acetic acid. After the mixture had stood at room temperature for 15 min. 650 ml. of water was added, and the milky solution was heated on a steam bath for 2 hr., the temperature not being allowed to rise above 60°. Crystals appeared during the heating. The reaction mixture was stored overnight in a refrigerator, and the light yellow precipitate collected by filtration, m.p. 72–74°, yield 5.47 g. (82%). The analytical sample was obtained by three recrystallizations from a mixture of low- and high-boiling petroleum ether, m.p. 77–78°.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.90; H, 6.46.

The compound takes up bromine in carbon tetrachloride and slowly decolorizes potassium permanganate solution. The infrared spectrum has a broad carbonyl absorption band (1665 cm.$^{-1}$), and bands at 695 and 760 cm.$^{-1}$, assignable to a monosubstituted phenyl group. The NMR spectrum (15%, carbon disulfide) contains aromatic peaks at 2.71 and 2.82 τ (relative area 10), an allylic proton band at 7.57 τ (multiplet, relative area 4), and a peak at 8.18 τ (multiplet, relative area 4) assignable to the homoallylic cyclohexene hydrogen atoms.

Catalytic dehydrogenation converted the compound into *o*-dibenzoylbenzene. A mixture of 0.340 g. (1.17 mmoles) of the dibenzoylcyclohexene and 34 mg. of 10% palladium-on-charcoal was heated at 275–295° for 1.5 hr. under nitrogen.

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[15] E. Clar, F. John, and B. Hawran, *Ber.*, **62*B***, 940 (1929).

Chromatographic separation on acid-washed alumina gave *trans*-1,2-dibenzoylcyclohexane and *o*-dibenzoylbenzene, m.p. 144.5–146°, yield 44 mg. (13%). The aromatized compound was identified by a mixture melting point with an authentic specimen.

1,2-Bis(3,4-dimethylbenzoyl)-1-cyclohexene, made in a similar way in 87% yield, was purified by successive recrystallization from high-boiling petroleum ether–chloroform, ethanol, and methanol, m.p. 137–138°.

Anal. Calcd. for $C_{24}H_{26}O_2$: C, 83.20; H, 7.56. Found: C, 83.28; H, 7.74.

The infrared spectrum shows one carbonyl group at 1655 cm.$^{-1}$ and a peak at 829 cm.$^{-1}$, assignable to the two adjacent hydrogen atoms of the 3,4-dimethylphenyl radical. The NMR spectrum is consistent only with a 1,2-diaroyl-1-cyclohexene structure.

***trans*-1,2-Bis(3,4-dimethylbenzoyl)cyclohexane.**—To an ice-cold mixture of *trans* hexahydrophthaloyl chloride (86.2 g., 0.412 mole), 200 ml. of *o*-xylene, and 500 ml. of methylene chloride was added over a 50-min. period 137.4 g. (1.030 moles) of aluminum chloride. The mixture was stirred for 1 hr. in an ice–salt bath, then warmed slowly and heated under reflux for 3 hr. By conventional procedures two products were isolated one of which separated from ethanol as colorless crystals, m.p. 166.5–167.5°.

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.51; H, 8.13.

That this compound is **2,2-bis(3,4-dimethylphenyl)hexahydrophthalide** is indicated by its infrared spectrum, which has a carbonyl band at 1775–1785 cm.$^{-1}$.

The second product, also recrystallized from ethanol, was identified as *trans*-1,2-bis(3,4-dimethylbenzoyl)cyclohexane, m.p. 107.5–109°. The yield of crude product was 21%.

Anal. Calcd. for $C_{24}H_{28}O_2$: C, 82.72; H, 8.10. Found: C, 82.87; H, 8.13.

The assigned structure is supported by a peak in the infrared spectrum for a carbonyl group (1670 cm.$^{-1}$) and peaks for a 1,2,4-trisubstituted aryl group (900, 834, and 823 cm.$^{-1}$).

2-Duroylcyclohexane-1-carboxylic Acid.—A solution of 16.2 g. (0.105 mole) of *cis* hexahydrophthalic anhydride and 14.1 g. (0.105 mole) of durene in 200 ml. of dry methylene chloride was stirred at 0° while 33.4 g. (0.250 mole) of aluminum chloride was added during a 15-min. period. The reaction mixture, after being allowed to come to room temperature, was heated under reflux for 4 hr. with continued stirring and poured into a mixture of ice and 10 ml. of concentrated hydrochloric acid. 2-Duroylcyclohexane-1-carboxylic acid, recrystallized from ethyl acetate, melted at 194–195°, yield 19.5 g. (65%).

Anal. Calcd. for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.84; H, 8.42.

The infrared spectrum shows adsorption in the 2500–3400-cm.$^{-1}$ region (hydroxyl group), at 1705–1710 cm.$^{-1}$ (aliphatic acid carbonyl group), at 1690 cm.$^{-1}$ (hindered ketone carbonyl group), and at 865 cm.$^{-1}$ (carbon-hydrogen deformation characteristic of the duryl group).

Beckmann Rearrangements in Alicyclic Systems. I. Spiro[5.6]dodecan-7-one Oxime[1]

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Received October 19, 1961

The Beckmann rearrangement of spiro[5.6]dodecan-7-one oxime under a variety of catalyic conditions is reported. Using polyphosphoric acid, 6-cyclohexylcaproamide was isolated as the only product af the rearrangement. Phosphorus pentachloride rearrangement yielded 6-(1′-cyclohexenyl)capronitrile, while concentrated sulfuric acid gave the corresponding amide, 6-(1′-cyclohexenyl)caproamide as the major reaction product. Benzenesulfonyl chloride and sodium hydroxide treatment of the oxime resulted in the formation of 7-azaspiro[5.7]tridecan-8-one rather than the expected nitrile from abnormal cleavage. Attempted Ritter reaction of the unsaturated nitrile using either concentrated sulfuric acid or polyphosphoric acid resulted in amide formation rather than cyclization to the lactam or α,β-unsaturated ketone as observed in other spiroketoxime systems.

Recently, the Beckmann rearrangement of several spiroketoximes in polyphosphoric acid leading to unusual products has been reported.[2] With the oximino group in a five-membered ring, rearrangement usually proceeded in high yield to an α,β-unsaturated ketone. However, with the oximino group in a six-membered ring, the yield of the unsaturated ketone sharply decreased and a second product, a saturated amide was also isolated in reasonable yield from the reaction mixtures.

The mechanism proposed for this reaction was initially identical to the course of rearrangement followed by a large number of α,α-disubstituted ketoximes[3] in that it was proposed that bond cleavage took place to produce an unsaturated nitrile. Such reactions have been observed in various nonprotonating media and in certain cases in protonating media to yield amides instead of the nitrile group through hydration. Indeed, this course for the rearrangement has been reported for such systems as the Beckmann rearrangement of α-keto and α-hydroxy ketoximes[4] and also reported in the low temperature Schmidt reactions

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[1] This work was supported by a Frederick Gardner Cottrell Grant from the Research Corporation and grants #B-2239 and B-3628 from the Department of Health, Education, and Welfare, Public Health Service.

[2] (a) R. K. Hill and R. T. Conley, *Chem. Ind.* (London), 1314 (1956); (b) R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960).

[3] For review see: L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, **11**, 1 (1960).

[4] (a) R. T. Conley and F. A. Mikulski, *Tetrahedron*, **3**, 90 (1958); (b) R. T. Conley and F. A. Mikulski, *J. Org. Chem.*, **24**, 97 (1959).