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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

The Reduction of Tetracyclone[1]

BY N. O. V. SONNTAG,[2] SEYMOUR LINDER, ERNEST I. BECKER AND PAUL E. SPOERRI

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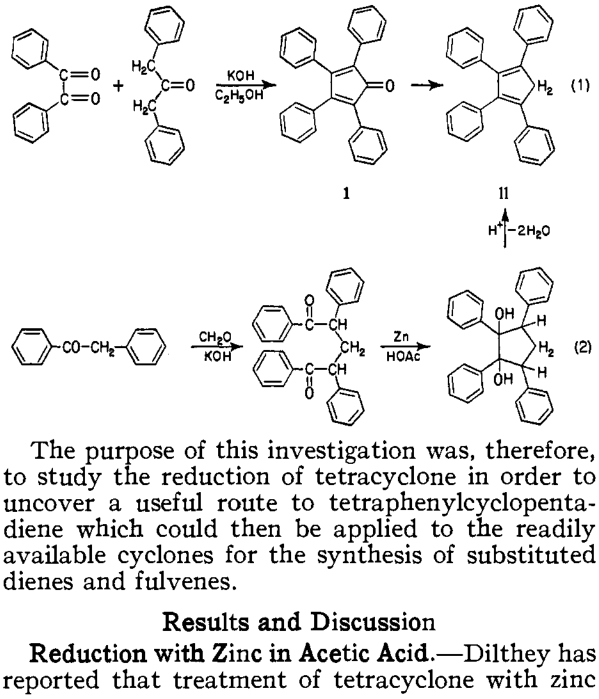
A study of the reduction of tetracyclone (I) (tetraphenylcyclopentadienone) has been undertaken to find a convenient synthetic route to tetraphenylcyclopentadiene (II), which lends itself to the synthesis of fulvenes. At room temperature reduction with zinc in acetic acid, I gives an acetic acid solvate of 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol (III) together with a smaller quantity of 2,3,4,5-tetraphenylcyclopenta-2-en-1-one (IV). At reflux IV predominates. III is isomerized to IV under the reflux conditions. Amalgamated zinc in acetic acid with hydrogen chloride also gives IV when the reaction is stopped immediately upon decolorization. When carried further, the products are 2,3,4,5-tetraphenylcyclopentanone (VI) (instead of the reported 2,3,4,5-tetraphenylcyclopenta-3-en-1-ol (V)), and also tetraphenylcyclopentene (VII) and 1,2,3,4-tetraphenylcyclopentane (VIII). I is also converted to IV by treatment with red phosphorus and hydriodic acid, toluene at 270°, catalytically with hydrogen over palladium-on-barium sulfate or with platinum in acetic acid and by means of the Meerwein–Ponndorf–Verley reduction. Hydrazine hydrate in ethanol gives IV at reflux. Over platinum in acetic acid I, II and VII all give VIII. Aluminum chloride in benzene has been also shown to give 1,3-dihydro-1,3-diphenyl-2-keto-2H-cyclopenta[*l*]phenanthrene (IX) and not VI as previously reported. At 0–10° addition of lithium aluminum hydride to I gives III. The reverse order of addition at 35° affords a mixture of II and IV. The Wolff–Kishner reduction of the 2,4-dinitrophenylhydrazone gives an anomalous product, 1-ethyl-2,3,4,5-tetraphenylcyclopentadiene (XVIII). A mixture of IV and XVIII is formed by the treatment of tetracyclone with hydrazine hydrate and alcoholic sodium ethoxide at 210°.

Introduction

In connection with a study of the absorption spectra of tetracyclone (I)[3] (tetraphenylcyclopentadienone), the related fulvenes were desired. These can be prepared from tetracyclone through dehydration of the tertiary alcohols formed by adding an appropriate Grignard reagent to tetracyclone[4,5] or by condensing 2,3,4,5-tetraphenylcyclopentadiene (II) with an appropriate carbonyl compound[4,5] or carbonyl analog.[6] The required dienes have thus far been available only by means of a lengthy procedure,[7,8] which has the additional drawback of being unsuited to the synthesis of unsymmetrical dienes (see equations 1 and 2).



The purpose of this investigation was, therefore, to study the reduction of tetracyclone in order to uncover a useful route to tetraphenylcyclopentadiene which could then be applied to the readily available cyclones for the synthesis of substituted dienes and fulvenes.

Results and Discussion

Reduction with Zinc in Acetic Acid.—Dilthey has reported that treatment of tetracyclone with zinc

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[1] This investigation was sponsored by the Signal Corps Engineering Laboratory under Contracts W36-039 sc44483 and DA36-039 sc15326, and was presented in part in Paper No. 116 at the 118th Meeting of the American Chemical Society, Chicago, Illinois, September, 1950, and in Paper No. 1 at the Meeting-in-Miniature of the Metropolitan Long Island Subsection of the New York Section of the American Chemical Society, Brooklyn, N. Y., March, 1951.

[2] The material reported here is taken in part from the Dissertation for the degree of Doctor of Philosophy presented by N. O. V. S. to the Graduate Faculty of the Polytechnic Institute of Brooklyn, June, 1951.

[3] Stephen B. Coan, D. E. Trucker and E. I. Becker, THIS JOURNAL, **75**, 900 (1953).

[4] W. Dilthey and P. Huchtemann, *J. prakt. Chem.*, **154**, 238 (1940).

[5] A. Löwenbein and G. Ulich, *Ber.*, **58**, 2662 (1925).

[6] D. Taber, D. E. Trucker, E. I. Becker and P. E. Spoerri, 118th Meeting of the American Chemical Society, Chicago, Ill., 1950.

[7] J. Wislicenus and H. Carpenter, *Ann.*, **302**, 223 (1898).

[8] K. Ziegler and B. Schnell, *ibid.*, **445**, 266 (1925).

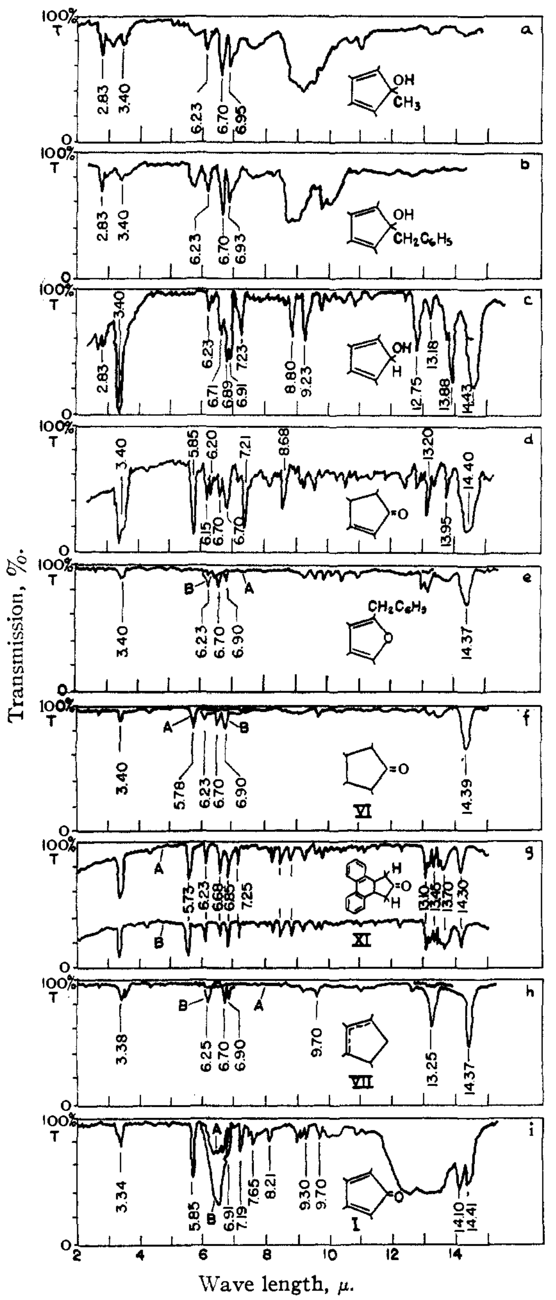

Fig. 1.—Infrared absorption spectra: a and b, 0.3 mm. cell, 20 mg./ml. chloroform; c and d, solid in petrolatum; e, 0.3 mm. cell; A, 6 mg./ml. carbon bisulfide, B, saturated solution in carbon tetrachloride; f, 0.3 mm. cell; A, 5.5 mg./ml. in carbon bisulfide. B, 5.5 mg./ml. in carbon tetrachloride; g, solid in petrolatum; A, product from phenanthrenequinone and dibenzyl ketone, B, product from tetracyclone, aluminum chloride and benzene; h, 0.3 mm. cell, 9.7 mg./ml. of (A) carbon bisulfide and (B) carbon tetrachloride; i, 0.3 mm. cell; A, 23 mg./ml. of carbon tetrachloride, B, carbon tetrachloride.

in refluxing acetic acid solution gives an acetic acid solvate of tetraphenylcyclopenta-2,4-dien-1-ol (III) and either 2,3,4,5-tetraphenylcyclopenta-2-en-1-one (IV)[9] or 2,3,4,5-tetraphenylcyclopenta-3-en-1-one (IVa),[10–12] the position of the double bond being uncertain. Repetition of these experiments confirmed the results. Positive demonstration of the hydroxyl group in III was obtained by comparison of the infrared and ultraviolet spectra of the acetic acid-free material with those of 1-methyl-(XV)[4] and 1-benzyltetraphenylcyclopentadien-1-ol (XVI).[4] The infrared absorption spectra (Fig. 1a, b and c) of the carbinols exhibit a strong band at 2.83 μ, which is characteristic for hydroxyl groups, and no band at 5.6–6.0 μ, the carbonyl region. Further, the ultraviolet absorption spectrum of III (Figs. 2 and 3) resembles that of II and not that of I or IV.

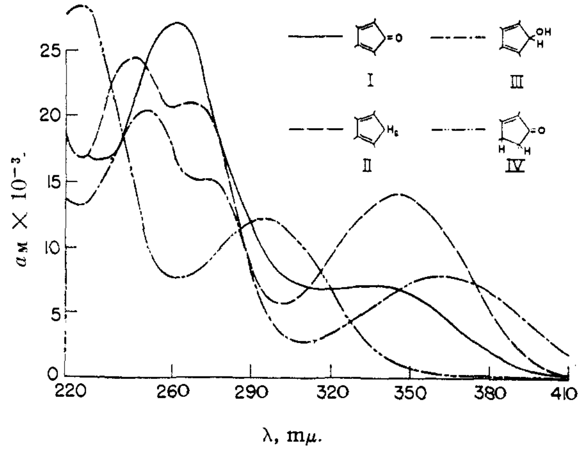

Fig. 2.

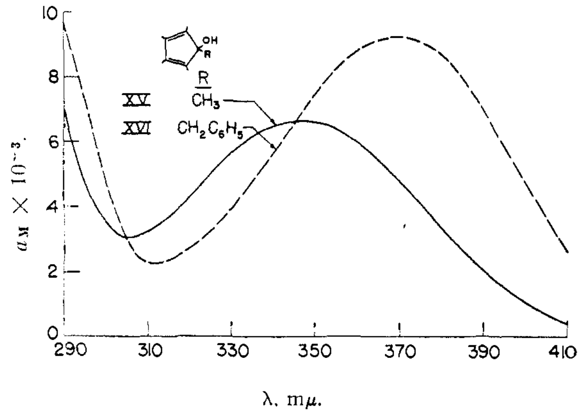

Fig. 3.

The previous assignment[10] of a carbonyl group in IV was a penetrating deduction since it did not form either an oxime or a phenylhydrazone.[10,13] Even under the anhydrous conditions of Szmant and McGinnis[14] it does not give a hydrazone but it does form a 2,4-dinitrophenylhydrazone under the forcing conditions of Josten,[15] *i.e.*, with sulfuric acid in dioxane. A sodium salt (XI), corresponding to $C_{29}H_{21}ONa$, speaks for the expected enolic hydrogen. The infrared spectrum (Fig. 1d) shows

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(9) W. Dilthey and F. Quint, *J. prakt. Chem.*, **128**, 139 (1930).

(10) W. Dilthey, W. Braun and O. Trösken, *ibid.*, **139**, 1 (1933).

(11) R. Pütter and W. Dilthey, *ibid.*, **149**, 183 (1937).

(12) It is not clear whether or not the zinc was amalgamated, compare references 9 and 10.

(13) G. G. Henderson and R. H. Corstorphine, *J. Chem. Soc.*, **79**, 1265 (1901).

(14) H. H. Szmant and C. McGinnis, This Journal, **72**, 2890 (1950).

(15) W. Josten, *Ber.*, **71**, 2230 (1938).

TABLE I

COMPARISON OF ANALYTICAL VALUES FOR COMPOUNDS PREPARED BY ALLEN AND VANALLAN AND THOSE PREPARED HERE

Compound	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Tetraphenylcyclopentanone (VI), m.p. 176°	$C_{29}H_{24}O$	89.65	89.52	6.23	6.11
Dihydrophencyclone (IX), from phenanthraquinone and dibenzyl ketone, m.p. 315–318°	$C_{29}H_{20}O$	90.60	90.41	5.24	5.39
Compound, m.p. 328° (A. and VA., IX)[a]			89.4		5.6
M.p. 325–326° (A. and VA., IX)[b]			89.41		5.19
			89.38		5.20
M.p. 320–323° (prepared here, IX)			90.29		5.21
Calculated for carbinol prepared by adding C_6H_5MgBr to VI	$C_{35}H_{30}O$	90.09		6.48	
Calculated for carbinol prepared by adding C_6H_5MgBr to IX	$C_{35}H_{26}O$	90.87		5.67	
Compound, m.p. 254° (A. + VA., prepared by adding C_6H_5MgBr to product m.p. 328°)[a]		90.3		5.9	

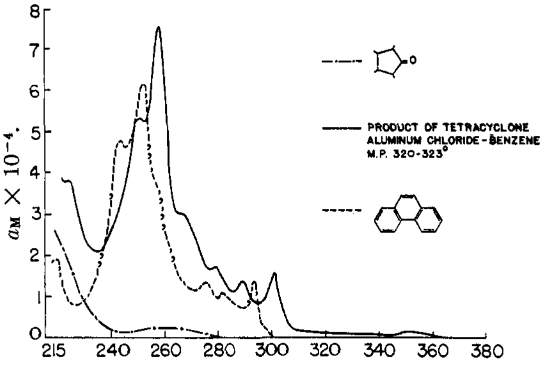
[a] C. F. H. Allen and J. A. VanAllan, THIS JOURNAL, **65**, 1384 (1943). [b] J. A. VanAllan, private communication, Nov. 8, 1950.

bands at 5.85 and 6.15 μ which are characteristic for an α,β-unsaturated carbonyl group. The ultraviolet absorption spectrum is shown in Fig. 2.

Reduction of tetracyclone with zinc and acetic acid at room temperature gave 72% of III and only 8.9% of IV. Apparently the formation of III is favored at room temperature and IV at high temperature. In either case, no one product was formed to the exclusion of the other. These facts suggested the possibility that the dienol is the initial reduction product at either temperature and that it is isomerized to the 2-en-1-one (IV) at the higher temperature. Substantiation of this hypothesis was obtained when it was found that III was isomerized to IV in 96% yield in refluxing acetic acid with added zinc.

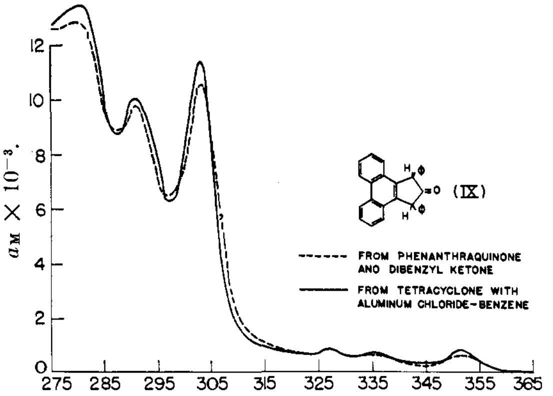
Clemmensen Reduction.—In our hands amalgamated zinc in acetic acid with dry hydrogen chloride reduced I to IV when the reduction was stopped immediately upon discharge of the purple-red cyclone color confirming Dilthey's[10] results. However, carrying the reaction an hour beyond this time gave a mixture of two products melting at 176[10] and 95° (a new product), respectively. The compound melting at 176° was assigned the structure 2,3,4,5-tetraphenylcyclopenta-3-en-1-ol, without proof.[10] Although the compound obtained here agreed in its physical properties and analysis with that of Dilthey, present theory would not predict this structure. Like IV it would not form a phenylhydrazone even under anhydrous conditions.[14] It did add phenylmagnesium bromide to give a pentaphenylcyclopentanol, while the infrared spectrum (Fig. 1f) showed no band in the hydroxyl region and a strong band at 5.78 μ, indicative of a carbonyl group in a strained ring.[16] Accordingly, the compound, m.p. 176°, was assigned the structure 2,3,4,5-tetraphenylcyclopentanone (VI).

Allen and VanAllan,[17] however, had already assigned this structure to a compound melting at 328° which they prepared by treating (I) with benzene and aluminum chloride to obtain a reduction similar to those observed by Fuson and coworkers[18] for certain α,β-unsaturated esters and ketones. A repetition of this experiment here gave a product melting at 320–323° which agreed in all respects with the one described. However, in disagreement with Allen and VanAllan it proved to be identical with dihydrophencyclone (1,3-dihydro-1,3-diphenyl-2-keto-2H-cyclopenta[*l*]phenanthrene) (IX), previously reported by Dilthey, *et al.*[19,20] The analyses reported[17] agree



λ, mμ.

Fig. 4.



λ, mμ.

Fig. 5.

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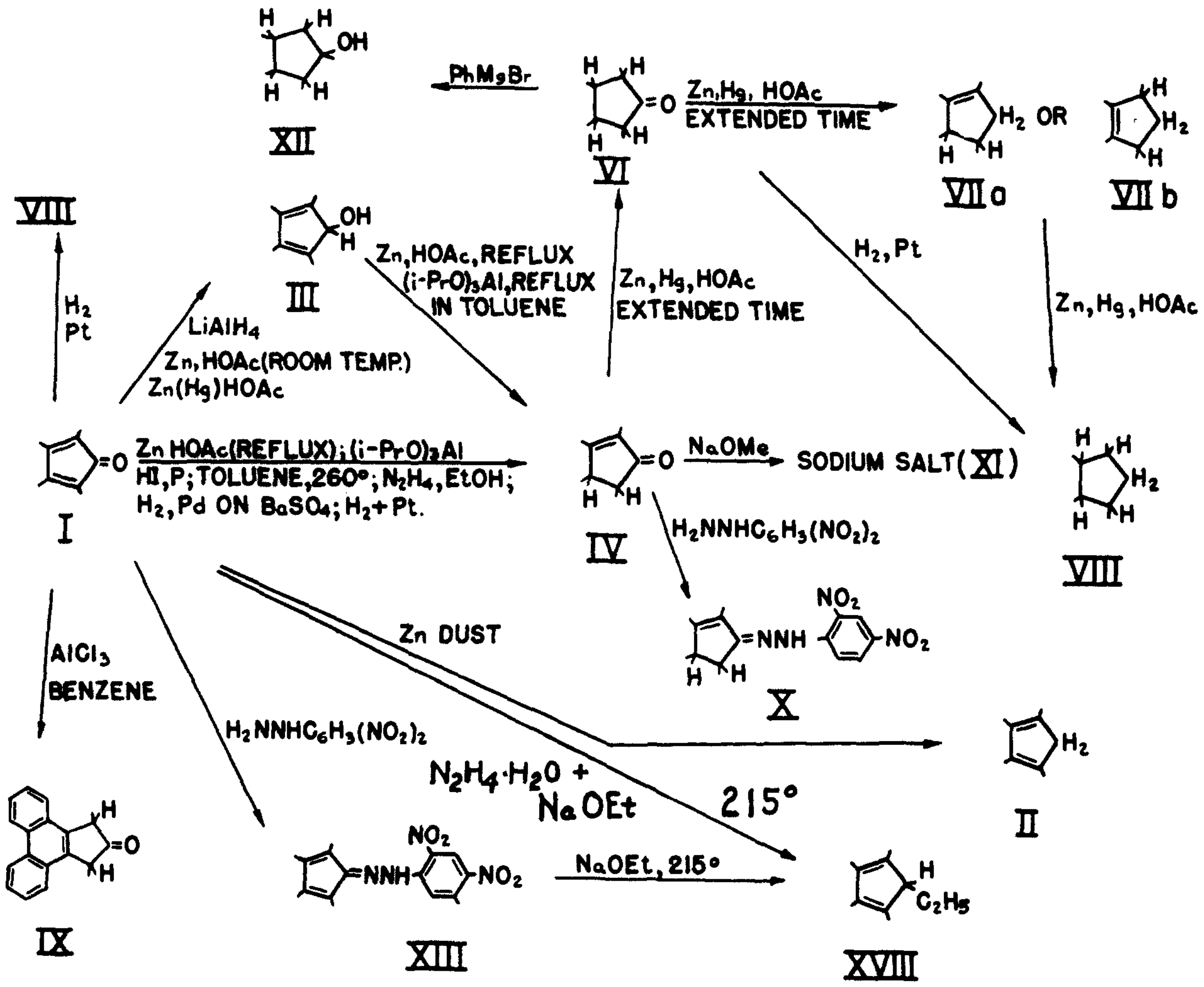
[16] Although the central ring is saturated and considered generally to be essentially strain-free, models show that there is considerable interference of the phenyl groups which may account for the strain.

[17] C. F. H. Allen and J. A. VanAllan, THIS JOURNAL, **65**, 1384 (1943).

[18] R. C. Fuson and H. G. Cooke, Jr., *ibid.*, **73**, 3515 (1951), and earlier papers.

[19] W. Dilthey, I. ter Horst and W. Schommer, *J. prakt. Chem.*, **143**, 189 (1935).

[20] W. Dilthey, S. Henkels and M. Leonhard, *ibid.*, **151**, 97 (1938).



XIV -4-NITROPHENYLHYDRAZONE

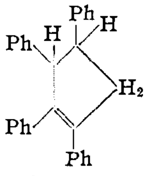
CHART I.

with IX better than with VI, and the analysis of the carbinol obtained by adding phenylmagnesium bromide agrees better with $C_{35}H_{30}O$[17] (see Table I). Finally, the identity of the infrared (Fig. 1g) and ultraviolet absorption spectra (Fig. 5) and the similarity of the latter to the ultraviolet absorption spectrum of phenanthrene itself (Fig. 4) prove that the 328° compound of Allen and Van-Allan is IX and not VI and that phenylmagnesium bromide adds to give 1,3-dihydro-1,2,3-triphenyl-2-hydroxy-2H-cyclopenta[*l*]phenanthrene and not pentaphenylcyclopentanol.

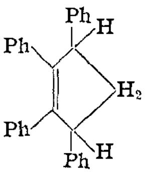
The conversion of tetracyclone to dihydrophencyclone is a new type of isomerization–cyclization and not a reduction. The scope and mechanism of this reaction will be the subject of a later paper.

Bergmann, *et al.*,[21] have also reported a tetraphenylcyclopentanone and this will be dealt with in the section on reduction with lithium aluminum hydride.

Analysis of the second product, m.p. 95°, obtained in the Clemmensen reduction of I was in accord with that for a tetraphenylcyclopentene. Although it gave no color, nor was it soluble in concentrated sulfuric acid, and was saturated toward bromine in carbon tetrachloride it absorbed one mole of hydrogen giving tetraphenylcyclopentane (VIII) (see below). Also, the ultraviolet absorption spectrum (Fig. 6) showed a peak at 270 mμ ($a_m = 9.97 \times 10^3$) reminiscent of that for *cis*-stilbene.[22] An attempt to hydroxylate the double bond[23] gave no reaction. The infrared absorption spectrum (Fig. 1h) shows a band at 6.90 μ in the C–H bending region which is evidence for a methylene group. Therefore, the compound melting at 95° is probably a tetraphenylcyclopentene, either (VIIa or b).



VIIa



VIIb

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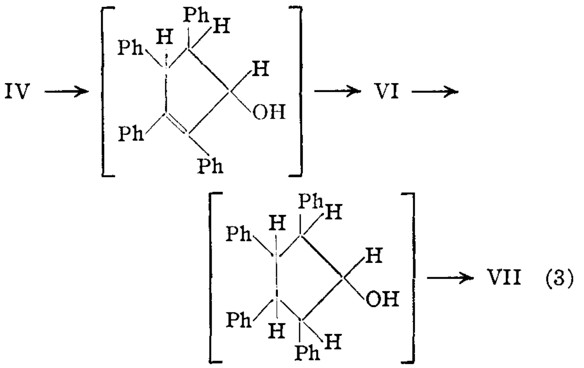
[21] E. D. Bergmann, G. Berthier, D. Ginsburg, Y. Hirshberg, D. Lavie, S. Pinchas, B. Pullman and A. Pullman, *Bull. soc. chim. France*, [5] **18**, 661 (1951).

[22] C. O. Parker, Ph.D. thesis, Polytechnic Institute of Brooklyn, June, 1950.

[23] D. Swern, G. N. Billen and J. T. Scanlan, THIS JOURNAL, **68**, 1504 (1946).

The correct position of the double bond remains to be ascertained.

The formation of a tetraphenylcyclopentene in the Clemmensen reduction of I in acetic acid may be explained as follows: First reduction takes place as in Chart I. This is repeated (equation 3) to give VI. Then VI may be reduced to a secondary alcohol which dehydrates under the acidic conditions to give the cyclopentene (VII) with the double bond in a more stable position between two phenyl rings. Hydrogenolysis of the first intermediate (equation 4) is an alternate possibility. A tetraphenylcyclopentene melting over 300° was reported by Henderson and Corstorphine,[13] but attempts to obtain this compound failed.



A more extended reduction of I in acetic acid produced, in addition to VII, a small quantity of VIII.

Other Reported Reductions.—The products which resulted when tetracyclone was subjected to reduction by means of red phosphorus and hydriodic acid,[10] hydrazine in alcohol,[15] hydrogen over palladium-in-acetic acid just to discharge the purple-red color[10] and hydrocarbons and ethanol at 140–300°[24] have now been shown to be IV. In the last-named reaction using toluene at 250–270° the only other compound identified proved to be benzaldehyde, identified by its odor, boiling point and its 2,4-dinitrophenylhydrazone. Bibenzyl, another possible oxidation product, was absent.

The catalytic reduction was examined further. When Adams catalyst in acetic acid was employed, I absorbed four moles of hydrogen giving a compound melting at 156°. This same compound was obtained by similar hydrogenation of II with the absorption of two moles of hydrogen and of VII with the absorption of one mole. Predicated on its mode of formation and analysis, it was assigned structure VIII, 1,2,3,4-tetraphenylcyclopentane.[25] Its ultraviolet absorption spectrum is shown in Fig. 6.

The ultraviolet absorption spectra of the condensation product of benzoin with dibenzyl ketone[9] has now shown it to be IV. The ultraviolet spectrum of 2,3,4,5-triphenyl-5-benzylfuran (XVII),[26] a reduction product related to I, has been recorded (Fig. 6). Finally, as reported by Dilthey[10] distillation of I with zinc dust gave II.

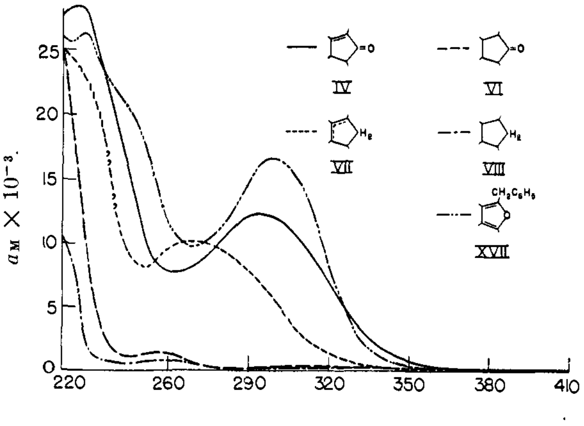


Fig. 6.

Meerwein–Ponndorf–Verley Reduction.—Aluminum isopropoxide gave no reduction of I in isopropyl alcohol–toluene until the isopropyl alcohol was distilled, whereupon IV was obtained. Refluxing toluene or isopropyl alcohol alone was without effect upon I. Under the conditions of this reaction, solvated III isomerized to IV. It thus appears that, as in the reductions with zinc in acetic acid, I is converted to III which is then isomerized to IV.[27]

Reduction with Lithium Aluminum Hydride.—The addition of lithium aluminum hydride to I at 0–10° gave an 81% yield of III. In contrast to this the reverse addition in refluxing solution gave 73% of IV and 12–17% of II. Hochstein and Brown[29] have discussed this change in the course of the reaction with the order of addition, but the appearance of II was not foreseen. It can be accounted for in two ways: IV may be reduced to an allylic alcohol intermediate which is dehydrated with rearrangement to II during the acid hydrolysis of the reaction mixture, or III may be hydrogenolyzed in a slower competitive reaction (equation 4). Trevoy and Brown[30] appear to be the first to have reported hydrogenolysis of a carbon–oxygen bond. Bergmann, *et al.*,[21] and Conover and Tarbell[31] have recorded hydrogenolyses of carbonyl and ester groups. It is significant that the hydrogenolysis reported here was observed

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(24) B. A. Arbuzov, V. S. Abramov and L. A. Shapshinskaya, *Compt. rend. acad. sci., U.R.S.S.*, **46**, 147 (1945); *C. A.*, **39**, 4849^5 (1945).

(25) A compound melting at 80.5° has also been reported to be a tetraphenylcyclopentane by Henderson and Corstorphine.[13] Conceivably this could be a *cis–trans* isomer of the compound melting at 156°; it was never isolated in any of the experiments in this Laboratory.

(26) R. Pütter and W. Dilthey, *J. prakt. Chem.*, **150**, 40 (1937).

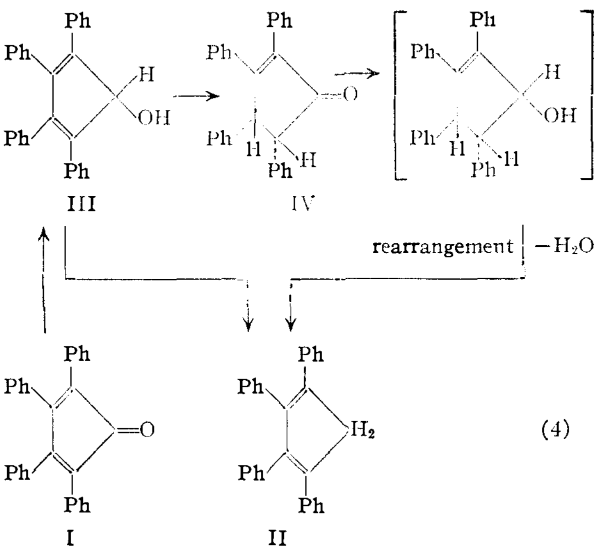
(27) An important contribution to the course of reduction of α,β-unsaturated ketones has been made, but the question is not completely resolved.[28] The present reduction seems certainly to take place as described and supports the tentative contention of Lutz and Gillespie.[28] Structural considerations render it unlikely that the phenyl rings are completely coplanar with the cyclopentadienone ring in tetracyclone. If the reduction indeed takes place through a cyclic mechanism, then in this case the only available space for the cycle is in that plane passing through the carbonyl group at right angles to the C_5-ring. The reaction must initially then take place by 1,2-addition to the carbonyl group.

(28) R. E. Lutz and J. S. Gillespie, Jr., THIS JOURNAL, **72**, 344 (1950).

(29) F. A. Hochstein and W. G. Brown, *ibid.*, **70**, 3484 (1948).

(30) L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

(31) H. Conover and D. S. Tarbell, *ibid.*, **72**, 3586 (1950).



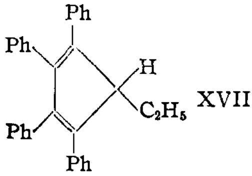
(4)

in refluxing ethyl ether while Bergmann's experiment was carried out in refluxing dioxane and those of Conover and Tarbell at 65–90°.

Bergmann,[21,31a] reported that the addition of tetracyclone (I) to lithium aluminum hydride in boiling dioxane gave 2,3,4,5-tetraphenylcyclopentan-1-one (VI). The evidence cited was the ultraviolet absorption spectrum ($\lambda_{\max.}$ 2950 Å., log E_m 4.13[32]) and the absence of C═C double bond absorption in the infrared (curve not given). However, the given melting point, 161°, compares favorably with that for IV, 161–162°, and not with that for VI, 175–176°. The ultraviolet absorption given is almost identical with that for IV (Fig. 6). Moreover, a saturated ketone, as claimed, would not be expected to show such a high intensity[33] (see Fig. 6). The infrared spectrum (Fig. 1d) obtained here shows absorption bands at 6.15 and 6.20 μ characteristic of conjugated double bonds.[34]

Repetition of the experiment gave 60% of (IV) and a trace of (II).

Wolff–Kishner Reduction.—The conversion of an α,β-unsaturated carbonyl compound to the corresponding olefin by heating its hydrazone, semicarbazone, pyrazoline or azine with alkali[39] could not be applied to the reduction of I because of the inability to prepare these derivatives. However, the 2,4-dinitrophenylhydrazone (XIII) was known[15] and a modification of the required procedure gave the 4-nitrophenylhydrazone (XIV) as well. Heating XIII in ethanolic sodium ethoxide at 210° for 16 hours did give 1-ethyl-2,3,4,5-tetraphenylcyclopentadiene (XVIII)[40] in about 25% yield.



XVIII

The Huang-Minlon[41] procedure did not give the expected product.

Although previous attempts to prepare the hydrazone of I resulted in reduction to IV, under Wolff–Kishner conditions hydrazine hydrate effected the reduction of I to a mixture of XVIII 26% and IV 15%.

Experimental

All melting points are corrected.

Reduction of Tetracyclone at the Reflux Temperature with Zinc and Acetic Acid.—One gram (2.6 mmoles) of tetracyclone was dissolved in 250 ml. of boiling acetic acid and zinc dust (about 2.5 g.) was slowly added. When the solution decolorized (about 15 minutes), it was decanted while hot from residual zinc. Cooling gave a crop of white crystals which were filtered, washed with water and then with glacial acetic acid. The major portion of the precipitate dissolved at this point. The insoluble material, evidently 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol-acetic acid solvate (0.25 g., 0.55 mmole, 21.7%), melted at 138–140° to a red liquid. The solvate rapidly reddened and lost its brilliant white fluorescence upon exposure to air.

The mother liquor from the dienol crystallization was evaporated to dryness at room temperature under reduced pressure. Chromatography of the residual solid from carbon tetrachloride solution on an alumina column (2.5 × 15 cm., F-20 Grade of alumina, Aluminum Company of America) gave two colorless bands, the upper one of which fluoresced in ultraviolet light. The lower band was obtained in the percolate and was concentrated to give 0.65 g. of crystals, m.p. 162–163°, evidently 2,3,4,5-tetraphenylcyclopentenone (IV) (1.69 mmoles, 64%). Displacement of the fluorescent upper band with isopropyl alcohol gave an additional 0.06 g. unsolvated dienol (III) (total yield 27% on unsolvated basis).

Reduction of Tetracyclone with Zinc and Acetic Acid at Room Temperature—2,3,4,5-Tetraphenylcyclopenta-2,4-dien-1-ol (III).—One gram (2.60 mmoles) of tetracyclone

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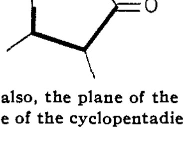
(31a) Without further experimental work Bergmann (*Bull. soc. chim. France*, 703 (1952)) has re-named this compound the enone (IV).

(32) The slight peak reported at 2200 Å.[21] does not appear to be as significant to the present authors because it is in the insensitive region of the Beckman model DU spectrophotometer; however, see Fig. 6.

(33) E. A. Braude, *Ann. Repts. on Progress Chem.* (*Chem. Soc. London*), **42**, 105 (1945).

(34) Bergmann, *et al.*,[21] did not isolate any III presumably because (1) the inverse addition appears to be required and (2) in refluxing dioxane III would probably isomerize to IV. The authors did not cite the work of Hochstein and Brown[29] in which the importance of the order of addition is stressed. Although it may indeed be that I is reduced to IV by a direct mechanism,[35] the isolation of III at low temperatures is difficult to encompass in the special hypothesis of Bergmann and Pullman[21] on the electronic state of the carbonyl group in tetracyclone. This problem will be treated in a forthcoming paper.

(35) A reasonable cyclic mechanism has been proposed for reduction of open-chain α,β-unsaturated ketones with lithium aluminum hydride.[36] In tetracyclone this mechanism would not seem to be operative because the atoms 1, 2, 3, 4 must lie in a plane. Assuming that the C–C distances for cyclopentadiene[37] apply here, the 1,4-distance is 3.5 Å. The Al–H distance is 1.63 Å.[38] which appears to be too small to close the ring. Here, also, the plane of the cycle would have to lie perpendicular to the plane of the cyclopentadienone ring.[27] At higher temperatures a direct attack at "4" would explain Bergmann's result. With inverse addition the product is III and the 6-membered cycle is not required.



(36) R. E. Lutz and J. S. Gillespie, Jr., THIS JOURNAL, **72**, 2002 (1950).

(37) V. Schomaker and L. Pauling, *ibid.*, **61**, 1769 (1939).

(38) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 168, 179.

(39) D. Todd in "Organic Reactions," vol. IV, edited by R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 378.

(40) To the authors' knowledge this unusual type of product has not previously been reported in a Wolff–Kishner reduction. A detailed discussion is in preparation.

(41) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

TABLE II

THE REDUCTION OF TETRACYCLONE

Name of reduction	Reagent and conditions	Product	M.p., °C.	Yield, %
Metal, acid	Zn, CH_3COOH, room temp.	III, solvate	140	72
	Zn, CH_3COOH, reflux until decolorized	IV	162	64
		III, solvate	140	27
Zn dust distln.	Zn, pyrolysis	II	180	5
Clemmensen	Zn(Hg), HCl, CH_3COOH reflux until decolorized	IV	162	84
	Zn(Hg), HCl, CH_3COOH extended reflux, 1 hr. after	VI	176	15.5
	decolorization	VII	95	11
	Zn(Hg), HCl, CH_3COOH extended reflux, 8 hr. after	VII	95	42
	decolorization	VIII	156	6
Meerwein–Ponndorf	$(i\text{-}C_3H_7O)_3Al$ in $C_6H_5CH_3$	IV	162	86
Hydriodic acid	HI, red P, 170°	IV	162	68
Hydrocarbon	$C_6H_5CH_3$ at 250–270° in sealed tube	IV, C_6H_5CHO	162	20
Catalytic, atmospheric pressure	H_2, 10% Pt, CH_3COOH, reflux	IV	162	69
	H_2, Pd–$BaSO_4$, CH_3COOH, reflux	IV	162	73
Catalytic, low pressure	10% Pd-on-C, Pt or Raney Ni in $CH_3COOC_2H_5$, or C_6H_6; Parr, 40 lb./in.^{2}, room temp., 2–3 hr.	No reduction	...	..
Catalytic, low pressure	Pt in CH_3COOH; Parr, 40 lb./in.^{2}, room temp., 45 min.	VIII	156	85
Hydrazine	$NH_2NH_2 \cdot H_2O$ in C_2H_5OH	IV	162	44
Wolff–Kishner	Tcy + $NH_2NH_2 \cdot H_2O$ + C_2H_5OH	XVIII	180	26
	heated 220° with $NaOC_2H_5$ in sealed tube, 16 hr.	IV	162	15
	Tcy 2,4-dinitrophenylhydrazone + $NaOC_2H_5$ + C_2H_5OH in sealed tube, 16 hr.	XVIII	180	40
Metal hydride	$LiAlH_4$, 0–10°, reagent added to cyclone	III	140	81
	$LiAlH_4$, in diethyl and dibutyl ethers, room temp.	IV	162	73
	reflux, cyclone added to excess reagent	II	180	18

TABLE III

PHYSICAL PROPERTIES OF COMPOUNDS

Compound	M.p., °C.	Color		Formula	Carbon, %		Hydrogen, %	
		Alone	In H_2SO_4		Calcd.	Found	Calcd.	Found
II	180	Colorless	Orange	$C_{29}H_{22}$	94.05	94.01	5.95	6.10
III	139–140[a]	Colorless	Red					
IV	162–163	Colorless	Yel.-green	$C_{29}H_{22}O$	90.11	89.94	5.74	5.60
VI	176	Colorless	Colorless	$C_{26}H_{24}O$	89.65	89.52	6.23	6.11
VIIa or b	95	Colorless	Colorless	$C_{29}H_{24}$	93.50	93.57	6.50	6.34
VIII	156	Colorless	Colorless	$C_{29}H_{26}$	93.00	92.79	7.00	7.31
IX	315–318[b]	Colorless	Colorless	$C_{29}H_{20}O$	90.60	90.41	5.24	5.39
X	260–261	Red-brown	Blue-green	$C_{35}H_{26}N_4O_4$	74.19	74.33	4.63	4.70[c]
XI	292–294	Colorless	Colorless	$C_{29}H_{21}NaO$	85.27	85.14	5.18	4.91
XII	244–246	Colorless	Pale yel.	$C_{29}H_{30}O$	90.09	89.79	6.48	6.55
XIV	244–245	Red-brown	Dark blue	$C_{35}H_{25}N_3O_2$	80.89	80.96	4.85	4.92[d]

[a] Ref. 9. [b] From phenanthrenequinone and dibenzyl ketone. [c] Calcd. for $C_{35}H_{26}N_4O_4$: N, 9.89. Found: N, 9.79. [d] Calcd. for $C_{35}H_{25}N_3O_2$: N, 8.09. Found: N, 7.92.

(m.p. 218–220°) was suspended in 40 ml. of acetic acid and 1.0 g. of zinc dust added. Decolorization was complete in about 10 minutes with precipitation of a curdy, gray solid. The solid was filtered, saving the filtrate, and washed successively with four 50-ml. portions of water and then four 25-ml. portions of warm acetone. The combined acetone washings were concentrated at reduced pressure under nitrogen at room temperature until a white compound precipitated, probably III. Upon exposure to light and air, it darkened rapidly. It fluoresced intensely under ultraviolet light and gave a dark red color in concentrated sulfuric acid. It became red at 138° and melted 140–148° (dec.).

After standing for two days in the ice-chest, the mother liquor which had been set aside deposited white crystals which were filtered, washed with 30 ml. of acetic acid and then 50 ml. of water. This compound was also sensitive to light and air although considerably less so than the previously described material. It melted sharply at 139–140° (to a red color). Under vacuum it quickly darkened to a violet brown mass and the odor of acetic acid was noticeable. The total yield of product was 0.72 g. (1.87 mmoles, 72% based on the unsolvated carbinol).

Careful evaporation of the second mother liquor to dryness, dissolution of the residue in carbon tetrachloride and chromatography through alumina gave 0.09 g. (0.23 mmole, 8.9%) of (IV), m.p. 162°.

1-Methyl-(XV) and 1-Benzyltetraphenylcyclopentadien-1-ol (XVI).—These were prepared in 77 and 87% yields, respectively, from tetracyclone and methylmagnesium iodide (rather than the bromide[4]) and benzylmagnesium chloride.[4,5] To ensure that 1,4-addition had not taken place,[17] each was dehydrated to the corresponding fulvene[4,5] using concentrated sulfuric acid in acetic acid rather than hydrogen chloride in acetic acid[4,5] or fusion with potassium acid sulfate[4]: 1,2,3,4-tetraphenylfulvene, 77%, m.p. 210–211° (reported[4] 211–212°) and 1,2,3,4,6-pentaphenylfulvene, 70%, m.p. 203–204° (reported[5] m.p. 204°).

2,3,4,5-Tetraphenylcyclopenta-2-en-1-one 2,4-Dinitrophenylhydrazone (X).—2,3,4,5-Tetraphenylcyclopenta-2-en-1-one, m.p. 162° (1.00 g., 2.59 mmoles) was dissolved in 50 ml. of dry dioxane and added to 0.62 g. of 2,4-dinitrophenylhydrazine, m.p. 197–200°, in 40 ml. of dioxane containing 1 ml. of concentrated sulfuric acid and the mixture refluxed two hours under nitrogen. Cooling and pouring into water gave a precipitate which was filtered, dried under vacuum, dissolved in the minimum quantity of dry benzene and chromatographed twice through a 25 × 2.5 cm. column packed with alumina. The lower dark green band was

TABLE IV

ULTRAVIOLET ABSORPTION MAXIMA

No.	Solvent[a]	λ (1)[b]	a_m(1)[c]	λ (2)[b]	a_m(2)[c]	λ (3)[b]	a_m(3)[c]
I	B			342	0.676		
	C	262	2.71	335	0.710	512	0.132
II	B					349	1.43
	C	245	2.44	269	2.09	346	1.40
III	C	250	2.03	272	1.50	364	0.777
IV	B			299	1.19		
	C	277	2.86	295	1.22		
VI	C	249	0.133	255	0.147	261	0.137
VIIa,b	C	270	.997				
VIII	C	249	.0733	255	0.0833	260	0.0733
IX	B	280	1.73	291	1.31	335	.0813
				303	1.41	351	.0853
XV	B	348	0.667				
XVI	B	370	0.924				
XVII	C	227	2.64	299	1.63		

[a] C = cyclohexane, B = benzene. [b] λ = wave length in mμ. [c] For use of a_m see M. Mellon, *Anal. Chem.*, 21, 3 (1949).

eluted with benzene and evaporated to dryness leaving 1.22 g. (2.16 mmoles, 83%) of red-brown (X), m.p. 260–261°. Recrystallization from benzene did not raise the melting point.

Sodium Salt (XI) of 2,3,4,5-Tetraphenylcyclopenta-2-en-1-one (IV).—A solution of 1.0 g. of the zinc–acetic acid reduction compound (IV), m.p. 162°, was refluxed in 50 ml. of methanol containing 1.0 g. of sodium for three hours. The solution became intensely yellow at the start. After standing overnight, it deposited colorless needles, m.p. 292–294°. These were insoluble in acetone, carbon tetrachloride, cold methanol and water. An alkaline ash remained upon ignition and it formed no color upon solution in sulfuric acid. A Zeisel test for methoxyl was negative.

Isomerization of (III) Acetic Acid Solvate to IV with Zinc in Acetic Acid.—III-solvate (0.30 g., 0.67 mmole) was dissolved in 10 ml. of acetic acid containing 0.02 g. of zinc dust and refluxed for 0.5 hour. The solution was cooled, diluted with 50 ml. of water to give a precipitate which was filtered, washed once with ether, and dried, m.p. 156–160°. Recrystallization gave 0.25 g. (0.64 mmole, 96%) of IV, m.p. 160–162°. A mixture melting point with a sample prepared by the zinc and acetic acid reduction of tetracyclone showed no depression.

Clemmensen Reduction of Tetracyclone—2,3,4,5-Tetraphenylcyclopenta-2-en-1-one (IV).—Five grams (13 mmoles) of tetracyclone (m.p. 218–220°) was dissolved in 100 ml. of acetic acid and 25 g. of amalgamated zinc dust added to the mixture. The solution was brought to reflux and dry hydrogen chloride was passed into the solution until the violet color had been discharged (about ten minutes). At this point the solution was quickly decanted from the residual amalgam into water, precipitating a white solid, weighing 4.8 g. after filtration and drying. Recrystallization from ethanol gave 4.2 g. (11 mmoles, 84%) of (IV), m.p. 160–162°. No depression was observed in a mixture melting point with a sample of tetraphenylcyclopenta-2-en-1-one produced from tetracyclone by reduction with zinc and acetic acid.

Clemmensen Reduction of Tetracyclone—2,3,4,5-Tetraphenylcyclopentan-1-one (VI) and Tetraphenylcyclopentene (VIIa or b).—Five grams (13 mmoles) of tetracyclone (m.p. 218–220°) was dissolved in 100 ml. of glacial acetic acid containing 25 g. of amalgamated zinc. The mixture was refluxed while dry hydrogen chloride was bubbled in until the tetracyclone color had disappeared, and for one hour longer. At this time the hot liquid was decanted from the amalgam into water, precipitating a white solid which melted at 80–90° after filtering and drying. It fluoresced intensely under ultraviolet light. Recrystallization twice from ethanol and once from petroleum ether (b.p. 90–100°) gave 0.78 g. (2.0 mmoles, 15.5%) of colorless (VI), m.p. 175–176°. The compound fluoresced blue-white under ultraviolet light and gave no color in concentrated sulfuric acid. A mixture melting point with authentic 2,3,4,5-tetraphenylcyclopenta-2,4-diene (m.p. 178–180°) melted at 168–173°.

The mother liquors from the above recrystallizations were combined and carefully evaporated to dryness. The thoroughly dried solid was then taken up in 35 ml. of petroleum ether (b.p. 90–100°) and chromatographed through a 2.5 × 25 cm. column of alumina. The lower blue fluorescing band (under ultraviolet light) was developed with petroleum ether (b.p. 90–100°) and then eluted with benzene. From the eluate of the lowest band, on careful evaporation, 0.4 g. of a white waxy solid was obtained, fluorescent under the mercury vapor lamp, sintering at 85° and melting at 91–95°. Rechromatographing this solid from benzene solution on alumina gave 0.53 g. (1.43 mmoles, 11%) of tetraphenylcyclopentene (VIIa or b), m.p. 95°. The hydrocarbon gave no coloration in concentrated sulfuric acid, and would not decolorize bromine in carbon tetrachloride. An attempt to hydroxylate the double bond with performic acid by the method of Swern, *et al.*,[23] gave back unreacted pentene.

1,2,3,4,5-Pentaphenylcyclopentan-1-ol (XII).—One-half gram (1.29 mmoles) of tetraphenylcyclopentanone (VI), m.p. 176°, was added under nitrogen to the Grignard reagent prepared from 1 g. of magnesium turnings and 0.5 g. of bromobenzene in 30 ml. of diethyl ether and the mixture was refluxed for 40 minutes. Hydrolysis with 10% aqueous ammonium chloride was followed by separation of the ethereal layer, drying it overnight with anhydrous potassium carbonate, and then concentrating to 10 ml. under nitrogen at reduced pressure. Cooling and the addition of 3 ml. of 95% ethanol precipitated white needles, m.p. 211–229° (after washing with ethanol). Recrystallization from benzene gave 0.23 g. (0.49 mmole, 38%) of (XII), m.p. 244–246° (to a red melt). For analysis the compound required extensive drying at 180° under vacuum. The carbinol dissolved in concentrated sulfuric acid with a pale yellow color.

Reaction of Tetracyclone with Aluminum Chloride in Benzene—Dihydrophencyclone, (1,3-Diphenyl-2-keto-1,3-dihydro-2H-cyclopenta[*l*]phenanthrene) (IX).—Tetracyclone (3.84 g., 10 mmoles) was suspended in 25 ml. of dry benzene and stirred while 1.34 g. (10 mmoles) of aluminum chloride was added portionwise. Some heat was generated. After one hour an additional 1.34 g. of aluminum chloride was added, and stirring continued at room temperature for 15 hours. Hydrolysis in dilute hydrochloric acid gave a tan precipitate which was filtered, dried, washed with acetone, and recrystallized twice from toluene to give 1.8 g. (4.6 mmoles, 46%) of pearly, colorless flakes, m.p. 320–323°. Concentration of the mother liquors gave an additional 0.3 g. A small portion of the latter fraction on a chromatographic column gave a single major band and a narrow, lower, violet fluorescing band under ultraviolet light. Elution of the latter afforded a trace of a low melting solid insufficient for further identification. The major product gave no color in concentrated sulfuric acid but a pale orange color in pyridine containing sodium ethoxide (active hydrogen). A mixture melting point with dihydrophencyclone, m.p. 315–318°, prepared from the condensation of phenanthrenequinone and dibenzyl ketone, melted sharply at 314–315° without sintering.

Catalytic Hydrogenation of Tetraphenylcyclopentene (VIIa or b) to Tetraphenylcyclopentane (VIII).—VIIa or b, m.p. 95°, (0.37 g., 10 mmoles) dissolved in 200 ml. of glacial acetic acid containing platinum black from 0.5 g. of platinum oxide was hydrogenated in the Parr apparatus at 40 p.s.i.g. In 30 minutes the equivalent of one molecule of hydrogen was absorbed. Filtration of the catalyst and concentration of the filtrate at reduced pressure gave a clear oil which crystallized upon the addition of 5 ml. of 95% ethanol and cooling, 0.315 g. Chromatography from heptane-on-alumina gave a lower, non-fluorescing band. Additional heptane washed this band into the eluate and on concentration afforded 0.31 g. of pearly, colorless compound, m.p. 154–156°. The compound was colorless in concentrated sulfuric acid and gave no depression in mixture melting points with tetraphenylcyclopentane, m.p. 156°, obtained from either the catalytic reduction of I or II.

Clemmensen Reduction of Tetracyclone–Tetraphenylcyclopentene and Tetraphenylcyclopentane.—In a repetition of the previously described Clemmensen reduction using identical quantities but an eight-hour reduction time, 5 g. (13 mmoles) of I afforded 2.15 g. (5.6 mmoles, 43%) of VIIa or b, m.p. 95° (from an upper ultraviolet fluorescing band of the chromatogram) and 0.3 g. (0.78 mmole, 6%) of VIII, m.p. 156° (from a lower, colorless, non-fluorescing band of the chromatogram).

Reduction of Tetracyclone by Zinc Dust Distillation.—One gram (2.59 mmoles) of I and 2 g. of zinc dust were intimately mixed and placed in a r.b. flask which was connected to a U-tube condenser. The flask was heated in an oil-bath at 270° for 1 hour. The condensate, after two crystallizations from ethanol afforded 27 mg. of 2,3,4,5-tetraphenylcyclopenta-2,4-diene (II), m.p. 180°. Reducing the pressure in the distillation yielded only 45 mg. of the diene (0.27 mmole, 5%). The product gave no depression in mixed melting point with an authentic sample of I, m.p. 180°.

Reduction of Tetracyclone with Toluene.[24]—One gram (2.6 mmoles) of I in 60 ml. of toluene was heated in a 100-ml. Carius tube for 48 hours at 250–270°. At this time the solution was still dark red-violet. The tube was cooled, opened, and the contents concentrated at reduced pressure, the distillate being collected. The residue from the evaporation was a viscous red-violet mass with an odor reminiscent of benzaldehyde. The residue dissolved in 10 ml. of boiling diethyl ether, which was then cooled in ice and filtered to give 0.52 g. of red-violet solid. Recrystallization from glacial acetic acid gave 0.35 g. of tetracyclone, m.p. 219–221° (no depression in mixed melting point with an authentic sample).

From the mother liquor of the original crop, a pale pink solid precipitated which was filtered, washed once with ether, 0.27 g., m.p. 153–158°, and recrystallized from acetic acid to give 0.2 g. (0.52 mmole, 20%) of IV, m.p. 160–162°. This material gave no depression in a mixture melting point with a sample of IV, m.p. 160–162°, produced from I by reduction with zinc and acetic acid.

Fractional distillation of the crudely distilled solvent gave a total of 58 ml. of toluene, b.p. 110–112°, and a residual higher boiling oil, (0.5 ml.) identified as benzaldehyde (odor, b.p. 178–179°, and 2,4-dinitrophenylhydrazone, m.p. 235–237°).

The combined mother liquors from all the crystallizations were evaporated to dryness, taken up in 60 ml. of petroleum ether, b.p. 90–100°, and chromatographed through a 25 × 2.5 cm. column of alumina. The characteristic violet fluorescing biphenyl band was not observed.

Effects of Solvents upon Tetracyclone at the Reflux Temperature. (A).—Two grams of (I) was refluxed in 150 ml. of dry isopropyl alcohol for 48 hours. Tests for acetone were made in the condensate every 15 minutes with 2,4-dinitrophenylhydrazine test solution for the first four hours, then at one-half hour intervals with negative results throughout. The solvent was distilled at reduced pressure giving 2.0 g. of residue, m.p. 219°. Fractionation of the solvent gave only isopropyl alcohol, b.p. 81–83°.

(B).—Two grams of tetracyclone (m.p. 218–220°) in 150 ml. of toluene and refluxed 48 hours again gave no decolorization. The solvent obtained by distillation at reduced pressure was fractionated and gave only toluene, b.p. 108–111°. The residue (2.0 g.) melted at 218–220°.

Meerwein–Ponndorf Reduction of Tetracyclone.—To a mixture of 250 ml. of dry isopropyl alcohol and 250 ml. of dry toluene there was added 2.84 g. (10 mmoles) of tetracyclone, m.p. 220°, and 6.12 g. (30 mmoles) of freshly distilled aluminum isopropoxide and the mixture was distilled slowly for two hours through a 38-cm. Vigreux column. No acetone was detected in the distillate with 2,4-dinitrophenylhydrazine reagent. At this time toluene was added and the isopropyl alcohol distilled. A positive test for acetone was then obtained in the distillate. After two additional hours of slow distillation, the solution was almost decolorized and acetone was no longer detected.

After decomposition of the mixture with 85 ml. of 10% sulfuric acid, the toluene layer was separated and washed successively with dilute ammonium hydroxide and then twice with water. Distillation of toluene at reduced pressure (room temperature) left a pink residue, m.p. 152–160°. One-half of this material was crystallized twice from acetone to give a colorless solid, m.p. 160–163°. The other portion melted at 160–162° after two crystallizations from acetic acid (total yield 3.3 g., 8.6 mmoles, 86%). These two compounds gave no depression in a mixture melting point. Each did not depress the melting point of IV melting at 162–163° obtained by the reduction of tetracyclone with zinc and acetic acid.

Isomerization of 2,3,4,5-Tetraphenylcyclopenta-2,4-diene-1-ol (III) to Tetraphenylcyclopenta-2-en-1-one (IV).—The solvate of III (0.3 g., 0.68 mmole) was dissolved in a mixture of 10 ml. of isopropyl alcohol, 90 ml. of toluene, and 0.6 g. of aluminum isopropoxide and refluxed for two hours. Acidification with 8.5 ml. of 10% sulfuric acid was followed by separation of the toluene layer and washing the latter with dilute ammonium hydroxide and then water. Evaporation to dryness at reduced pressure gave a pink solid which was colorless after crystallization from acetic acid, m.p. 160–161° (0.23 g., 0.60 mmole, 88.5%). No depression in a mixture melting point was observed with an authentic sample of IV, m.p. 162°, from the reduction of tetracyclone with zinc and acetic acid.

Catalytic Hydrogenation of Tetracyclone with 10% Platinum.[42]—One gram (2.6 mmoles) of I, m.p. 218–220°, and 0.1 g. of platinum black in 100 ml. of acetic acid (distilled over potassium permanganate) was refluxed while hydrogen was bubbled into the mixture until the color was discharged. The hot solution was filtered and poured into water. The colorless solid was crystallized twice from acetone to give 0.72 g. (1.86 mmoles, 73%) of IV, m.p. 162°, identical with that of previous authentic samples.

Catalytic Hydrogenation of Tetracyclone with Platinum in the Parr Apparatus.—Two hundred milliliters of a saturated acetic acid solution of I (0.54 g., 1.4 mmoles), containing platinum black from 0.5 g. of platinum oxide was hydrogenated at 40 p.s.i. at a shaking rate of 235 strokes per minute. In 30–45 minutes four moles of hydrogen was absorbed. After filtration of the catalyst the solution was concentrated at reduced pressure under nitrogen to give a clear, colorless oil which solidified on standing. Recrystallization twice from 95% ethanol gave silky colorless needles of tetraphenylcyclopentane (VIII), m.p. 156° (0.46 g., 1.19 mmoles, 85%). A mixture melting point with authentic (IV), m.p. 162°, sintered at 138° and melted at 141–149°. For analysis, drying for four hours at 140° in the Abderhalden pistol was necessary. The hydrocarbon was colorless in concentrated sulfuric acid and was faintly blue-violet fluorescent under ultraviolet light as a solid, but not in cyclohexane solution.

The catalytic hydrogenation of tetracyclone in the Parr apparatus could not be accomplished by the use of 10% platinum-on-charcoal in acetic acid, ethyl acetate or benzene; or by platinum in ethyl acetate or benzene; or with freshly prepared Raney nickel in ethyl acetate or benzene.

Catalytic Hydrogenation of 2,3,4,5-Tetraphenylcyclopenta-2,4-diene (II) in the Parr Apparatus.—II (0.2 g., 0.54 mmole), in 200 ml. of acetic acid containing platinum black (from 0.2 g. of platinum oxide) was hydrogenated at 40 p.s.i. Two moles of hydrogen was absorbed in 30 minutes. After filtration of the catalyst, concentration of the solution at reduced pressure under nitrogen gave a colorless oil which solidified. Two recrystallizations from ethanol afforded 0.18 g. (0.49 mmole, 90%) of VIII, m.p. 156°. The product gave no depression in mixture melting point with the hydrocarbon, m.p. 156°, obtained by the catalytic hydrogenation of tetracyclone.

Reduction of Tetracyclone with Hydrazine Hydrate.—One gram of I (2.6 mmoles), m.p. 218–220°, was heated with 1 ml. of hydrazine hydrate (85% in water) in 40 ml. of absolute ethanol at reflux for two hours. At the conclusion of this time the solution was clear orange. After cooling and standing two days, colorless crystals appeared which were filtered and dried in air, 40 mg., m.p. 162°. The solid did not fluoresce under ultraviolet light. It gave no depression in a mixture melting point with an authentic sample of IV, m.p. 162°. Concentration of the filtrate to one-third its volume at reduced pressure and room temperature afforded an additional 0.4 g. of the same compound (total 0.44 g., 1.14 mmoles, 44%).

Reduction of Tetracyclone with Lithium Aluminum Hydride at 0–10°.—A solution of 1.0 g. (2.6 mmoles) of lithium aluminum hydride in 50 ml. of diethyl ether was added to a solution of 1.0 g. (2.6 mmoles) of I in 50 ml. of *n*-butyl ether maintained at 0–10°. After one hour the purple color changed to pale yellow and after an additional two hours of stirring the mixture was hydrolyzed by adding dilute hydrochloric acid and ice.

The ether layer was separated, dried over anhydrous magnesium sulfate, filtered, and distilled under nitrogen to one-fourth its volume. Cooling gave 0.82 g., 2.07 mmoles, 81%

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[42] See footnote 9 for the corresponding experiment with palladium or barium sulfate as catalyst.

of slightly pink crystals of III melting at 139–140°. No depression was observed in a mixture melting point with the acetic acid solvate of III, m.p. 138–140°, obtained by reduction of I with zinc in acetic acid. The crystals gave a deep red color in concentrated sulfuric acid.

Reduction of Tetracyclone with Lithium Aluminum Hydride at Reflux in Ether.—Two grams (5.2 mmoles) of I in 200 ml. of dry dibutyl ether was added dropwise with stirring at room temperature to a solution of 2 g. (0.052 mole) of lithium aluminum hydride in 200 ml. of dry ethyl ether. The mixture was stirred one hour at room temperature then refluxed two hours. After decomposition of the mixture by dropwise addition with cooling of 50 ml. of dilute (1:10) hydrochloric acid, the ether layer was decanted, dried over anhydrous potassium carbonate, and concentrated to give white crystals, m.p. 153–156°; upon standing an additional crop deposited. Recrystallization from ethanol gave needle-like clusters, m.p. 162°. No depression was observed with authentic IV, m.p. 162°. The alcohol was distilled, the residue taken up in benzene, combined with the ether filtrate, and chromatographed through an alumina column 2.5 × 75 cm. With the aid of an ultraviolet lamp a white fluorescing band was separated which upon evaporation of the solvent and addition of ethanol, precipitated white crystals, m.p. 180°. Continued development gave 12–17% of faintly pink diene. Evaporation of the solvent and addition of ethanol gave more IV, m.p. 161° (total yield 1.4–1.5 g., 3.0 mmoles, 75%). A third band was eluted and afforded 11 mg. of white needles, crystallizing in star-like clusters, m.p. 231–233°. No further work was done on this material.

Reduction with Lithium Aluminum Hydride in Dioxane.—According to Bergmann,[21] 3.5 g. (9.1 mmoles) of I in 20 ml. of dioxane was added in 5 min. to 0.4 g. (10.5 mmoles) of lithium aluminum hydride in 20 ml. of dioxane and refluxed for 3 hr. After hydrolysis with 30 ml. of dilute hydrochloric acid (1:10), the mixture was extracted with ether, and the solvents distilled at reduced pressure to give a pink residue. Crystallization from 50 ml. of acetic acid gave 1.16 g. of colorless solid, m.p. 161.3–162.4°. No depression was observed with the Meerwein–Ponndorf–Verley product (IV). Two additional crops from the filtrate gave 1.13 g., m.p. 159–161° (2.29 g., 5.9 mmoles, 65%). Distillation of the acetic acid and chromatography of the residue in heptane solution on alumina gave 7 mg. of II, no depression with authentic diene, m.p. 180°.

Tetracyclone 2,4-Dinitrophenylhydrazone (XIII).—The procedure followed is modified from that of Josten.[15] One gram (5.0 mmoles) of 2,4-dinitrophenylhydrazine was dissolved in 40 ml. of purified dioxane in a 3-neck r.b. flask fitted with a gas-inlet tube, a condenser and a dropping funnel. Two milliliters of concentrated sulfuric acid was added and the solution was brought to reflux. At this point a solution of 1.9 g. (5.0 mmoles) of I in 40 ml. of dioxane was added during 15 minutes and reflux was continued for two hours. During the entire operation nitrogen was slowly passed through the flask. The mixture was then poured into 2 l. of water and the precipitated brown solids filtered, dried in a desiccator, taken up in 150–200 ml. of dry benzene, and chromatographed through a 100 × 2.5 cm. column of alumina. The lower red-brown band separated from the small upper red band (unreacted 2,4-dinitrophenylhydrazine) and was concentrated under nitrogen at reduced pressure to give 2.54 g. (4.5 mmoles, 91%) of the 2,4-dinitrophenylhydrazone of tetracyclone, m.p. 271°, violet-brown (red-brown streak on porcelain). The derivative gave a blue-violet color in concentrated sulfuric acid. The reported yield is "about 70%."[16]

Tetracyclone 4-Nitrophenylhydrazone (XIV).—In an exactly analogous manner there was obtained from 1.9 g. (5 mmoles) of I and 0.76 g. of 4-nitrophenylhydrazine 1.98 g. (3.8 mmoles, 76%) of the red-brown 4-nitrophenylhydrazone of tetracyclone (XIII), m.p. 244–245°. The derivative gave a dark blue color in concentrated sulfuric acid and a blue-green color in alcoholic potassium hydroxide.

Wolff–Kishner Reduction of the 2,4-Dinitrophenylhydrazone of Tetracyclone.—One gram (1.77 mmoles) of the 2,4-dinitrophenylhydrazone in a solution of ethanolic sodium ethoxide (prepared by dissolving 1 g. of sodium in 40 ml. of absolute ethanol) was sealed into a 100-ml. Carius tube and heated at 210–220° for 16 hours. After cooling, the tube contained a white solid suspended in a dark brown solution. The solid was filtered and the filtrate was added to water giving an intense green suspension which coagulated on standing in the cold. The filtered solid was dried at reduced pressure, dissolved in 100 ml. of benzene (leaving a small residue), chromatographed through a 2.5 × 25 cm. column of alumina and eluted successively with benzene and chloroform to give the following bands.

Band	Color under U.V. light	Solvent	Volume, ml.	Quantity material on evap.
I (lowest)	Colorless (forerun)	C_6H_6	200	....
II	Blue-violet	C_6H_6	150	0.237 g. white solid m.p. 177–179°
III	Pale yellow	$C_6H_6 + CHCl_3$	200	Trace
IV (top)	Apple-green (small)	$CHCl_3$	150	None

The solid from the evaporation of the eluate of band II gave a depression in mixture melting point with II prepared by the Ziegler–Schnell synthesis. The hydrocarbon fluoresced under ultraviolet light and gave a slight orange color in concentrated sulfuric acid.

The green suspension which had coagulated was filtered, the filtrate extracted with ether and the ether distilled. The solid remaining was combined with the coagulum, dissolved in 70 ml. of benzene and chromatographed on alumina as before using benzene, chloroform and isopropyl alcohol as eluants.

Band	Color under U.V. light	Solvent	Volume, ml.	Quantity material on evap.
I (lowest)	Colorless (prerun)	C_6H_4	175	....
II	Blue-violet	C_6H_6	75	0.025 g. white solid, m.p. 178–180°
III	Colorless (sli. pink in daylight)	$CHCl_3$	100	3 mg. red-violet solid, m.p. 221°
IV	Dark green-black (green in daylight)	$CHCl_3 + C_3H_7OH$	50	0.2 g. black oil

Evaporation of the eluate from band II gave an additional quantity of XVIII (total yield 0.262 g., 0.71 mmole, 40%). The trace of red-violet solid, m.p. 221°, from the evaporation of the eluate of band III was identified as I by melting point and mixture melting point. The oil in band IV was not further investigated.

Wolff–Kishner Reduction of Tetracyclone with Hydrazine Hydrate. 1-Ethyl-2,3,4,5-tetraphenylcyclopenta-2,4-diene (XVIII) and 2,3,4,5-Tetraphenylcyclopenta-2-en-1-one (IV).—One gram (2.6 mmoles) of I and 1.0 ml. of hydrazine hydrate (85% in water) were refluxed in 40 ml. of absolute ethanol for 15 minutes. This solution was combined with a solution of 1 g. of sodium in 30 ml. of absolute ethanol sealed into a 100-ml. Carius tube and heated at a temperature of 210–220° for 16 hours. After cooling, a clear yellow solution remained above a white precipitate which fluoresced with ultraviolet light. The tube was opened, the solution filtered, and the precipitate sucked dry, giving a m.p. 177–179°. One recrystallization from acetone gave 0.25 g. (0.65 mmole, 26%) of white flakes, m.p. 180°, identified as XVIII by mixture melting point with an authentic sample, m.p. 180°.

The initial filtrate was poured into water precipitating a light brown oily solid. Two recrystallizations from acetone-ethanol gave 0.15 g. (0.39 mmole, 15%) of colorless solid, m.p. 160°, identified as IV by mixture melting point with a known sample, m.p. 161°.

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Brooklyn, N. Y.