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3,384,658

PROCESS FOR DIMERIZING ARYL ALKANES

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9 Claims. (Cl. 260—515)

ABSTRACT OF THE DISCLOSURE

A process for dimerizing an aryl alkane by subjecting an aryl alkane to the influence of ultraviolet radiation in the presence of a diaryl ketone and to certain compounds resulting from such process.

This invention relates to a process for dimerizing an aryl alkane and to certain of said dimers as new compounds.

We have found that aryl alkanes can effectively be dimerized in the presence of a diaryl ketone under the influence of ultraviolet radiation.

Aryl alkanes that can be dimerized in accordance with the dictates of this invention can be represented in general by the following structural formula:

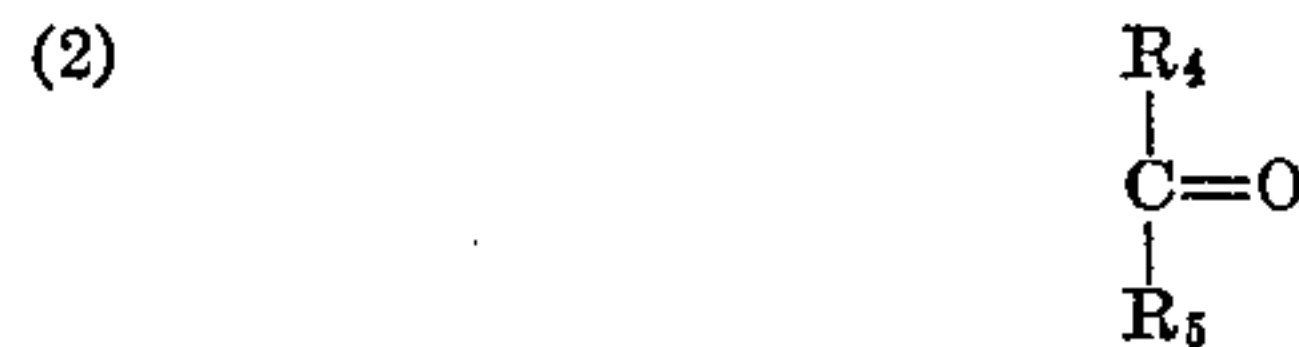


wherein R_1 is an alkyl radical having from one to 16 carbon atoms, preferably from one to eight carbon atoms, such as, methyl, ethyl, n-propyl, isopropyl, isobutyl, amyl, isoamyl, hexyl, isooctyl, decyl, tetradecyl, hexadecyl, etc.; R_2 is an aryl radical containing one or more rings, at least one of which is an aromatic ring, directly attached to the carbon in said formula, such as phenyl, biphenyl, naphthyl, phenanthryl, anthryl, indyl, dihydronaphthyl, cyclohexylphenyl, etc., the substituents on said aryl radicals preferably being hydrogen or alkyl radicals having from one to eight carbon atoms, preferably from one to three carbon atoms, such as, methyl, ethyl, n-propyl, isobutyl, amyl, isooctyl, etc., but can include such diverse radicals as F, Cl, Br, I, NO_2 , SO_3H , $COOH$, $COOR$, wherein R is an alkyl radical, NH_2 , OH, etc.; and R_3 is a radical selected from the group consisting of alkyl radicals defined by R_1 and aryl radicals defined by R_2 , but preferably being an aryl radical defined by R_2 . Examples of aryl alkanes that can be employed include cumene, 1-ethyl, 1-phenylbutane, 1-octyl, 1-tolyldecane, 1-dodecyl, 1-(3,4-dicarboxyphenyl) hexadecane, 1,1-diphenylethane, 1,1-di (paratolyl) ethane, 1,1-di (orthotolyl) ethane, 1-orthotolyl, 1-paratolyl ethane, 1,1-bis (3,4-dimethylphenyl) ethane, 1,1-bis (2,3-dimethylphenyl) ethane, and 1-(2,3-dimethylphenyl), 1-(3,4-dimethylphenyl) ethane, 1,1-bis (2-ethylphenyl) ethane, 1-(4-propylphenyl), 1-(4-methylphenyl) pentane, 1,1-bis(2-methylanthryl) butane, 1-(2-methyl, 4-chlorophenyl), 1-(2-ethylphenyl) octane, 1,1-bis (tetramethylphenyl) decane, 1-(2-methyl, 4-isopropylphenyl), 1-(4-methyl-2-nitrophenyl) ethane, 1,1-bis (2,4-diisopropylphenyl) hexadecane, 1,1-bis (2-ethyl, 4-butylphenyl) isobutane, 1,1-bis (2-hexylphenanthryl), 3,3-dimethylpentane, 1-(2-propyl, 3-carboxynaphthyl), 1-(4-butylphenyl) hexane, 1-(5-octyl, 1,4-dihydronaphthyl), 1-(2-methylnaphthyl)-dodecane, 1-(1-bromo, 9,10-dihydrophenanthryl), 1-(2-ethylphenyl)-decane, 1-(2-propyl, 3-aminophenyl), 1-(4-methyl-2-sulfophenyl)-ethane, etc.

The diarylketone that must be present in the dimeriza-

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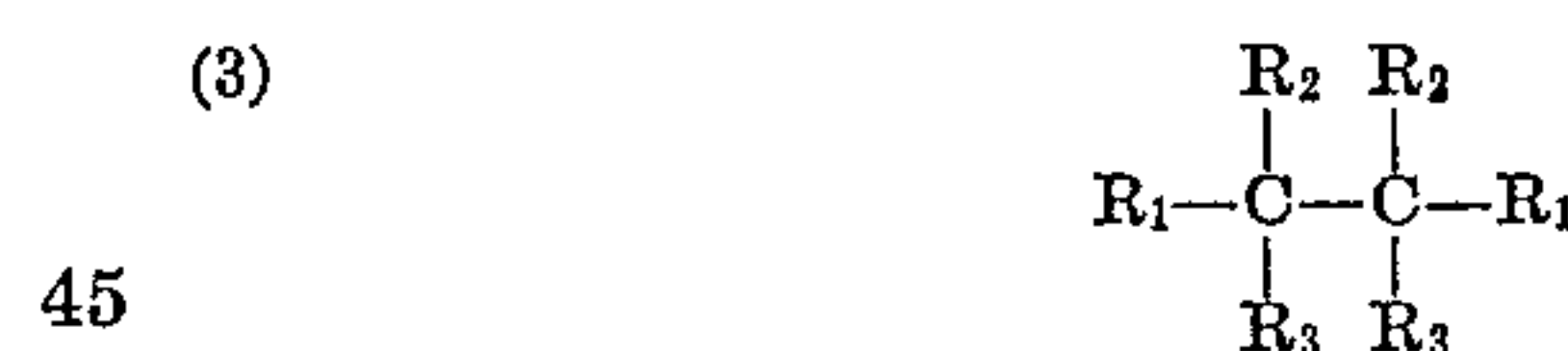
tion procedure described and claimed herein can be represented in general by the following structural formula:



wherein R_4 and R_5 , the same or different, are aryl radicals defined by R_2 . Examples of benzophenones that can be employed include benzophenone, 2,4'-dimethylbenzophenone, 4,4' - dimethylbenzophenone, 3,4,3',4' - tetramethylbenzophenone, 2,2' - dichloro, 5,5' - diethylbenzophenone, 3,3'-dinitrobenzophenone, 4-sulfobenzophenone, 4 - carboxybenzophenone, 4,4' - dicarbomethoxybenzophenone, 2,4,2',4' - tetracarboethoxybenzophenone, 2-chloro, 4'-carboxybenzophenone, dinaphthylketone, phenylnaphthylketone, etc. Of these we prefer to employ benzophenone 2,4' - dimethylbenzophenone, 4,4' - dimethylbenzophenone, 3,4,3',4',-tetramethylbenzophenone, 4,4'-dicarbomethoxybenzophenone and 2,4,2',4' - tetracarbo-methoxybenzophenone.

The procedure defined herein involves bringing together the aryl alkane and the benzophenone defined above and maintaining the same in intimate contact with each other while the same are subjected to the influence of ultraviolet radiation. By "ultraviolet radiation" we mean to include light having a wave length from about 2000 to about 4000 Å. Temperature and pressure employed during the reaction are not critical and can vary over a wide range. Thus, for example, the temperature can be from about 0° to about 400° C., preferably from about 0° to about 150° C., and the pressure can be from about 0 to about 1000 pounds per square inch gauge. Reaction time is not critical, but a greater amount of reaction occurs as the reaction period is lengthened. Thus a period of at least about 10 minutes can be employed, but a period of about one to about 200 hours is preferred. Although the charge aryl alkane and diaryl ketone can be employed in any amounts, we prefer to employ approximately equal molar amounts thereof.

As a result of the above the following desirable dimer is produced:



wherein R_1 , R_2 and R_3 are as defined above. Examples of such dimers are those obtained when one of the aryl alkanes defined above loses its tertiary hydrogen and the radical so formed couples with a similar radical similarly formed. At the same time the following additional dimer is produced.



wherein R_4 and R_5 are as defined above. Examples of the latter dimers are those substituted glycols formed by the coupling of two radicals arising out of the addition of a hydrogen to the oxygen in any one of the specific benzophenones defined above.

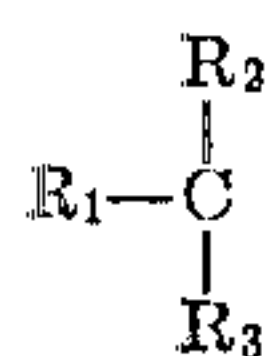
The formation of Compounds 3 and 4 solely is entirely unexpected and fortuitous. While we are not certain, we believe Compound 2 under the influence of ultraviolet radiation becomes highly activated and abstracts a tertiary hydrogen from Compound 1, resulting the following radicals, respectively:



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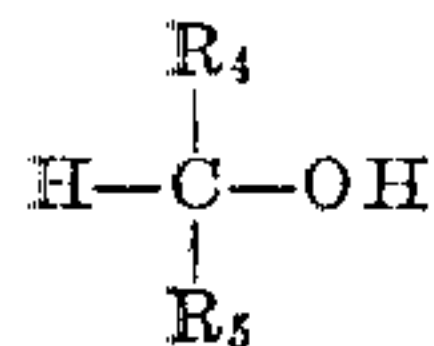
and

(6)



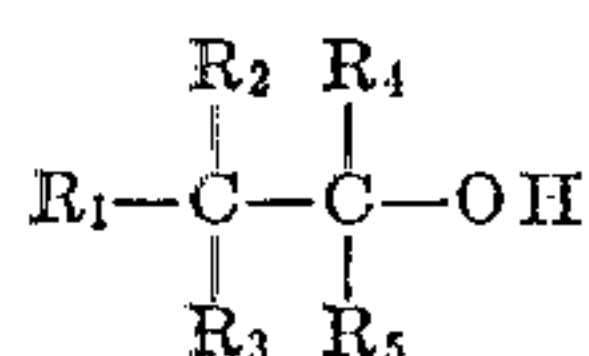
It would be expected at this point that Radical 6 would extract a tertiary hydrogen from Compound 1 and thereby would be reconverted to Compound 1. At the same time it would be expected that Radical 5 would abstract a tertiary hydrogen from Compound 1 resulting in the following benzhydrol:

(7)



Additionally, it might be expected that Radicals 5 and 6 would combine with each other to form the following compound:

(8)

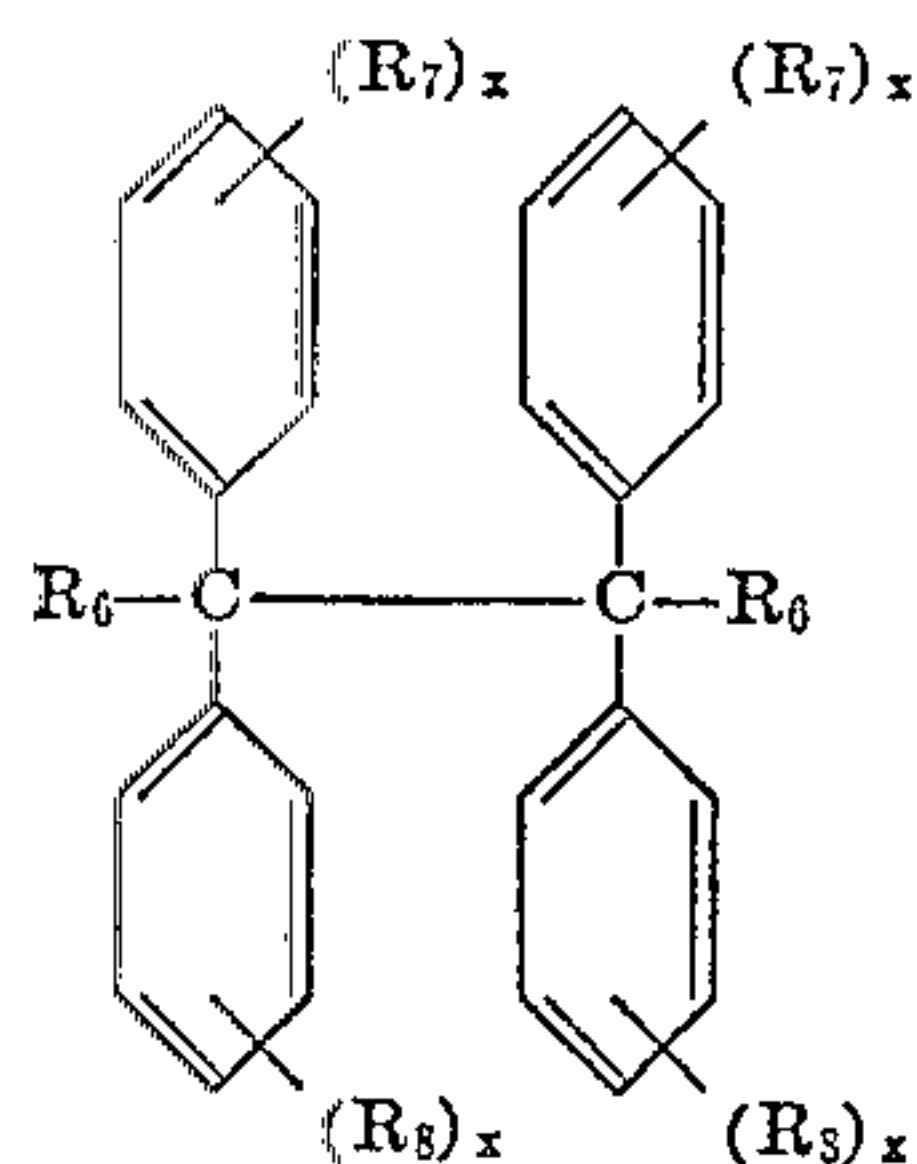


However, we have found, unexpectedly and desirably, that Radicals 5 and 6 combine solely with each other to form Compounds 4 and 3, respectively, but no evidence of the presence of Compounds 7 and 8. The presence of Compound 4, a pinacol, is desirable, since it can be regenerated by oxidation, for example, with lead tetraacetate in acetic acid (Cordner and Pausacker, Journal Of The Chemical Society, 1953, page 102), to the charge diaryl ketone, Compound 2, for reuse in the process.

The recovery of the desired product can be effected in any suitable manner. Thus, in general the pinacol, Compound 4, will crystallize out of solution and can be recovered from the reaction product by filtration and can be regenerated, if desired, to the diarylketone initially employed. The remainder of the product can then be subjected to distillation, for example, at a temperature of about 100° to about 350° C. and a pressure of about 0.5 to about 760 millimeters of mercury to remove therefrom unreacted aryl alkane and/or diaryl ketone which may be present. Left behind will be the hydrocarbon dimer, Compound 3.

We have also found that Compound 3 wherein R_1 is an alkyl radical and R_2 and R_3 are aryl radicals carrying at least one alkyl radical, preferably from one to two alkyl radicals, namely a compound of the following general structural formula:

(9)

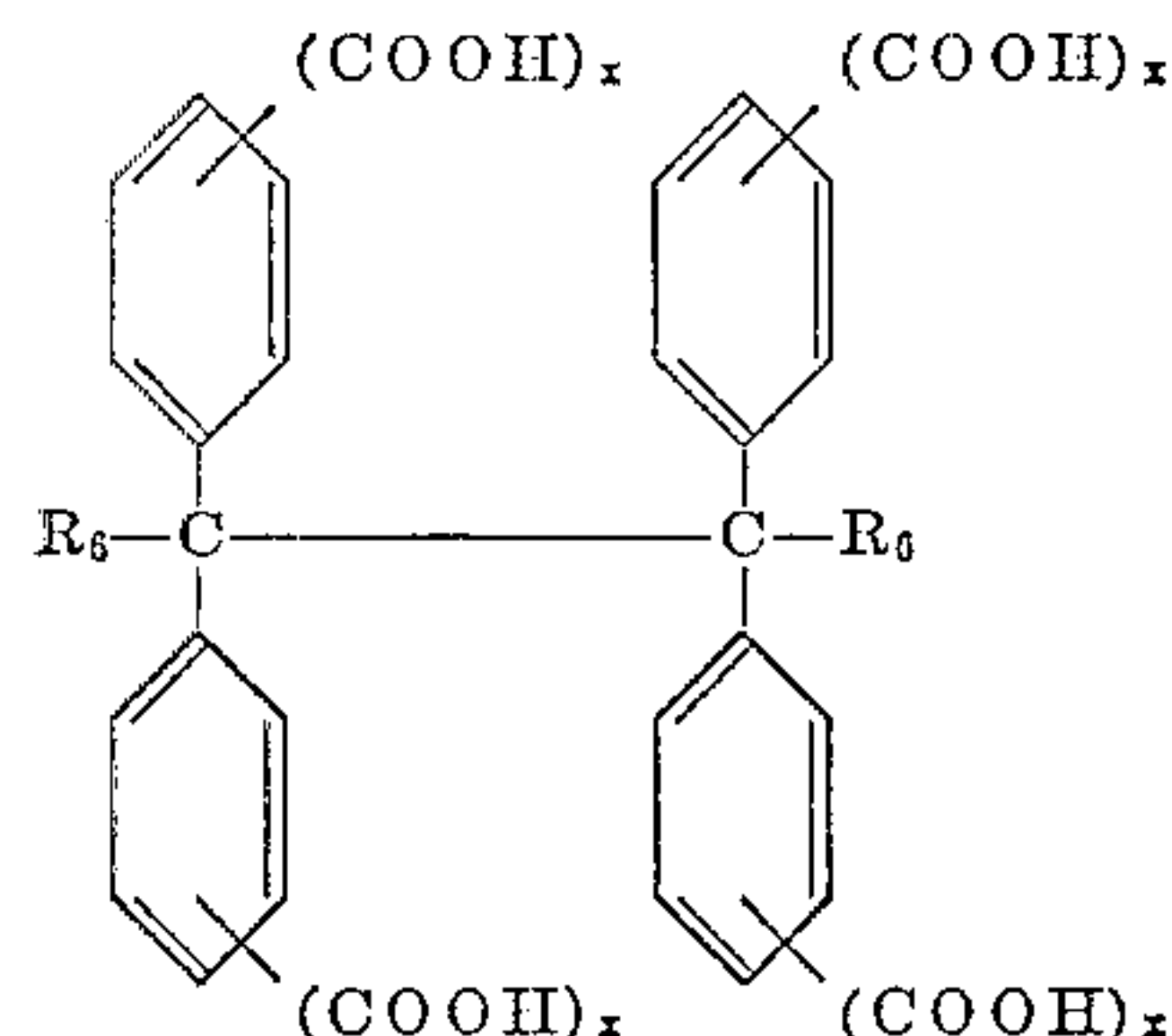


wherein R_6 is an alkyl radical having from one to 16 carbon atoms, preferably from one to eight carbon atoms, such as defined hereinabove, R_7 and R_8 are alkyl radicals having from one to eight carbon atoms, preferably from one to three carbon atoms, such as defined hereinabove, and x is an integer from one to five, preferably from one

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to two, and acids corresponding to Compound 9, namely an acid of the following general structural formula:

5 (10)



wherein R_6 and x are as defined above are new compounds. Examples of Compound 9 are those dimers formed, as defined herein, from the dimerization of the alkyl substituted diphenyl alkanes defined hereinabove and examples of Compound 10 are the acids resulting from the oxidation, as defined herein, of the dimers defined as Compound 9. Compound 10 can be obtained from Compound 9 in any suitable manner, but preferably by subjecting the latter to oxidation with nitric acid having a concentration of about five to about 70 percent at a temperature of about 150° to about 250° C. and a pressure of about atmospheric to about 500 pounds per square inch gauge for about 10 minutes to about five hours. At the end of the reaction period Compound 10 can be recovered from the reaction mixture, for example, by extracting the same with acetone. Since Compound 10 is not soluble in acetone it will be left behind as a solid crystalline material.

The invention can further be illustrated by the following:

Example I

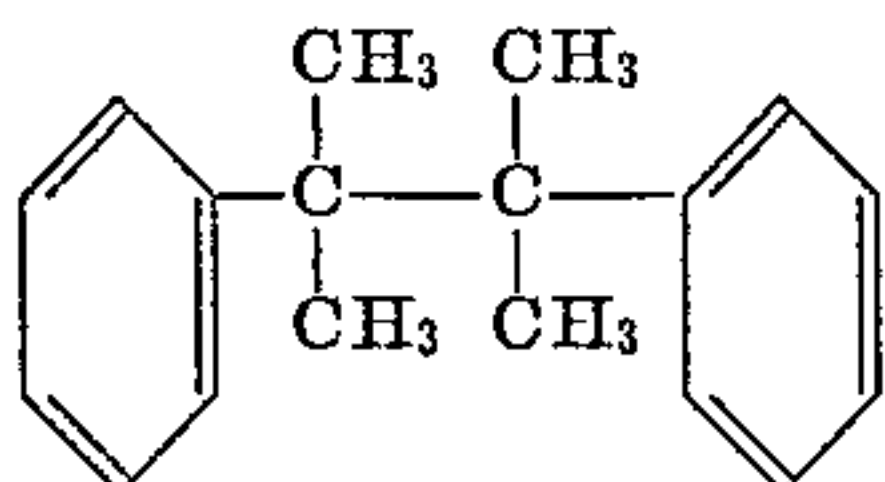
Into the center of a glass cylinder there was placed a quartz well and in the latter there was placed a Hanovia High Pressure Mercury Lamp, Model No. 654, manufactured by Hanovia Lamp Division, Engelhard Hanovia, Inc., Newark, N.J. The lamp during the procedures defined herein was operated at 280 volts and consumed one ampere while emitting ultraviolet light of a wave length in a region of 2400 to 4000 Å. In the portion of the cylinder between the inner wall thereof and the outer wall of said quartz well there were placed 91 grams of benzophenone and 650 grams of 1,1-ditolylethane. The latter mixture was then subjected to ultraviolet radiation at atmospheric pressure and at a temperature of 29° C. over a period of 144 hours. The reaction mixture at the end of the reaction period was subjected to filtration and there was recovered, as determined by its infrared spectrum and by its melting point of 185.0° C., 25.3 grams of benzopinacol. The filtrate, which amounted to 712.2 grams, was distilled at a temperature of 130° C. and a pressure of two millimeters of mercury to remove overhead unreacted benzophenone and ditolylethane. There was left behind 53.3 grams of a semi-solid yellow product consisting of 11.0 grams of benzopinacol and 42.0 grams of another compound having a molecular weight of 418 which was identified as 2,2,3,3-tetratolylbutane.

Example II

Using the same apparatus of Example I there was subjected to ultraviolet radiation at a temperature of 25° C. and atmospheric pressure over a period of 118 hours 91 grams of benzophenone and 600 grams of cumene. From the reaction product there was recovered 26.5

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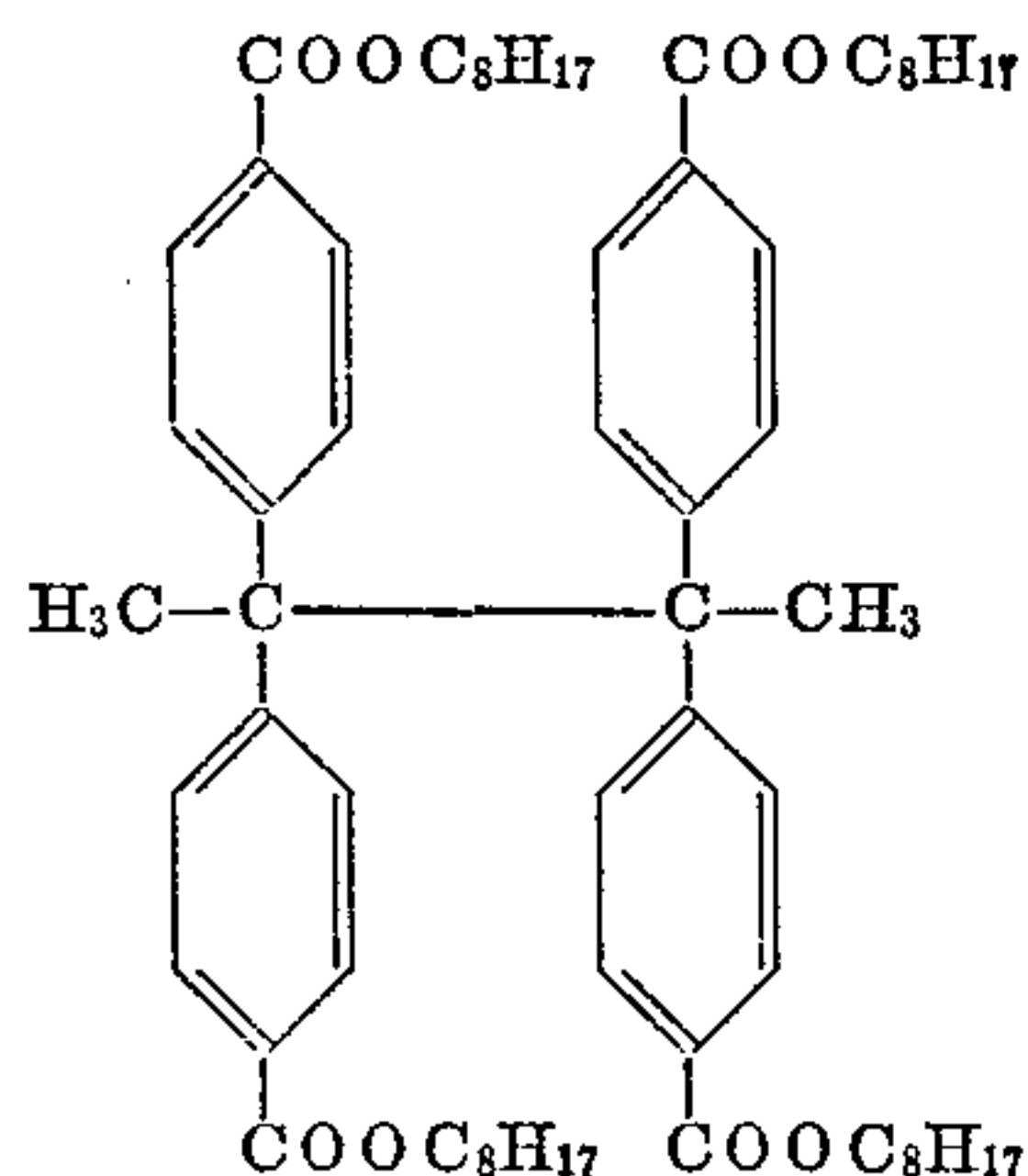
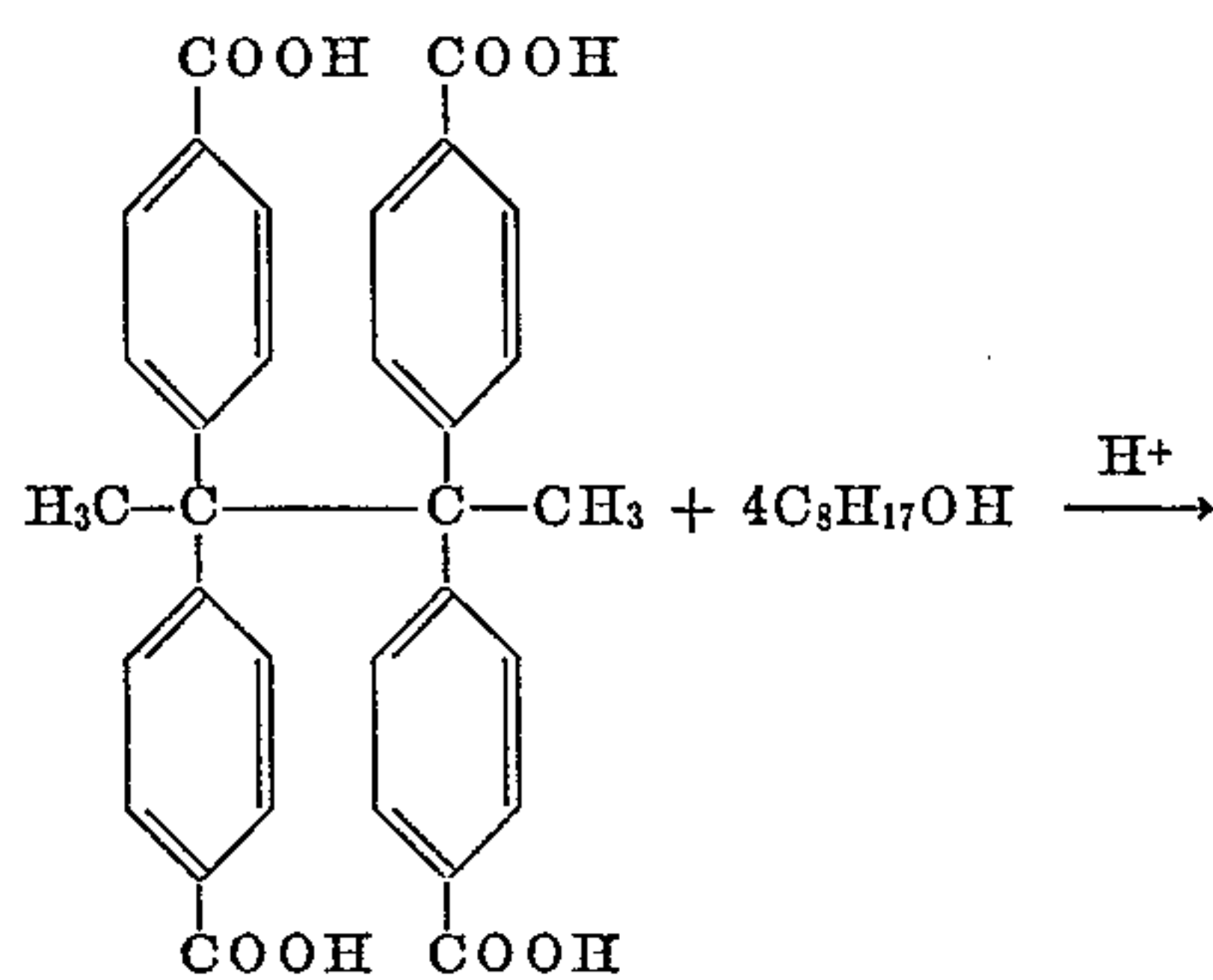
grams of benzopinacol by filtration. The reaction mixture remaining was subjected to distillation at a temperature of 152° C. at atmospheric pressure to remove unreacted cumene therefrom and to leave behind 106.9 grams of a yellow viscous mass. From the latter there was recrystallized from acetone 15.7 grams of a white solid having a melting point of 120° to 121° C. which was identified as dicumyl:



Example III

Into a one liter autoclave there was placed 51.1 grams of the 2,2,3,3-tetratolylbutane produced in Example I and 260 grams of 30 percent aqueous nitric acid. The contents of the reactor were held at 170° C. for one hour and at 200° C. for an additional two hours. The pressure during the reaction was maintained at 200 pounds per square inch gauge. The reaction product obtained was then extracted at a temperature of 50° C. and a pressure of 0 pounds per square inch gauge with 200 grams of acetone, leaving behind 23.2 grams of a light yellow solid having a neutral equivalent of 137.5 (theoretical for 2,2,3,3-tetracarboxyphenylbutane: 135.0). Its infrared spectrum indicated no alcoholic hydroxyl or ketone absorption. The product obtained therefore is 2,2,3,3-tetracarboxyphenylbutane.

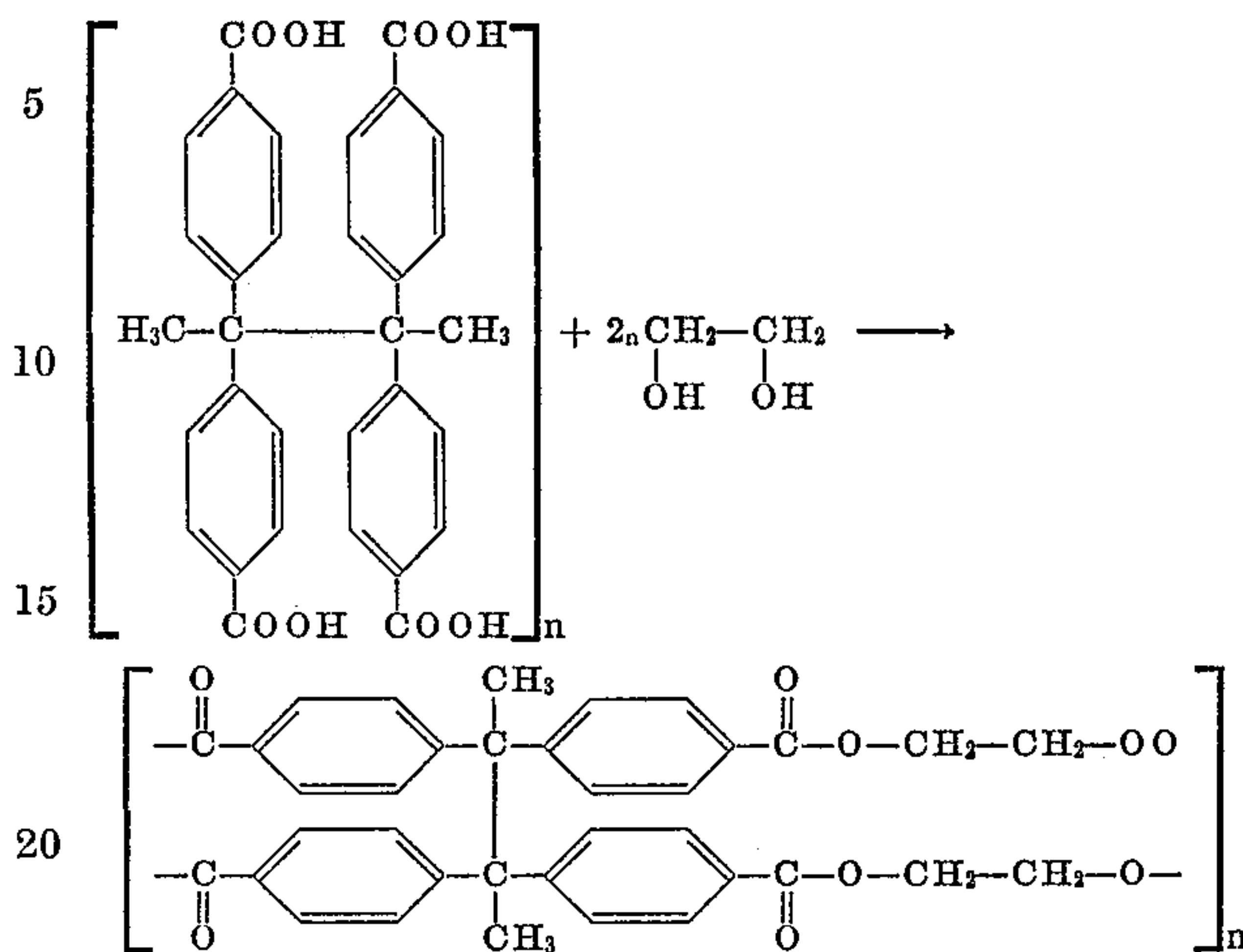
The aryl alkane dimers produced herein can be employed as intermediates in the preparation of the corresponding acids as defined hereinabove. Thus, for example, the tetraacid obtained by the nitric acid oxidation of 2,2,3,3-tetratolylbutane can be esterified with n-octyl alcohol to form tetra-n-octyl ester which can be used as a plasticizer for vinyl resins:



Reaction of the acid (2,2,3,3-tetracarboxyphenylbutane) 75

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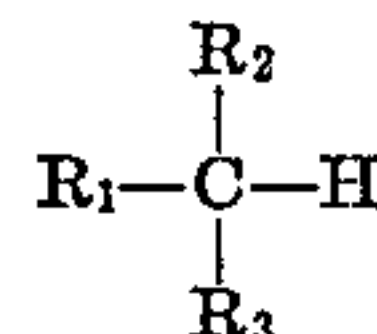
with glycol will produce a highly crosslinked polyester for use in the manufacture of plastic matrixes:



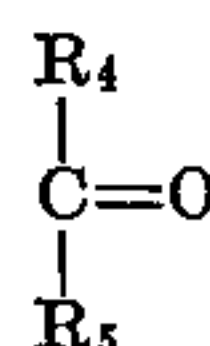
Obviously, many modifications and variations of the invention, as hereinabove set forth, can be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

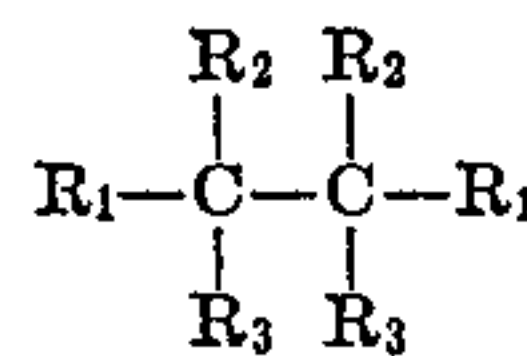
1. A process for dimerizing an aryl alkane of the following general formula:



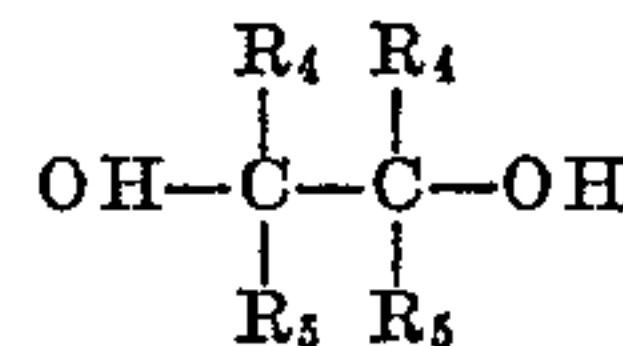
wherein R₁ is an alkyl radical, R₂ is an aryl radical and R₃ is a radical selected from the group consisting of radicals defined by R₁ and R₂, which comprises subjecting said aryl alkane to ultraviolet radiation for at least about ten minutes in the presence of a diaryl ketone of the following general formula:



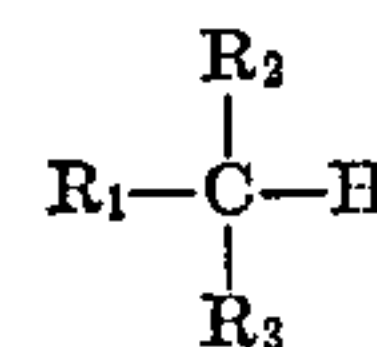
wherein R₄ and R₅ are aryl radicals to produce the following dimer:



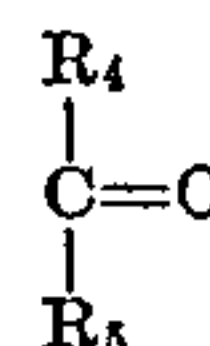
and the following pinacol



2. A process for dimerizing an aryl alkane of the following general formula:

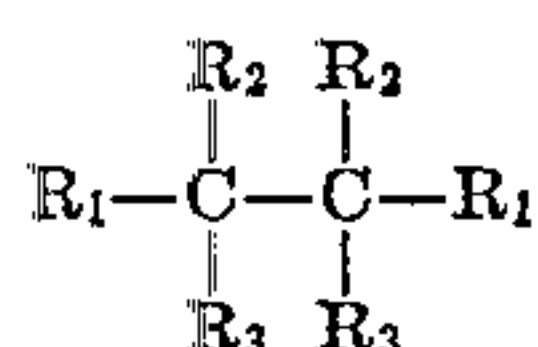


wherein R₁ is an alkyl radical and R₂ and R₃ are phenyl radicals, which comprises subjecting said aryl alkane to ultraviolet radiation for at least about ten minutes in the presence of a diarylketone of the following general formula:

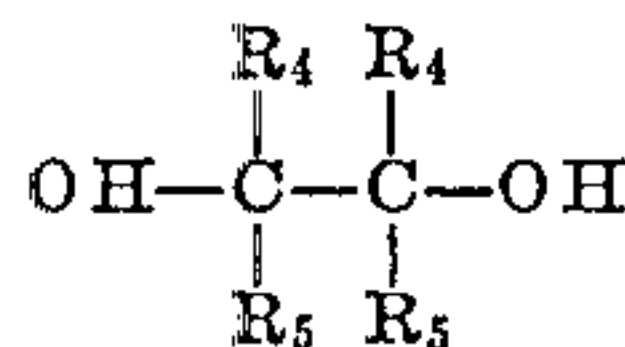


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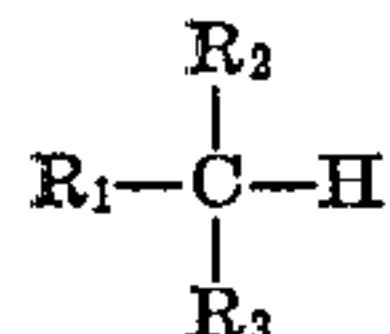
wherein R_4 and R_5 are phenyl radicals to produce the following dimer:



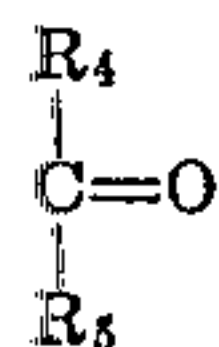
and the following pinacol



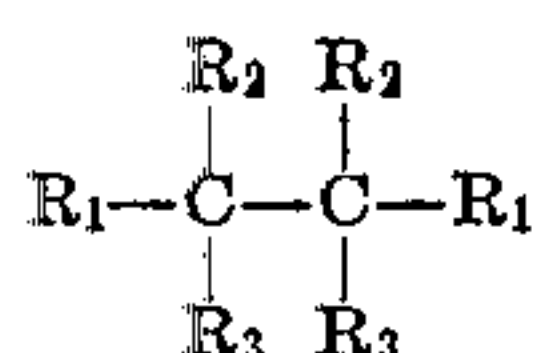
3. A process for dimerizing an aryl alkane of the following general formula:



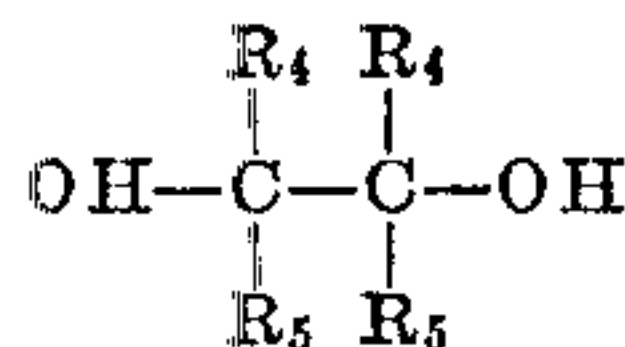
wherein R_1 is an alkyl radical and R_2 and R_3 are phenyl radicals carrying at least one alkyl radical which comprises subjecting said aryl alkane to ultraviolet radiation for at least about ten minutes in the presence of a diarylketone of the following general formula:



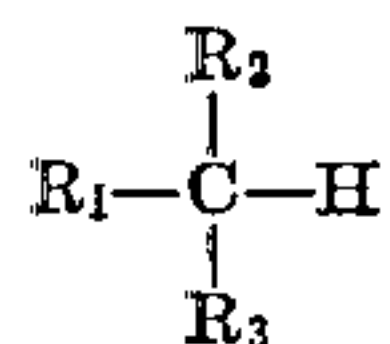
wherein R_4 and R_5 are phenyl radicals to produce the following dimer:



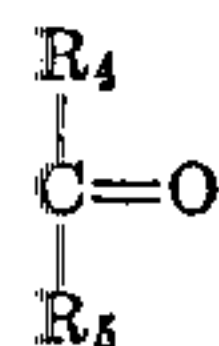
and the following pinacol



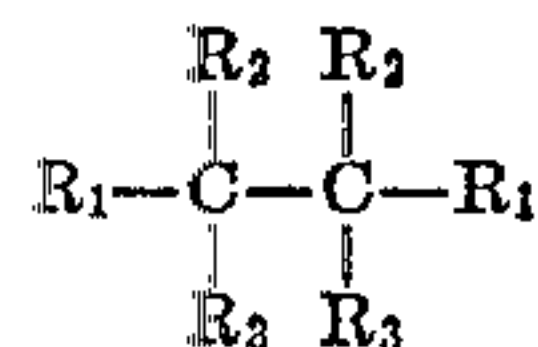
4. A process for dimerizing an aryl alkane of the following general formula:



wherein R_1 and R_3 are alkyl radicals and R_2 is a phenyl radical, which comprises subjecting said aryl alkane to ultraviolet radiation for at least about ten minutes in the presence of a diarylketone of the following general formula:

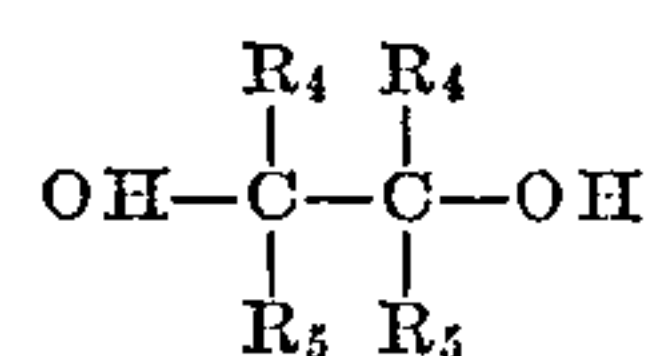


wherein R_4 and R_5 are phenyl radicals to produce the following dimer:



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and the following pinacol

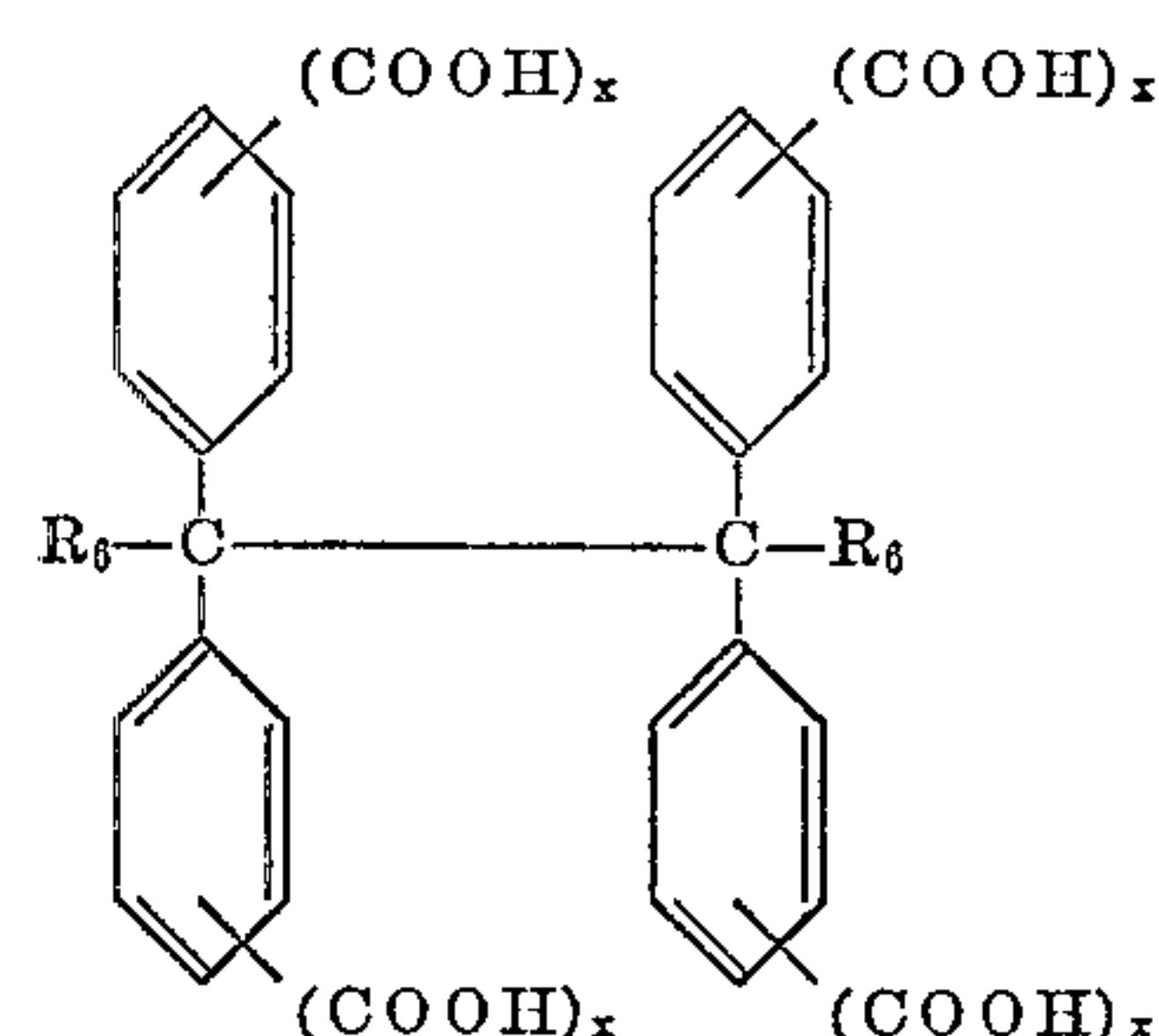


5. A process for dimerizing 1,1-ditolylethane which comprises subjecting the same to ultraviolet radiation in the presence of benzophenone for at least about ten minutes to produce 2,2,3,3-tetratolylbutane and benzopinacol.

6. A process for dimerizing cumene which comprises subjecting the same to ultraviolet radiation in the presence of benzophenone for at least about ten minutes to produce dicumyl and benzopinacol.

7. A process for dimerizing 1,1-ditolylethane which comprises subjecting the same to ultraviolet radiation for at least about ten minutes in the presence of benzophenone to produce 2,2,3,3-tetratolylbutane and benzopinacol, recovering said benzopinacol and thereafter regenerating the latter to benzophenone.

8. A new compound of the following general formula:



wherein R_6 is an alkyl radical and x is an integer from one to five.

9. As a new compound 2,2,3,3-tetracarboxyphenylbutane.

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K. ROSE, M. WEBSTER, M. G. BERGER,

Assistant Examiners.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,384,658

May 21, 1968

John H. McCracken et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, lines 17 to 23, that portion of the formula reading

-CH₂-OO

should read

-CH₂-O-

Signed and sealed this 21st day of October 1969.

SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.

Commissioner of Patents