fractions of a c.p.s. from our findings of 11.2 c.p.s. for the unsubstituted and 10.8 c.p.s. for the substituted *trans*-cyclohexane diols. The value of this sum may, therefore, be regarded as a useful numerical index of configuration for this type of compound, since the characteristic value obtainable for the analogous *cis* isomer from the data reported by Musher is about 50% greater (16.6 c.p.s.).

The effects of inversion barriers of the different configurations on the chemical shift of the methyl groups in the diacetates are also very analogous to the effects observed in the diols. Though the details have been omitted from the text, it is clear from the reproduced spectra that the four differing environments of the methyl groups are averaged by inversion in the *trans* isomer only. Rapid inversion in the *trans* isomer can be expected to average the chemical shift to two lines (even in the case of rapid inversion, it can be seen that there are two distinct environments for the four methyl groups in this molecule), which is exactly what the spectrum shows. On the other hand, the spectrum of the *cis* isomer includes three methyl signals, one of which appears from the intensity and line width to result from two overlapping lines. The absence of rapid inversion thereby indicated confirms the validity of the use of this feature in our work to assign the conformation of *cis*-dimethylcyclohexane diol.

TABLE OF STRUCTURAL ASSIGNMENTS

	Isomer designation	Structural assignment confirmed	Melting point	Reference to preparation method
Resorcitols	I	*trans*	116.0–116.5°	28
	II	*cis*	86–87°	28
5,5-Dimethylresorcitols	III	*trans*	108–109°	14
	IV	*cis*	146–147°	14

Experimental

The procedures followed in the preparation and purification of all the diols used were the same as those described in the references given in the accompanying table. Their physical constants, including m.p. and infrared spectral data where available, agreed well with those recorded in the literature in all cases.

Conclusion

On the basis of the arguments presented above, the structural assignments we have listed in the accompanying table seem to accord best with the observed NMR spectra of the individual isomers.

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(28) M. F. Clark and L. N. Owen, *J. Chem. Soc.*, 2105 (1950).

Synthesis of Spiroundecatrienones from 2,6-Di-*t*-butylquinone Methide and Butadienes

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Spiro[5.5]undeca-1,4,8,-trien-3-ones (IIIa,b,c) were obtained as Diels-Alder adducts from the reactions of 2,6-di-*t*-butylquinone methide (II) with butadiene, isoprene, and chloroprene. The structure assigned to the butadiene product was unequivocally proved primarily by alternate synthesis of its hydrogenation product, 2,4-di-*t*-butylspiro[5.5]undeca-3-one (IV). The key step in the synthetic scheme was the conversion of 2,6-di-*t*-butyl-4-(5-tosyloxypentyl)phenol (Vb) to 2,4-di-*t*-butylspiro[5.5]undeca-1,4-dien-3-one (VI) in almost quantitative yield by Ar_1-5 participation reaction.

Although several highly substituted homologs of *p*-quinone methide are well authenticated compounds[1] only one, 10-methyleneanthrone[2] has been reported which contains its methide double bond terminally. With fewer substituents on the ring, the terminal quinone methides become much less stable, and attempts to isolate the simpler ones such as the 2,6-dimethyl[3] or 2,6-di-*t*-butyl compounds[4] have led only to dimeric products. Most recently, Filar and Winstein[5] have published spectroscopic evidence for the existence of both 2,6-dimethylquinone methide and 2,6-di-*t*-butylquinone methide in dilute hydrocarbon solution, although once again the quinone methides could not be isolated. 2,6-Di-*t*-butyl-4-methylene-2,5-cyclohexadienone[5] (II) was reported to be formed by treatment of 3,5-di-*t*-butyl-4-hydroxybenzyl bromide with triethylamine or by oxidation of 2,6-di-*t* butyl-4-methylphenol with lead dioxide.

Complementing the work of Filar and Winstein, we have found that it is possible to trap the reactive intermediate, 2,6-di-*t*-butylquinone methide (II), as a Diels-Alder adduct with butadienes. Thus, spiro[5.5]undeca-1,4,8-trien-3-ones (IIIa,b,c) were

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(1) C. D. Cook and B. E. Norcross, *J. Am. Chem. Soc.*, **78**, 3797 (1956); *ibid.*, **81**, 1176 (1959).

(2) E. Clar, *Ber.*, **69**, 1686 (1936).

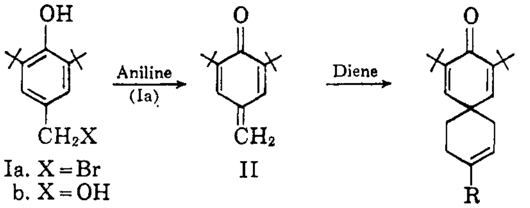
(3) K. Fries and E. Brandes, *Ann.*, **542**, 48 (1939); H. Von Euler, E. Alder, J. O. Cedwell, and O. Törngren, *Arkiv-Kem. Mineral Geol.*, **15A**, No. 11 (1942).

(4) T. Fujisaki, *J. Chem. Soc. Japan*, **77**, 730 (1956).

(5) L. J. Filar and S. Winstein, *Tetrahedron Letters*, **25**, 9 (1960).

isolated by treatment of a dilute solution (10^{-1} *M*) of 3,5-di-*t*-butyl-4-hydroxybenzyl bromide (Ia) in diene with the base, aniline. The yields of the adducts varied greatly with the nature of the diolefin, as butadiene, isoprene, and chloroprene afforded products in 10, 44, and 93% yields, respectively. The only other product identified under these conditions was 3,5,3′,5′-tetra-*t*-butylstilbene-4,4′-quinone. The chloroprene adduct was also isolated in 9% yield when 2,6-di-*t*-butylquinone methide was generated from 3,5-di-*t*-butyl-4-hydroxybenzyl alcohol[6] (Ib) and a catalytic amount of sulfuric acid. Here, the principal product was 3,5-di-*t*-butyl-4-hydroxybenzyl ether.

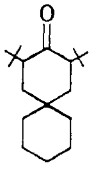
Although two structural isomers were possible as products from the reactions with both isoprene and chloroprene, only one[7] adduct was isolated in each case. The position of the methyl or chloro substituent was not firmly established in the present work; however, in view of the observation[8] that the *para* isomer always greatly predominated in the adduct from the Diels-Alder reaction of monosubstituted olefins with 2-substituted 1,3-butadienes, it seems reasonable that both the methyl and chloro substituent are at position 9 (IIIb,c) rather than 8.



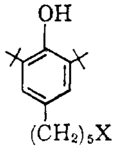
Ia. X = Br
b. X = OH

II

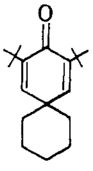
IIIa. R = H
b. R = CH_3
c. R = Cl



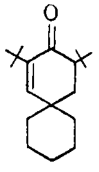
IV



Va. X = Cl
b. X = $SO_3C_6H_4CH_3$



VI



VII

The assignment of the structure, 2,4-di-*t*-butylspiro[5.5]undeca-1,4,8-trien-3-one (IIIa), to the butadiene adduct was based on elemental analysis, absorption spectral data, and upon the nature of its hydrogenation product. The infrared spectrum of IIIa exhibited a triplet in the 6-μ region indicative of a cyclohexadienone structure. The ultraviolet absorption spectrum showed a λ maximum at 247 mμ in ethanol solution which is near that of 242.5 mμ reported for spiro[5.5]undeca-1,4,dien-3-one.[9] The presence of the α-*t*-butyl groups on IIIa would be expected to increase the wave length of absorption[10] by about 10 mμ. Hydrogenation of IIIa with palladium-on-carbon catalyst proceeded with absorption of three mole equivalents of hydrogen to give a product (82% yield) identical with 2,4-di-*t*-butylspiro[5.5]undeca-3-one (IV), prepared by alternate unequivocal synthesis.

Compound IV was prepared as follows. Reaction of 2,6-di-*t*-butylphenol[11] with potassium *t*-butoxide and 1-borm-5-chloropentane produced 2,6-di-*t*-butyl-4-(5-chloropentyl)phenol, Va, (19% yield) as well as 1-(2,6-di-*t*-butylphenoxy)-5-chloropentane (31% yield) and 5-chloro-1-pentene (34% yield). Treatment of Va with silver tosylate in acetonitrile solution at 120° gave 2,6-di-*t*-butyl-4-(5-tosyloxypentyl)phenol (Vb) in 90% yield. Refluxing a dilute solution of Vb in *t*-butyl alcohol with potassium *t*-butoxide afforded 2,4-di-*t*-butylspiro[5.5]undeca-1,4-dien-3-one (VI) in 98% yield. This spirodienone absorbed two mole equivalents of hydrogen on hydrogenation with palladium-on-carbon catalyst to yield IV[12] in 88% yield.

The yield of spirodienone, VI, appears to be the highest ever reported for this type of Ar_1 participation reaction.[13] In other examples cited in the literature the yield of spirodienone is reduced due to intermolecular reaction. This type of side reaction is suppressed by the very high degree of steric hindrance about the phenolic oxygen in Vb.

Hydrogenation of the 2,6-di-*t*-butylquinone methide–chloroprene adduct with palladium-on-carbon catalyst afforded 2,4-di-*t*-butylspiro[5.5.]-undeca-1-en-3-one (VII) in 65% yield. The structure was evident from spectral data (reported in the Experimental) and further quantitative hydrogenation with fresh catalyst to 2,4-di-*t*-butylspiro[5.5]-undeca-3-one (IV).

Several years ago, Hatchard[14] reported the isolation of a 1:1 adduct (34–75% yield) from the oxidation of 2,6-di-*t*-butyl-4-methylphenol with lead dioxide or potassium ferricyanide in the presence of chloroprene. A structure of type IIIc (chlorine atom not specified) was postulated primarily on the basis of absorption spectral evidence. A mechanism was suggested for the formation of the spiro adduct involving the addition of hydroxy-di-*t*-butylbenzyl radical to chloroprene to form an an allylic radical, VIII. The latter was specified to add intramolecularly to the aromatic system with subsequent oxidation converting the resulting radical to IIIc. This adduct has been found to be identical with that isolated by us from the reaction

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[6] Filar and Winstein did not report formation of the quinone methide by reaction of this alcohol with acid.

[7] The presence of a small (less than 5%) amount of the second isomer was not completely excluded, particularly in the case of the isoprene product.

[8] Y. Titov and A. I. Kuznstosova, *Dokl. Nauk. USSR,* **126,** 586 (1959).

[9] A. S. Dreiding, *Helv. Chim. Acta,* **40,** 1812 (1957).

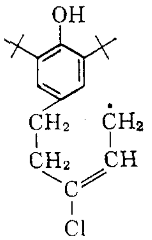
[10] L. Dorfman, *Chem. Rev.,* **53,** 47 (1953).

[11] N. Fernblum and R. Seltzer, *J. Am. Chem. Soc.,* **83,** 3668 (1961).

[12] Only one of the two possible geometrical isomers was isolated.

[13] S. Winstein and R. Baird, *J. Am. Chem. Soc.,* **79,** 756 (1957); S. Masamune, *ibid.,* **83,** 1009 (1961) and references cited therein.

[14] W. R. Hatchard, *ibid.,* **80,** 3640 (1958).



VIII

of 2,6-di-*t*-butylquinone methide with chloroprene. In view of the present experiments which demonstrate that chloroprene is an exceptionally good trap for the quinone methide and the observations of Filar and Winstein[5] that lead dioxide oxidation forms the quinone methide, we prefer to interpret Hatchard's experiments as involving a Diels-Alder type reaction between 2,6-di-*t*-butylquinone methide and chloroprene rather than classical radical addition.

Experimental

3,5-Di-*t*-butyl-4-hydroxybenzyl Bromide (Ia).—Hydrogen bromide was bubbled through a stirred suspension of 3,5-di-*t*-butyl-4-hydroxybenzyl alcohol (118 g., 0.5 mole) in 300 ml. of isopentane at 20–25° for 30 min. beyond when all of the solid had dissolved. The solution was washed three times with water, dried, and concentrated to a volume of 300 ml. Upon cooling to −5°, 3,5-di-*t*-butyl-4-hydroxybenzyl bromide[15] slowly crystallized as pale yellow plates, m.p. 52–54° (100 g., 74% yield).

2,4-Di-*t*-butyl-9-methylspiro[5.5]undeca-1,4,8-trien-3-one (IIIb).—A solution of aniline (10.3 g., 0.11 mole) in 30 ml. of isoprene was added dropwise over a 30-min. period to a stirred solution of Ia (30 g., 0.1 mole) in 900 ml. of isoprene at 15–20. Stirring was continued under nitrogen at 20–25° for 72 hr. The precipitated aniline hydrobromide (17.5 g., 101%) was collected and washed several times with ether. The filtrate was washed with 10% hydrochloric acid, then 10% sodium bicarbonate, and dried. Removal of the solvent under vacuum gave 28.0 g. of residual oil.

The product was placed on a column containing 1750 g. of activated alumina (grade 1) using *n*-hexane as solvent and eluted with hexane containing increasing percentages of benzene. Crude 2,4-di-*t*-butyl-9-methylspiro[5.5]undeca-1,4,8-trien-3-one (12.5 g., 44% yield), m.p. 60–65°, came off with 10–20% benzene. Sublimation followed by recrystallization from 95% ethanol yielded 10 g. of white plates, m.p. 73–74°.

Anal. Calcd. for $C_{20}H_{30}O$: C, 83.9; H, 10.5. Found: C, 83.8; H, 10.4.

Absorption spectra showed dienone bands at 6.03, 6.10, and 6.15 μ in carbon tetrachloride solution in the infrared and a high intensity maximum at 242 mμ (ϵ 12,000) in isooctane solution in the ultraviolet.

Further elution with 30–50% benzene gave the 3,5,3′,5′-tetra-*t*-butylstilbene-4,4′-quinone[16] (8.5 g., 38% yield), identified by the melting point of an admixture with an authentic sample.

2,4-Di-*t*-butylspiro[5.5]undeca-1,4,8-trien-3-one (IIIa).—Aniline (10.3 g., 0.11 mole) was added dropwise over a 15-min. period to an agitated solution of Ia (30 g., 0.1 mole) and butadiene (400 g.) in 400 ml. of *n*-hexane at 0° contained in a pressure bottle. The mixture was cooled to −50° and air was displaced with nitrogen. The pressure bottle was sealed and tumbled at 20–25° for 72 hr. Aniline hydrobromide (17.4 g.) was collected and washed with ether, and the filtrate washed with 10% hydrochloric acid, then 10% sodium bicarbonate, and dried. Removal of the solvent under reduced pressure gave 27 g. of residual solid.

The product was chromatographed on a column containing 2000 g. of activated alumina (grade 1). Elution with 15–30% benzene in hexane gave 2,4-di-*t*-butylspiro[5.5]-undeca-1,4,8-trien-3-one (2.7 g., 10% yield), m.p. 66–70°. Sublimation followed by recrystallization from 95% ethanol yielded 2.3 g. of white plates, m.p., 76–76.5°.

Anal. Calcd. for $C_{19}H_{28}O$: C, 83.8; H, 10.3. Found: C, 83.9; H, 10.2.

The infrared spectrum exhibited maximum at 6.04, 6.10, and 6.16 μ in carbon tetrachloride solution. The ultraviolet spectrum showed a high intensity maximum at 247 mμ (ϵ 11,600) in ethanol solution.

2,4-Di-*t*-butyl-9-chlorospiro[5.5]undeca-1,4,8-trien-3-one (IIIc).—A solution of aniline (2.0 g., 0.021 mole) in 10 ml. of benzene was added dropwise over a 15-min. period to a stirred solution of Ia (6.0 g., 0.02 mole) and chloroprene (125 g.) in 125 ml. of benzene at 15–20°. Stirring was continued under nitrogen at 20–25° for 24 hr. Aniline hydrobromide (3.6 g., 103%) was collected by filtration and washed with ether. The filtrate was concentrated under vacuum and the residue taken up in ether and washed with 10% hydrochloric acid, then 10% sodium bicarbonate, and dried. Evaporation of the solvent gave a solid residue which was recrystallized from methanol to yield IIIc as pale yellow crystals (5.7 g., 93% yield), m.p. 109–111°. Treatment with decolorizing charcoal in ethyl alcohol gave white needles, m.p. 111–112°.

Anal. Calcd. for $C_{19}H_{27}OCl$: C, 74.4; H, 8.87; Cl, 11.6. Found: C, 74.5; H, 8.95; Cl, 11.9.

The ultraviolet spectrum showed a high intensity maximum at 242 mμ (ϵ 9200) in isooctane solution.

2,4-Di-*t*-butyl-9-chlorospiro[5.5]undeca-1,4,8-trien-3-one (IIIc) from 3,5-Di-*t*-butyl-4-hydroxybenzyl Alcohol and Isoprene.—A solution of Ib (35.5 g., 0.15 mole), chloroprene (140 g.), and sulfuric acid (2.0 g.) in 250 ml. of ether was stirred at 23–25° for 18 hr. Then, sulfuric acid (1.0 g.) was added and stirring continued for 24 hr. at 25°. The solution was washed with 10% sodium bicarbonate, dried, and the solvent removed under vacuum to give 38 g. of solid residue. Recrystallization from *n*-hexane gave 20 g. of pale yellow crystals, m.p. 128–132°. A second recrystallization from *n*-hexane afforded white plates of 3,5 di-*t*-butyl-4-hydroxybenzyl ether, m.p., 133–135°, identified by the melting point of an admixture with an authentic sample.[17] An additional crop (8.0 g.) of very crude ether was obtained by concentrating the *n*-hexane solution.

The residue obtained by removal of the hexane under vacuum was crystallized from methanol to give 4.0 g. (9% yield) of pale yellow crystals, m.p. 105–107°. After an additional recrystallization from methanol, 2,4-di-*t*-butyl-9-chlorospiro[5.5]undeca-1,4,8-trien-3-one was obtained as white needles, m.p. 110–111°.

2,6-Di-*t*-butyl-4-(5-chloropentyl)phenol (Va).—Potassium *t*-butoxide *t*-butyl alcoholate (55.5 g., 0.3 mole) was added cautiously to a stirred solution of 2,6-di-*t*-butylphenol (61.8 g., 0.3 mole) in 750 ml. of tetraethylene glycol dimethyl ether under nitrogen at 10–20°. After stirring 1 hr., a solution of 55.8 g., (0.3 mole) of 1-bromo-5-chloropentane (Aldrich, fractionally distilled, $n^{25}\text{D}$ 1.4818) in 75 ml. of tetraethylene glycol dimethyl ether was added. The resulting green solution was stirred under nitrogen at 20–25° for 72 hr. at which time 97% of the *t*-butoxide had been consumed. The mixture was diluted with 2000 ml. of water, made acidic with dilute hydrochloric acid, and extracted with three 500-ml. portions of benzene. The organic extract was washed with six 1000-ml. portions of water and dried.

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(15) C. D. Cook, N. G. Nash, and H. R. Flanagan, *J. Am. Chem. Soc.*, **77**, 1783 (1955).

(16) C. D. Cook, *J. Org. Chem.*, **18**, 261 (1953).

(17) Unpublished work of Dr. A. L. Rocklin, Shell Development Co.

Benzene and readily volatile reaction products were removed by vacuum distillation. Fractional distillation of this distillate through a semimicro spinning-band column gave 5-chloropentene-1, 8.5 g., b.p. 104–105° (750 mm.), and forerun, 4.0 g., b.p. 87–103° (750 mm.), estimated to contain 50% 5-chloropentene-1 by infrared spectroscopy (34% total yield); n^{20}_D 1.4310 (reported[18] n^{19}_D 1.4305).

Anal. Calcd. for C_5H_9Cl: C, 57.4; H, 8.64; Cl, 34.0. Found: C, 57.8; H, 8.70; Cl, 33.5.

The infrared spectrum exhibited absorption peaks at 6.12, 10.10, and 10.95 μ characteristic of $-CH=CH_2$.

The residual liquid was fractionally distilled from sodium carbonate (1 g.) through a Vigreux column at 0.1 mm. to give the following: fraction 1, 2,6-di-*t*-butylphenol, 27 g., b.p. 60–65° (m.p. 34–37°); fraction 2, 2.5 g., b.p. 70–135°, and fraction 3, 46 g., b.p. 134–140°.

To a vigorously stirred solution of fraction 3 in 250 ml. of toluene under nitrogen was added potassium *t*-butoxide *t*-butyl alcoholate (11 g., 0.06 mole). Stirring was continued at 20–25° for 12 hr. The *t*-butyl alcohol and most of the toluene were removed at 35–40° with a stream of nitrogen. Residual solid, diluted with 300 ml. of *n*-hexane, was collected and washed with *n*-hexane in a drybox.

The solid was added to 300 ml. of 10% hydrochloric acid and the acidic mixture extracted twice with *n*-hexane. The organic extract was washed with 5% sodium bicarbonate, dried, and the solvent removed under vacuum. Distillation of the residual liquid from sodium carbonate (0.5 g.) gave 17 g. (19% yield) of 2,6-di-*t*-butyl-4-(5-chloropentyl)phenol (Va), b.p. 138–140° (0.1 mm.) which failed to crystallize on cooling.

Anal. Calcd. for $C_{19}H_{31}OCl$: C, 73.4; H, 10.0; Cl, 11.4; phenolic acidity, 0.32 eq/100 g. Found: C, 73.4; H, 10.1; Cl, 11.8; phenolic acidity 0.32 eq/100 g.

The *n*-hexane filtrate was washed with 10% hydrochloric acid, then 10% sodium bicarbonate, dried, and the solvent removed under vacuum. Distillation of the residual liquid gave 28 g. (31% yield) of 1-(2,6-di-*t*-butylphenoxy)-5-chloropentane, b.p. 130–132° (0.1 mm.).

Anal. Calcd. for $C_{19}H_{31}OCl$: C, 73.5; H, 10.0; Cl, 11.4. Found: C, 73.7; H, 10.1; Cl, 11.2.

The infrared spectrum exhibited absorption at 9.93 μ characteristic of an ether linkage and showed no bands characteristic of phenolic hydroxyl.

2,6-Di-*t*-butyl-4-(5-tosyloxypentyl)phenol (Vb).—A mixture of Va (5 g., 0.016 mole), silver *p*-toluenesulfonate (7.5 g., 0.27 mole), and 100 ml. of acetonitrile was placed in a pressure bottle under nitrogen and tumbled at 120–125° for 20 hr. The mixture was filtered (2.15 g. of silver chloride, 94%) and the filtrate evaporated under vacuum to give 6.8 g. (90% yield) of a yellow oil. The *p*-toluenesulfonate (estimated to be 95% pure) would not crystallize and was used without further purification.

Anal. Calcd. for $C_{26}H_{38}SO_4$: C, 69.9; H, 8.58; S, 7.20. Found: C, 70.5; H, 8.50; S, 6.7; Cl, 0.4.

2,4-Di-5-butylspiro[5.5]undeca-1,4-dien-3-one (VI).—A solution of Vb (5.2 g., 0.0111 mole) and potassium *t*-butoxide *t*-butyl alcoholate (2.6 g., 0.014 mole) in 1200 ml. of *t*-butyl alcohol was refluxed (83°) under nitrogen for 16 hr. Most of the *t*-butyl alcohol was removed by vacuum distillation. The residual liquid was diluted with 300 ml. of water and extracted twice with ether. Drying and removal of the solvent gave 3.0 g. (98% yield) of pale yellow crystals, m.p. 99–102°. Recrystallization from ethanol gave VI as white needles, m.p. 106–106.5°.

Anal. Calcd. for $C_{19}H_{30}O$: C, 83.2; H, 11.0. Found: C, 83.4; H, 11.1.

Absorption spectra showed dienone bands at 6.04, 6.11, and 6.17 μ in carbon tetrachloride solution in the infrared and a high intensity maximum at 242 mμ (ε 13,000) in isooctane solution in the ultraviolet.

Hydrogenation of 2,4-Di-*t*-butylspiro[5.5]undeca-1,4-diene-3-one (VI).—A mixture of VI (0.9 g., 0.0033 mole), 10% palladium-on-carbon catalyst (0.5 g.), and 50 ml. of absolute ethanol shaken at 25° under 40 p.s.i. of hydrogen pressure absorbed 2.1 moles of hydrogen per mole of spirodienone in 2 hr. The reaction mixture was filtered and the filtrate concentrated to give a colorless oil which crystallized on standing. Recrystallization from 95% ethanol yielded 0.8 g. (88% yield) of white needles, m.p. 48–50°. Further recrystallization gave pure 2,4-di-*t*-butylspiro[5.5]undeca-3-one (IV), m.p. 53–54°.

Anal. Calcd. for $C_{19}H_{34}O$: C, 82.0; H, 12.3. Found: C, 82.0; H, 12.3.

The infrared spectrum showed a carbonyl band at 5.85 μ in carbon tetrachloride solution.

Hydrogenation of 2,4-Di-*t*-butylspiro[5.5]undeca-1,4,8-trien-3-one (IIIa).—A mixture of IIIa (0.6 g., 0.0022 mole), 10% palladium-on-carbon catalyst (0.3 g.), and 30 ml. of absolute ethanol shaken at 25° under 40 p.s.i. of hydrogen pressure absorbed 2.9 moles of hydrogen per mole of substrate in 2 hr. The reaction mixture was filtered and the filtrate concentrated to give a straw colored oil which crystallized on cooling. Recrystallization from 95% ethanol gave 0.5 g. (82% yield) of pale yellow needles, m.p. 46–50°. A second recrystallization yielded white needles, m.p. 52.5–53.5°. No depression in melting point was observed for an admixture with authentic 2,4-di-*t*-butylspiro[5.5]undeca-3-one (IV). The infrared spectrum was identical with that of the authentic sample.

Anal. Calcd. for $C_{19}H_{34}O$: C, 82.0; H, 12.3. Found: C, 82.1; H, 12.3.

Hydrogenation of 2,4-Di-*t*-butyl-9-chlorospiro[5.5]undeca-1,4,8-trien-3-one (IIIc).—A solution of IIc (2.0 g., 0.065 mole) in 30 ml. of absolute ethanol was subjected at 25° to 40 p.s.i. of hydrogen pressure in the presence of 0.3 g. of 10% palladium-on-carbon catalyst. After being shaken for 90 min. (3.0 moles of hydrogen absorbed per mole of substrate), the reaction mixture was filtered, diluted with water, and extracted with ether. The ether extract was washed with 5% sodium bicarbonate, dried, and evaporated to give an oil which deposited crystals on standing in an ice water bath. Recrystallization from 95% ethanol yielded 1.2 g. (65% yield) of white crystals, m.p. 43–45°. An additional recrystallization gave pure 2,4-di-*t*-butylspiro[5.5]undeca-1-en-3-one (VII), m.p. 44–45°.

Anal. Calcd. for $C_{19}H_{32}O$: C, 82.5; H, 11.7. Found: C, 82.2; H, 11.9.

The infrared spectrum showed α,β-unsaturated carbonyl bands at 5.95 and 6.02 μ and an ultraviolet absorption maximum was found at 234 mμ (ε 8300) in ethanol solution.

A mixture of VII (0.5 g., 0.002 mole) 10% palladium-on-carbon (0.3 g.) and 25 ml. of absolute ethanol shaken at 25° under 40 p.s.i. of hydrogen pressure absorbed 1.0 mole of hydrogen per mole of substrate in 1 hr. Work-up in the usual manner afforded 0.4 g. (80% yield) of 2,4-di-*t*-butylspiro[5.5]undeca-3-one, m.p. 52.5–53.5°. The mixed melting point with an authentic sample was undepressed.

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[18] R. Paul, *Compt. rend.*, **193**, 599 (1931).