(**C**).—Five drops of concentrated sulfuric acid was added to a solution of 5 g. of 5-amino-3-methyl-1-phenylpyrazole and 1 ml. of 90% hydrogen peroxide[27] in 30 ml. of glacial acetic acid, cooled in ice so that the temperature remained below 40° (otherwise the reaction is very exothermic). The deep-red solution was evaporated *in vacuo*. Extraction of the red oil with 95% alcohol left a residue of 1.8–2.0 g. of compound IX. The sticky red-brown semi-solid left on evaporation of the alcohol was extracted with ether to give 0.1 g. of tan needles, m.p. 113°; mixed m.p. with products from (B) and (C) undepressed. (In one experiment 0.2 g. of orange-red needles, m.p. 70–80°, was obtained from this ether solution (lit. m.p. for Quilico and Justoni's isomer,[14] 81°). On recrystallization from dilute ethanol it was converted to light tan needles, m.p. 103–106°.) The infrared spectrum was characterized by prominent bands at 2.96, 3.15, 3.28, 3.42, 3.53, 5.9, 6.1, 6.18, 6.25, 6.54, 6.66, 6.76, 6.87, 7.18, 7.63, 10.1, 10.9, 11.9 and 13.1 μ.

Anal. Calcd. for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.5; C-methyl, 1.0; mol. wt., 205. Found: C, 58.22; H, 5.42; N, 19.8; C-methyl, 0.96; mol. wt., 188.

In the early stages of this work, when this compound was thought possibly to be "azipyrazole," its dipole moment was determined to check the possibility of a mesoionic structure. The dielectric constant of benzene solutions was determined by the standing microwave technique.[28] The calculated dipole moment was 0.86 *D*.

3-(Phenylazo)-crotononitrile (Azipyrazole). (**A**).—To 0.05 g. of 3-(phenyl-NON-azoxy)-crotonamide dissolved in 15 ml. of chloroform at 0°, 0.05 ml. of phosphorus trichloride was added, and the solution was refluxed 1 hr. After cooling, 25 ml. of water was added and the mixture was made alkaline with sodium hydroxide. The chloroform layer was dried with sodium sulfate and the solvent then was removed *in vacuo*. The light brown residual solid was sublimed at 90° (0.05 mm.) to give 10 mg. (30%) of ivory-white needles, m.p. 109°. The m.p. was unchanged after recrystallization from dilute alcohol.

(**B**).—Vacuum sublimation of the red oil described in (C) for the azoxy compound gave 20 mg. of the same product.

(**C**).—To a solution of 1.0 g. of diacetonitrile phenylhydrazone in 35 ml. of absolute alcohol was added 2 g. of yellow mercuric oxide, and the mixture was refluxed for 2 hr. The free mercury was filtered off and most of the alcohol distilled off, leaving a red oil. This was partially soluble in light petroleum ether; the insoluble part was then dissolved in ethyl ether. Evaporation of the solvent from the ethyl ether solution gave 0.3 g. of tan needles, m.p. 105–107°. Vacuum sublimation as described above gave 0.20 g. (26%) of ivory-colored needles, m.p. 109°. The mixed melting points of the 109° products from these three methods were undepressed and all had the same infrared spectrum. The latter was characterized by prominent bands at 4.45, 6.20 and 6.25 μ, as well as at 3.53, 3.44, 5.80, 5.87, 5.93, 6.07, 6.31, 6.65, 6.73, 7.31, 7.95 and 8.25 μ.

Anal. Calcd. for $C_{10}H_9N_3$: N, 24.55. Found: N, 24.22.

Derivatives were prepared as follows: **5-amino-3-methyl-1-phenylpyrazole**, m.p. 113–115° (lit.[26] m.p. 115–116°), when azipyrazole was boiled a few minutes in 10% sodium hydrosulfite solution and filtered. **5-Amino-4-iodo-3-methyl-1-phenylpyrazole**, m.p. 75° (lit.[1a] m.p. 75°), when azipyrazole was warmed a few minutes with concentrated hydriodic acid, followed by saturating the solution with sodium hydroxide, extracting with ether and removing the ether from the extract by evaporation. **5-Amino-4-bromo-3-methyl-1-phenylpyrazole**, m.p. 105° (lit.[1a] m.p. 106.5° and mixed m.p. with azipyrazole 83–99°), was obtained by the same procedure using 48% hydrobromic acid.

Evaporation of the solvent from the petroleum ether extract of the reaction mixture in (C) left 50 mg. of stout red needles, m.p. 73–76°; after recrystallization from alcohol they melted at 82–83°.

Anal. Calcd. for $C_{10}H_9N_3$: N, 24.55. Found: N, 24.83.

3-(Phenylazo)-crotononamide (V).—Ethyl 3-(phenylazo)-crotonate was prepared in 10% yield by the reaction of mercuric oxide on ethyl acetoacetate phenylhydrazone[9]; red crystals, m.p. 50°. A solution of 80 mg. of this azo-ester and 2 g. of dry ammonia in 10 ml. of absolute ethanol was heated in a sealed tube 10 hr. at 110°. On subsequent evaporation of the solvent 60 mg. (90%) of a black crystalline solid, m.p. 74°, remained. (In another run the yield on this reaction was 60%.)

Anal. Calcd. for $C_{10}H_{11}N_3O$: N, 22.22. Found: N, 21.92.

The above amide (40 mg.) was added to 5 ml. of an ether solution of monoperphthalic acid,[29] containing 1×10^{-3} mole of the latter. After standing two days, sodium bicarbonate was added to neutralize the acid present. The ether solution was separated, dried and evaporated *in vacuo*, leaving tan needles, melting at 113°, identical with the 3-(phenyl-NON-azoxy)-crotonamide previously described.

Azipyrazole from V.—Phosphoric anhydride (100 mg.) was added to a solution of 50 mg. of 3-(phenylazo)-crotonamide in 15 ml. of benzene. The mixture was refluxed 30 minutes, cooled and filtered. The solvent was removed from the filtrate *in vacuo*. The white needles obtained (about 15 mg.) melted at 109° and the mixed melting point with azipyrazole prepared by other methods was also 109°.

Acknowledgments.—We wish to thank Dr. John G. Erickson for his kind encouragement and valuable comments, Dr. Louis D. Ellsworth for his aid with the dipole moment measurement and Dr. Basil Curnutte for his assistance in selecting the N–O bands in the infrared spectra of the azoxy compounds.

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[27] The generous gift of Becco Chemical Division, Food Machinery and Chemical Corporation, Buffalo, New York.

[28] M. G. Haugen and W. B. Westphal, N.D.R.C. Report 541, Insulation Res. Lab., Mass. Inst. Tech., Oct., 1945.

[29] H. Bohme, *Org. Syntheses*, **20**, 70 (1940).

MANHATTAN, KANSAS

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORIES OF HARVARD UNIVERSITY]

Preparation and Thermal Rearrangement of Several Dicyclopentadiene Derivatives

BY MYRON ROSENBLUM[1]

RECEIVED DECEMBER 20, 1956

Oxidation of dicyclopentadiene with selenium dioxide in aqueous dioxane solutions has been shown to yield 1-dicyclopentadienol. The oxidation of this alcohol under Oppenauer conditions affords 1-dicyclopentadienone, and its pyrolysis leads to the formation of cyclopentadiene and 2-cyclopentenone. Treatment of 1-dicyclopentadienone with both methyl and phenyl Grignards leads to the formation of the corresponding tertiary alcohols, 1-methyldicyclopentadiene-1-ol and 1-phenyldicyclopentadiene-1-ol. Pyrolysis of 1-acetoxydicyclopentadiene, prepared by acetylation of 1-dicyclopentadienol, affords azulene in low yield.

The synthesis of oxygenated derivatives of dicyclopentadiene has hitherto been confined to the di- and tetrahydro members of the parent diene,[2] although a considerable number of polyalkyl,

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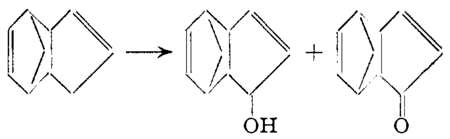
[1] Department of Chemistry, The Illinois Institute of Technology, Chicago 16, Ill.

[2] *Cf.* "Elsevier's Encyclopedia of Organic Chemistry," Vol. XIII, Elsevier Publishing Co., N. Y., 1946, pp. 1018–1032.

polyaryl and polyhalo dicyclopentadienes possessing oxygen functions at either or both positions 1 and 8 of the tricyclic system are known.[3,4]

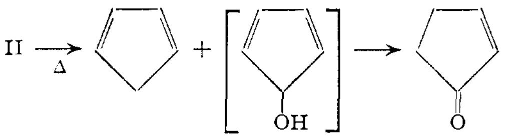
The present paper describes the preparation of several new oxygenated derivatives of dicyclopentadiene and includes a preliminary account of the behavior of some of these on pyrolysis.

Oxidation of dicyclopentadiene (I) with selenium dioxide in dioxane–water solutions afforded 1-dicyclopentadienol (II) in 57% yield, together with a small amount of 1-dicyclopentadienone (III). This alcohol had previously been prepared by Vanelli[5] by hydrolysis of 1-acetoxydicyclopentadiene (IV), obtained by treatment of dicyclopentadiene with selenium dioxide in acetic acid medium.



I II III

Slow distillation of II at atmospheric pressure gave cyclopentadiene and 2-cyclopentenone (V) in 42% yield, while vapor phase pyrolysis at reduced pressures resulted in an essentially quantitative conversion of II to V and cyclopentadiene. The formation of V may be viewed as proceeding *via* an initial reverse Diels–Alder reaction followed by isomerization of the transient 2,4-cyclopentadienol (VI).

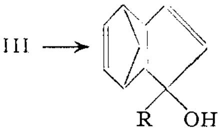


VI V

The reaction sequence I → II → V constitutes a useful procedure for the preparation of 2-cyclopentenone which has heretofore been obtained either by allylic oxidation of cyclopentene[6] or by dehydrohalogenation of 1-halocyclopentanone.[7] Of these methods only that of Treibs[6b] and of Corey[7c] are of preparative value.

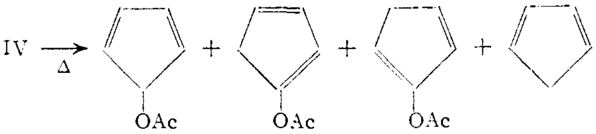
Oppenauer oxidation of II, employing *p*-quinone as oxidant, gave 1-dicyclopentadienone (III) in 79% yield.[8] Attempts to effect the thermal reversal of III to cyclopentadiene and the unknown cyclopentadienone were unsuccessful. Unlike II, the ketone III resisted pyrolysis at temperatures well above those sufficient to effect reversal of II to its diene and dienophile components.

Treatment of II with both methyl and phenyl Grignards afforded the corresponding tertiary alcohols, 1-methyldicyclopentadiene-1-ol (VII) and 1-phenyldicyclopentadiene-1-ol (VIII). The pyrolysis of these compounds has not as yet been explored.



VII, R = Me
VIII, R = C_6H_5

Pyrolysis of 1-acetoxydicyclopentadiene, prepared by acetylation of II, led to the formation of cyclopentadiene and a mixture of acetoxycyclopentadienes (IX, X, XI).[5] When this mixture was heated at 150° for 3 hr. and then repyrolyzed at atmospheric pressure, acetic acid was evolved and azulene, identified by its melting point and its ultraviolet absorption spectrum,[9] was isolated in low yield.



IX X XI

The identity of the isomer, present in the complex mixture of diacetoxydicyclopentadienes formed by dimerization of IX, X and XI, which on rearrangement gives rise to azulene, is being investigated.

Acknowledgment.—We are indebted to Professor R. B. Woodward, who suggested this problem, for many valuable discussions during the course of the investigation.

Experimental

1-Dicyclopentadienol (II).—Freshly distilled dicyclopentadiene, 185 g. (1.4 moles), was dissolved in a mixture of 500 ml. of dioxane and 50 ml. of water. Selenium dioxide, 66.5 g. (0.6 mole), was added, and the solution was stirred and heated under reflux for 3 hr. The resulting dark brown mixture was then filtered from selenium and poured into two liters of water. The heavy dark oil was drawn off and the aqueous solution was extracted with 600 ml. of ether in three portions. The organic solutions were combined, washed with water and dried over magnesium sulfate. Removal of solvent, followed by fractionation of the crude product, gave 1-dicyclopentadienol as a pale yellow, viscous oil; yield 100.2 g. (57%), b.p.'s 84° (3 mm.), 90° (5 mm.) and 106° (7 mm.). Redistillation resulted in a colorless product whose infrared spectrum was identical with that of II prepared earlier by Vanelli[5] by hydrolysis of 1-acetoxydicyclopentadiene.

1-Dicyclopentadienone (III).—A mixture of 52.5 g. of 1-dicyclopentadienol (0.36 mole), 48.0 g. of *p*-quinone (0.45 mole) and 87.0 g. of aluminum *t*-butoxide (0.36 mole) in 650 ml. of dry benzene was stirred at 50° for 6 hr. At the end of this period, the dark purple solution was allowed to cool and was decomposed with water. Aluminum hydroxide was filtered off and washed thoroughly with ether. The combined benzene–ether solution was extracted five times with 100-ml. portions of 5% sodium hydroxide solution, washed with water to neutrality and finally dried over magnesium sulfate. After evaporation of solvent, the product was distilled at 82–87° (4 mm.) as a pale yellow oil, which crystallized on being cooled to room temperature; yield 41.0 g. (79%). A portion was recrystallized several times from low boiling petroleum ether to give the pure ketone as colorless plates, m.p. 59.0–59.5°.

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[3] *Cf.* C. F. H. Allen, *Chem. Revs.*, **37**, 209 (1945).

[4] E. T. McBee and R. K. Meyers, THIS JOURNAL, **77**, 88 (1955).

[5] R. Vanelli, Ph.D. Thesis, Harvard University, 1950.

[6] (a) E. Dane and K. Eder, *Ann.*, **539**, 207 (1939). (b) W. Treibs, B. Franke, G. Leichsenring and H. Roder, *Ber.*, **86**, 616 (1953).

[7] (a) M. Godchot and F. Taboury, *Bull. soc. chim. France*, **13**, 545 (1913); (b) M. Mousseron, R. Jacquier and A. Fontaine, *ibid.*, 767 (1952); (c) E. J. Corey and Kunizo Osugi, *Pharm. Bull. Japan*, 1, 99 (1953).

[8] H. Hock and F. Depke, *Ber.*, **84**, 356 (1951), have reported the isolation of a ketone $C_{10}H_{10}O$ from the air oxidation of dicyclopentadiene to which they ascribe the structure of 1-dicyclopentadienone (III). However, their observation that the substance was an oil which resisted crystallization must cast doubt upon its identity, since the ketone prepared as described in this report is a readily crystallizable solid melting at 59°.

[9] Pl. A. Plattner and E. Heilbronner, *Helv. Chim. Acta*, **31**, 804 (1948).

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.67; H, 7.18.

A 2,4-dinitrophenylhydrazone derivative, crystallized from ethyl alcohol, melted at 203.5–204.0°.

Anal. Calcd. for $C_{16}H_{14}N_4O_4$: C, 58.89; H, 4.32; N, 17.17. Found: C, 58.71; H, 4.54; N, 17.13.

1-Acetoxydicyclopentadiene (IV).—1-Dicyclopentadienol, 50 g., was dissolved in 130 ml. of pyridine containing 100 ml. of acetic anhydride. After standing at room temperature for 12 hr., the solution was poured onto ice and the heavy dark oil was separated. The aqueous solution was extracted twice with 100-ml. portions of ether, and these extracts were combined with the oil. The organic solution was washed several times with dilute hydrochloric acid and then with water to neutrality. After drying the solution over Drierite, solvent was evaporated and the residue was fractionated. The ester distilled at 118.5–120.5° (14.5 mm.), yield 55.6 g. (87%). Its infrared spectrum was identical with that of 1-acetoxydicyclopentadiene prepared earlier by Vanelli.[5]

2-Cyclopentenone (V). **By Pyrolysis of 1-Dicyclopentadienol at Atmospheric Pressures.**—1-Dicyclopentadienol, 48.85 g., was placed in a 250-ml. claisen flask having a six-inch side arm. The flask was heated over a free flame as a slow stream of dry nitrogen was passed through the alcohol. The distillate temperature was maintained at 140–150°. A slower rate of distillation resulted generally in greater polymerization of the material in the distilling flask. The distillate, containing unchanged alcohol, cyclopentadiene and 2-cyclopentenone, was fractionated to give 8.29 g. of ketone V, b.p. 50° (15 mm.), n^{25}D 1.4753 (lit.[7c] b.p. 53° (16 mm.), $n^{18.2}$D 1.4780), and 13.13 g. of unchanged 1-dicyclopentadienol. The yield of 2-cyclopentenone, corrected for recovered alcohol, was 42%. Its dinitrophenylhydrazone derivative, m.p. 169–171°, was identical by mixed m.p. determination with that prepared from an authentic sample of 2-cyclopentenone.

2-Cyclopentenone (V). **By Vapor Phase Pyrolysis** of **1-Dicyclopentadienol at Reduced Pressures.**—The apparatus used in these and later experiments consisted of a 25-ml. round-bottom flask, surmounted by a small addition funnel. One of two side-arm tubes joined to the flask served as an inlet for nitrogen while the other led directly to the pyrolysis chamber. The latter consisted of a horizontally mounted Pyrex tube, 30 cm. in length and 1.8 cm. in diameter, heated by means of a multiple unit electric furnace. The pyrolysis tube was connected to a receiver flask, vacuum gage and pump. Temperatures within the pyrolysis chamber were measured by means of an iron–constantan thermocouple.

With the apparatus evacuated to a pressure of 5–7 mm. (nitrogen atmosphere) and the pyrolysis tube heated to a temperature of 450°, the alcohol was allowed to drop slowly from the addition funnel into the distilling flask, heated by means of a oil-bath to 200°. The alcohol was thus immediately volatilized and swept into the pyrolysis chamber by the nitrogen stream and thence into the receiver flask cooled in a Dry Ice–acetone-bath. Infrared spectra taken of the products of several runs, after allowing the cyclopentadiene to evaporate, failed to reveal the presence of any unchanged alcohol and were essentially identical with that of 2-cyclopentenone obtained by pyrolysis of II at atmospheric pressures. Polymeric residues in the distillation flask and the pyrolysis chamber were negligible.

Attempted Pyrolysis of **1-Dicyclopentadienone** (III).—When small amounts of the ketone III were heated in a distilling flask at 200–250° in an attempt to effect a reverse Diels–Alder reaction, a part of the ketone distilled unchanged while the remainder polymerized in the distilling flask.

1-Methyldicyclopentadiene-1-ol (VII).—1-Dicyclopentadienone, 10.0 g. (0.069 mole), dissolved in 20 ml. of anhydrous ether, was added dropwise to a stirred solution of methylmagnesium iodide prepared from 1.75 g. (0.069 mole) of magnesium turnings and 12.0 g. (0.085 mole) of methyl iodide in 40 ml. of anhydrous ether. The solution was refluxed on the steam-bath for 30 minutes following addition of the ketone and was then cooled and decomposed with saturated ammonium chloride solution. The aqueous phase was separated, extracted several times with ether, and the ethereal extracts were combined, washed to neutrality with water and dried over calcium sulfate. Evaporation of solvent left 7.85 g. (70%) of pale yellow oil which solidified on cooling. A portion of this material, after several recrystallizations from low boiling petroleum ether, followed by sublimation, yielded pure 1-methyldicyclopentadiene-1-ol as fine colorless needles, m.p. 49.0–49.5°.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.50; H, 8.70. Found: C, 81.50, 80.71; H, 9.08, 8.77.

1-Phenyldicyclopentadiene-1-ol (VIII).—1-Dicyclopentadienone, 2.0 g. (0.014 mole), dissolved in 10 ml. of anhydrous ether, was added dropwise to a stirred solution of phenylmagnesium bromide prepared from 2.15 g. (0.14 mole) of bromobenzene and 0.38 g. (0.016 mole) of magnesium turnings in 45 ml. of anhydrous ether. The solution was refluxed on the steam-bath for 30 minutes following addition of the ketone and was then cooled and decomposed with saturated ammonium chloride solution. The aqueous phase was separated and extracted several times with ether. The ether solutions were combined, washed to neutrality and dried over calcium sulfate. The crude solid, isolated on evaporation of solvent, was recrystallized twice from low boiling petroleum ether to give 0.75 g. (33%) of 1-phenyldicyclopentadiene-1-ol, m.p. 65.5–66.5°.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 86.28, 85.76, 85.79; H, 7.33, 7.39, 7.22.

Azulene. By Pyrolysis of 1-Acetoxydicyclopentadiene.—The apparatus described above in the pyrolysis of 1-dicyclopentadienol was employed in this experiment. The acetate, 10.4 g., was allowed to drop slowly into the distilling flask which was heated to a temperature of 190–200°. A pressure of 5–7 mm. (nitrogen atmosphere) was maintained during the course of the pyrolysis, and the pyrolysis chamber was heated to 440–475°. At the end of 1 hr. addition of the acetate was complete, and 10.4 g. of orange oil had been collected in the receiver flask. The product was heated in an atmosphere of nitrogen at a temperature of 150° for 3 hr. A portion of this material, 7.8 g., was placed in a short path distillation flask containing 1.95 g. of calcium oxide powder, and the flask was immersed in a Woods metal-bath preheated to 240°. A slow stream of nitrogen was bubbled through the mixture during the course of the pyrolysis. After the contents of the flask had been heated for 15 minutes and the bath had reached a temperature of 255°, vacuum was applied, and 1.70 g. of pale blue distillate was collected. Following another brief period of heating, when the bath temperature had risen to 265°, vacuum was again applied, and an additional 1.12 g. of dark blue liquid was collected. The two distillate fractions were combined and placed on a chromatographic column prepared from 16 g. of alumina. On elution with low boiling petroleum ether, the blue component moved rapidly down the column as a well defined zone. This material was rechromatographed three times on 8-g. alumina columns, and in this manner 2.5 mg. of dark blue crystalline material, m.p. 92–95° (with sublimation), was isolated after removal of solvent. The ultraviolet spectrum of the product, taken in 95% ethanol solution, was identical with that of azulene reported by Plattner and Heilbronner.[9]

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