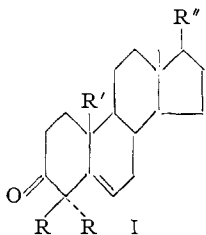
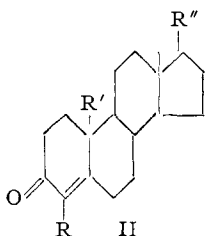


prepared through the enol lactone by the general method of Fujimoto⁵ (m.p. 167–168.5°; calcd. for C₂₀H₃₀O₂: C, 79.42; H, 10.00. Found: C, 79.21; H, 10.29). The third peak comprised recovered testosterone (recovery 33%) and was eluted with ethyl acetate–benzene (1:9 and 1:4). Yields of Ia and IIa were thus 14% and 66%, respectively. No evidence of O-alkylation at the 17-hydroxyl was obtained.



- I
a, R = CH₃; R' = CH₃; R'' = OH
b, R = allyl; R' = CH₃; R'' = OH
c, R = CH₃; R' = H; R'' = OH



- II
a, R = CH₃; R' = CH₃; R'' = OH
b, R = allyl; R' = CH₃; R'' = OH
c, R = *n*-butyl; R' = CH₃; R'' = OH
d, R = CH₃; R' = H; R'' = OH
e, R = CH₃; R' = H; R'' = OCOCH₃

Testosterone on similar alkylation with allyl bromide followed by chromatography of the crude product on silica gave 17 β -hydroxy-4,4-diallyl-androst-5-en-3-one (Ib) (conversion 11%; yield 14%; m.p. 108–109.5°; [α]_D –12° (*c* 0.66); infrared 2.92 μ , 5.84 μ , 5.93 μ , 6.04 μ , 6.11 μ ; Calcd. for C₂₅H₃₆O₂: C, 81.47; H, 9.85. Found: C, 81.13; H, 9.84.) on elution with ethyl acetate–benzene (1:19) and 4-allyltestosterone (IIb) (conversion 46%; yield 55%; m.p. 124.5–125° with presoftening; [α]_D +125° (*c* 1.11); λ_{\max} . 250m μ (ϵ 15,000); infrared 2.87 μ , 2.94 μ , 6.04 μ , 6.25 μ ; calcd. for C₂₂H₃₂O₂: C, 80.44; H, 9.82. Found: C, 80.64; H, 9.99) with ethyl acetate–benzene (1:9). Testosterone (recovery 16%) was eluted with ethyl acetate–benzene (1:4). When *n*-butyl iodide was used in the alkylation 4-*n*-butyltestosterone (IIc) (62%; m.p. 127.5–128.5°; [α]_D +113° (*c* 1.02); λ_{\max} . 251m μ (ϵ 15,000); infrared 3.11 μ , 6.00 μ , 6.23 μ ; calcd. for C₂₃H₃₆O₂: C, 80.18; H, 10.53. Found: C, 80.24; H, 10.73) was obtained. A material (10%) was eluted from the column before IIc which showed no ultraviolet absorption in the region of 250 m μ and was assumed, without further characterization, to be the dialkylated product.

19-Nortestosterone (with 1.25 moles methyl iodide) gave 17 β -hydroxy-4,4-dimethyl-19-norandrost-5-en-3-one (Ic) (16%; m.p. 149.5–150°; [α]_D +33° (*c* 0.36); infrared 3.01 μ , 5.85 μ , 6.06 μ ; calcd. for C₂₀H₃₀O₂: C, 79.42; H, 10.00. Found: C, 79.02; H, 9.96) and 4-methyl-19-nortestosterone

(5) G. I. Fujimoto, *THIS JOURNAL*, **73**, 1856 (1951).

(IIId) (50%; m.p. 158–159°; [α]_D +52° (*c* 0.74); λ_{\max} . 250 m μ (ϵ 15,400); infrared 2.82 μ , 6.04 μ , 6.22 μ). This material was shown to be identical on the basis of its infrared spectrum and a mixture m.p. with a sample of the compound prepared through the enol lactone (m.p. 154–158.5°; calcd. for C₁₉H₂₈O₂: C, 79.12; H, 9.78. Found: C, 78.99; H, 9.63); acetate⁶ (IIe; m.p. 128–129°; [α]_D +42° (*c* 0.85); λ_{\max} . 249.5 m μ (ϵ 17,100); calcd. for C₂₁H₃₀O₃: C, 76.32; H, 9.15. Found: C, 76.03; H, 9.06).

(6) J. A. Hartman, A. J. Tomaszewski and A. S. Dreiding, *ibid.*, **78**, 5662 (1956).

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RECEIVED AUGUST 30, 1957

THE ADDITION OF TETRACYANOETHYLENE TO DIPHENYLDIMETHYLENECYCLOBUTENE

Sir:

Possible synthetic routes to the still unknown genuine cyclobutadienes, which might be effected under mild conditions, are Diels–Alder additions with dimethylenecyclobutenes. The principal objective of the reported synthesis of diphenyldimethylenecyclobutene (I)¹ was, in fact, to investigate this approach. We now wish to report the first results of this study.

It was found that the triene I was unreactive toward maleic anhydride, *N*-phenylmaleimide and acetylene dicarboxylic ester at moderate temperatures (25–75°), in sharp contrast to the high Diels–Alder activity of the closely related model compound 1,2-dimethylenecyclobutane.² At elevated temperatures polymerization occurred in all instances with no isolable crystalline products being realized. Thus, from the reaction of I with acetylenedicarboxylic ester at 150°, there was obtained, after careful chromatography, an amorphous product in low yield which decomposed at 160–170°, depending upon the rate of heating. *Anal.* Calcd. for (C₂₄H₂₀O₄)_n: C, 77.40; H, 15.41. Found: C, 77.60; H, 15.53. The infrared spectrum of this polymeric product indicated that it comprised combined I and dienophile.

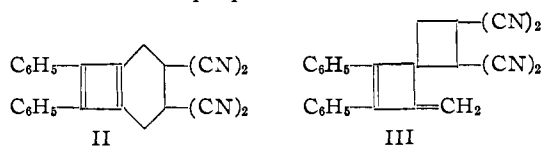
The foregoing suggested that a dienophile of unusual activity would be required to coax the triene I into undergoing a Diels–Alder addition. The recently described tetracyanoethylene³ appeared uniquely attractive for this purpose. From this and I, in benzene at room temperature, there was obtained a colorless crystalline stable adduct (*ca.* 40% yield), m.p. 175–176° (dec.) after recrystallization from ether. Calcd. for C₃₄H₁₄N₄: C, 80.43; H, 3.94; N, 15.63. Found: C, 80.73; H, 4.08; N, 15.39. The mild conditions employed for the addition suggested that the adduct had either the cyclobutadiene structure II or the spiran structure III, resulting from 1,4- or 1,2-addition

(1) A. T. Blomquist and Y. C. Meinwald, *THIS JOURNAL*, **79**, 5317 (1957).

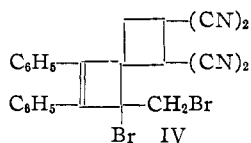
(2) A. T. Blomquist and J. A. Verdol, *ibid.*, **77**, 1806 (1955).

(3) T. L. Cairns, R. A. Carboni, D. D. Coffman, V. A. Engelhardt, R. E. Heckert, E. L. Little, E. G. McGeer, B. C. McKusick and W. J. Middleton, *ibid.*, **79**, 2340 (1957).

respectively. Only structure III was in accord with all of the observed properties of the adduct.



In the ultraviolet the adduct, in isoöctane, showed λ_{\max} 245 $m\mu$ (broad) ($\log \epsilon$ 4.30) and λ_{\max} 308 $m\mu$ ($\log \epsilon$ 4.07). The infrared spectrum showed weak absorption at 4.46 μ ($-\text{C}\equiv\text{N}$), characteristic aromatic absorption and absorption at 5.97, 11.40 and 11.60 μ characteristic of the methylenecyclobutene system.⁴ In carbon tetrachloride at room temperature the adduct absorbed one molar equivalent of bromine to give a crystalline dibromide IV, m.p. 162.5–163°. *Anal.* Calcd. for $\text{C}_{24}\text{H}_{14}\text{N}_4\text{Br}_2$: C, 55.62; H, 2.72; N, 10.81; Br, 30.84. Found: C, 55.92; H, 2.92; N, 10.73; Br, 31.07. The infrared and ultraviolet spectra of IV were similar



to those of the tetrabromide of I.¹ IV showed weak absorption at 6.06 μ in the infrared and λ_{\max} 285 $m\mu$ ($\log \epsilon$ 4.25) in the ultraviolet (chloroform solution).

Finally, the nuclear magnetic resonance spectrum of the adduct in hexadeuteroacetone solution shows three peaks approximately in the weight 5:1:1 and at about the correct positions for phenyl hydrogen (C_6H_5-), exomethylenic hydrogen ($=\text{CH}_2$) and saturated ring methylene hydrogen ($-\text{CH}_2-$) respectively.

This unique cycloaddition of tetracyanoethylene to form a four-membered carbon ring under such mild conditions is attributed to the extreme reactivity of the reactants and their refusal to form a stable, isolable cyclobutadiene. Further study of the triene I and related compounds is in progress.

Acknowledgment.—Support of this investigation by a Research Grant from the National Science Foundation is gratefully acknowledged. The authors also wish to express their thanks to Dr. T. L. Cairns of the du Pont Co. for supplying a quantity of tetracyanoethylene.

(4) D. E. Applequist and J. D. Roberts, *THIS JOURNAL*, **76**, 4012 (1956).

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RECEIVED AUGUST 6, 1957

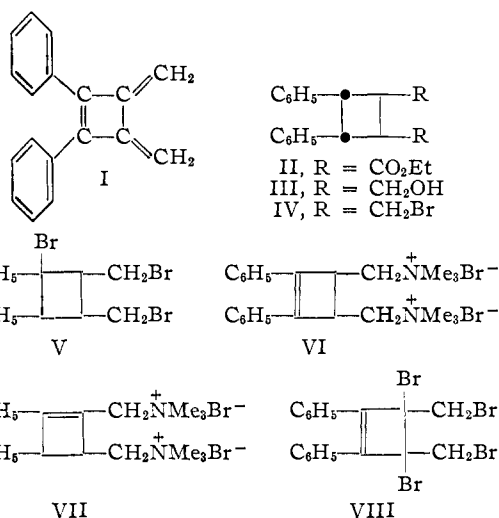
DIPHENYLDIMETHYLENOCYCLOBUTENE

Sir:

We wish to report the synthesis of diphenyldimethylenecyclobutene (I), the most highly unsaturated four-membered ring hydrocarbon known.¹

(1) For an interesting theoretical discussion of this system see J. D. Roberts, A. Streitwieser and C. M. Regan, *THIS JOURNAL*, **74**, 4579 (1952).

It is isoelectronic with the recently reported "Cyclobutadienoquinones."²



Diethyl β -truxinate³ (II) was reduced with lithium aluminum hydride to give the glycol III, m.p. 110–111°. *Anal.* Calcd. for $\text{C}_{18}\text{H}_{20}\text{O}_2$: C, 80.56; H, 7.51. Found: C, 80.83; H, 7.23. Treatment of III with phosphorus tribromide gave the dibromide IV, m.p. 95.5–96.5°. *Anal.* Calcd. for $\text{C}_{18}\text{H}_{16}\text{Br}_2$: C, 54.85; H, 4.60; Br, 40.55. Found: C, 55.04; H, 4.64; Br, 40.40. IV reacted smoothly with one equivalent of N-bromosuccinimide in refluxing carbon tetrachloride yielding the tribromo compound V, m.p. 105–105.5° (dec). *Anal.* Calcd. for $\text{C}_{18}\text{H}_{17}\text{Br}_3$: C, 45.70; H, 3.62; Br, 50.68. Found: C, 45.74; H, 3.61; Br, 49.96. Simultaneous elimination and displacement could be brought about by treatment of V with excess trimethylamine at 50°. The bis-quaternary salts, VI and VII, were separated by virtue of their differing solubility in methylene chloride. The more soluble isomer was recrystallized from water to give colorless needles, m.p. 185–187° (dec). *Anal.* Calcd. for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{Br}_2$: C, 56.48; H, 6.71; N, 5.49; Br, 31.32. Found: C, 56.23; H, 6.76; N, 5.49; Br, 31.46. The less soluble isomer, m.p. 200–202° (dec.), was characterized as its dipicrate, m.p. 228–230° (dec.). *Anal.* Calcd. for $\text{C}_{36}\text{H}_{38}\text{O}_{14}\text{N}_8$: C, 53.60; H, 4.75; N, 13.89. Found: C, 53.73; H, 4.61; N, 13.95. Either isomer, when converted to the bis-quaternary hydroxide and subjected to Hofmann degradation at 120–140° (0.5 mm.), yielded the triene I as a colorless crystalline solid. After resublimation at 40° (0.3 mm.), I showed m.p. 44–45°. *Anal.* Calcd. for $\text{C}_{18}\text{H}_{14}$: C, 93.87; H, 6.13. Found: C, 93.65; H, 6.05. The triene I could be kept at 0° under nitrogen for several days without visible change. However, at room temperature it rapidly turned yellow within a few hours and eventually formed a polymer. In the ultraviolet I (isoöctane soln.) showed the following maxima ($\log \epsilon$'s in parentheses): 237 $m\mu$ (4.42); 262 $m\mu$ (4.50); 328 $m\mu$ (4.20). The infrared spectrum revealed

(2) E. J. Smutny and J. D. Roberts, *ibid.*, **77**, 3420 (1955); M. P. Cava and D. R. Napier, *ibid.*, **79**, 3606 (1957).

(3) H. I. Bernstein and W. C. Quimby, *ibid.*, **65**, 1845 (1943).