The product obtained from band 5 consisted of alcohol and glycol components and resisted attempts at crystallization.

Resistance of 1,2-Diacetylferrocene (VIa) to Further Acetylation. A. Room Temperature Reaction.—A solution containing 0.90 cc. (0.113 mole) of acetyl chloride and 1.10 g. (8.3 mmoles) of aluminum chloride in 10 cc. of methylene chloride (dried over Drierite) was prepared and filtered through glass wool into the reaction vessel. The solution was stirred at room temperature in an atmosphere of dry nitrogen while 0.070 g. (0.26 mmole) of 1,2-diacetylferrocene dissolved in 10 cc. of dry methylene chloride was added over a period of 15 minutes. After stirring at room temperature for four hours, the intensely violet solution was cooled and decomposed with water. The aqueous phase was separated, extracted with ether until colorless, and the combined organic solutions were washed to neutrality and dried. Removal of solvent *in vacuo* left 0.111 g. of partially crystalline material. This was taken up in a small volume of benzene and chromatographed on 10 g. of alumina. After developing the chromatogram by elution with benzene, the alumina was withdrawn from the column, and the broad orange band was cut away from resinous material at the top of the column and extracted thoroughly with chloroform. Removal of chloroform *in vacuo* left 60 mg. of product, m.p. 84–94°, which after one recrystallization from ether–petroleum ether yielded 45 mg. of material, m.p. 95–97°, identical by mixed melting point with 1,2-diacetylferrocene. From the mother liquors, after several recrystallizations, an additional 3 mg. of 1,2-diacetylferrocene was recovered.

B. **Reaction at 40°.**—1,2-Diacetylferrocene (0.135 g., 0.5 mmole) dissolved in 10 cc. of dry methylene chloride was added to a stirred suspension containing 0.70 g. of aluminum chloride and 0.30 cc. of acetyl chloride in 20 cc. of the same solvent. No evolution of hydrogen chloride was evident either on mixing the reactants or during the subsequent two hours when the mixture was stirred at room temperature. At the end of this period an additional 0.70 g. of aluminum chloride and 0.30 cc. of acetyl chloride were added and the reaction mixture was warmed on the steam-bath for 1.25 hours. During this period hydrogen chloride was evolved slowly. When 8.6 cc. of 0.1 *N* sodium hydroxide solution had been titrated by the emergent gas, the reaction was cooled, decomposed with ice and filtered from alumina. The aqueous solution was separated, washed several times with chloroform, and the combined organic solutions were washed to neutrality and dried. Solvent was removed *in vacuo*, leaving a dark red gum. The crude product was taken up in benzene and chromatographed on 25 g. of alumina. Of the three bands which appeared on the column, the first was eluted with 5% chloroform–benzene, the second with 20% chloroform–benzene, and the third with 50% chloroform–benzene.

Fraction 1 was recrystallized twice from ether–petroleum ether to give 21 mg. of product, m.p. 96.5–98.0°, identical with 1,2-diacetylferrocene by mixed melting point. Neither fraction 2 nor 3 could be crystallized; the spectra of both of these possessed bands at 9.00 and 9.95 μ in the infrared.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE]

Reactions of Active Methylene Compounds in Pyridine Solution. I. The Ionic Autoxidation of Fluorene and its Derivatives[1]

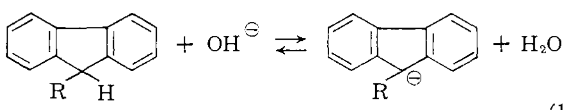
BY YAÏR SPRINZAK

RECEIVED APRIL 7, 1958

Fluorenes are oxidized smoothly by oxygen to fluorenones in pyridine solution and in the presence of benzyltrimethylammonium hydroxide. 9-Alkylfluorenes give 9-hydroperoxy-9-alkylfluorenes and 9-alkylfluorenols. This high reactivity is attributed to the presence of appreciable concentration of carbanions, recognizable by the color of their solutions. The reaction provides a convenient method for the preparation in high yields of oxygen compounds belonging to the above three classes. Low temperature oxidation of 2,3-diphenylindene affords 2,3-diphenylindone and a tertiary hydroperoxide, identified as 1-hydroperoxy-1,2-diphenylindene.

The present work was undertaken following the observation that substituted fluorenes, such as 2-nitro and 2,7-dibromofluorene, are oxidized by silver acetate in pyridine solution, at ordinary temperatures, to yield polymeric substances.[1] This reactivity was attributed to an increased ionizability of the hydrogen atoms at the 9-position of the fluorene molecule both owing to the presence of appropriate substituents and to the influence of the medium. It was therefore anticipated that a strong base, such as the hydroxide ion, might, in the same solvent, produce carbanions in appreciable concentration from fluorene and its derivatives.

Thus, when benzyltrimethylammonium hydroxide (Triton B), an alkali-like compound remarkable for its solubility in non-hydroxylic solvents, is added to a solution of fluorene in pyridine, an orange-yellow color develops. The color fades gradually with the addition of a foreign solvent (*e. g.*. water, alcohol, benzene, heptane), but reappears when sufficient pyridine is subsequently added to the mixture. It is assumed that the appearance of color is indicative of an ionization process wherein colored fluoryl ions are formed (eq. 1, R = H), and that the fading of the color brought about by changing the composition of the medium represents a reversal of the process.[2]



(1)

The faculty of developing a color under the action of Triton B in pyridine appears to be shared by all hydrocarbons of the cyclopentadiene series in which at least one hydrogen atom of the active methylene group is present. Thus, 1,2,3,4-tetraphenylcyclopentadiene, 2,3-diphenylindene and 9-ethylfluorene form reddish solutions, while indene

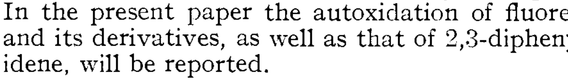
---

[1] Presented in part at the XIVth International Congress of Pure and Applied Chemistry, Zurich, July 1955; Congress Handbook, p. 66.

[2] While it is felt that the bulk of the observations here reported provide substantial support for this assumption, experiments are in progress with a view to obtaining more direct evidence as to the presence of carbanions under the prescribed conditions as distinct from related systems (*e.g.*, a solution of fluorene in alcoholic sodium hydroxide) where the formation of carbanions is generally postulated to account for chemical reactions (see A. Alexander, "Principles of Organic Ionic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 123 ff.).

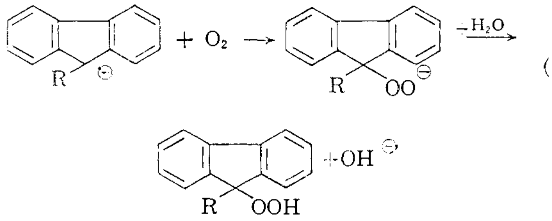
gives a yellow solution. In addition, phenylacetonitrile and related compounds exhibit the same property, giving yellow solutions. All the colored solutions obtained in the manner described above exhibit high reactivity toward a variety of reagents. In the present paper the autoxidation of fluorene and its derivatives, as well as that of 2,3-diphenylidene, will be reported.

When a solution of fluorene in pyridine is stirred in an atmosphere of oxygen at room temperature in the presence of a small amount of Triton B, one mole of oxygen per mole of fluorene is absorbed with heat evolution, and fluorenone is formed in almost quantitative yield (eq. 2).[3] The reaction is not sensitive to light and begins without an induction period. When 9-benzylfluorene is used and the oxidation is carried out at 40°, one-half mole of oxygen is consumed per mole of hydrocarbon, and the product is 9-benzylfluorenol. The end of the reaction is marked by the fading of the red color of the solution.

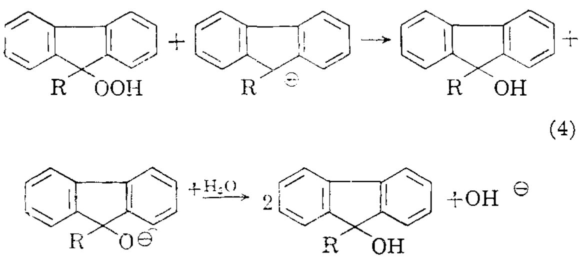


(2)

The autoxidation apparently proceeds by an ionic mechanism and, in the case of a 9-alkylfluorene, may be represented by the scheme[4]



(3)



(4)

In fact, not only can the presence of a hydroperoxide be detected in the crude product, but, when the oxidation of a 9-alkylfluorene is carried out at a temperature sufficiently low (−15°), reaction 4 becomes slow relatively to reaction 3 and the solution can be made to absorb one mole of oxygen per mole of hydrocarbon.[5] The hydroperoxide, a stable, crystalline compound, can be isolated readily in a high yield. Furthermore, the addition at room temperature of one equivalent of the hydroperoxide to a pyridine solution containing one equivalent of the parent hydrocarbon and a catalytic amount of Triton B (in an atmosphere of nitrogen) resulted in the formation of two equivalents of the corresponding fluorenol (eq. 4). The end of the reaction was indicated by the disappearance of the pink color of the solution.

With purely aliphatic alkylfluorenes, such as 9-methyl- and 9-ethylfluorene, a considerable amount of hydroperoxide was produced along with the corresponding carbinol even when the oxidation was performed at 40°. The reduction of the hydroperoxide (eq. 4) seems therefore to be relatively slower in these cases than in the case of 9-benzylfluorene. Thus, the oxygen uptake was ordinarily higher than 0.5 mole per mole of hydrocarbon, the actual volume absorbed in each case being closer to this lower limit the slower the agitation (that is, the slower the oxygen supply to the solution). With 9-phenylfluorene, on the other hand, an appreciable amount of 9-phenylfluorenol is formed even at −15°, a lower temperature (−40°) being necessary in order to suppress reaction of the intermediate hydroperoxide with the hydrocarbon (eq. 4).

No hydroperoxide could be detected in the product of the oxidation of fluorene (eq. 2) even when the reaction was carried out at −40°. Presumably the hydroperoxide formed is rapidly converted to fluorenone, by a mechanism previously suggested by Kornblum[6] for the dehydration of secondary hydroperoxides under alkaline conditions. The high instability of 9-hydroperoxyfluorene and its almost instantaneous conversion to fluorenone under the reaction conditions was confirmed by an experiment in which a pyridine solution of the peroxide[7] was treated with Triton B at −40°.

The present autoxidation reaction[8] constitutes a

---

[3] A. A. Vanscheidt [*C. A.*, **29**, 2160 (1935)] suggests a color test for fluorenes, based on the observation that a change of color, due to oxidation, is produced when a boiling solution of the hydrocarbon in acetone or pyridine is shaken with methanolic potassium hydroxide. Previously [*Ber.*, **59B**, 2092 (1926)] the same author reported the autoxidation of 1,2,7,8-dibenzofluorene to the corresponding fluorenone under similar conditions, using acetone, as well as the autoxidation of dibiphenylene-ethane and related compounds to the corresponding dibiphenylene-ethenes in hot pyridine and in the presence of methanolic potassium hydroxide [*C. A.*, **21**, 3616 (1927)].

[4] The following observations indicate that the rate of oxidation (eq. 3) is determined by the ionization step: when stirring is speeded up to a certain point, the solution becomes colorless, and further speeding does not further increase the rate of absorption of oxygen. When the stirring is stopped or slowed down sufficiently, the pink color of the solution reappears.

[5] A free radical mechanism, proceeding by an ion-radical chain and involving a peroxy radical has been proposed recently by G. A. Russell [THIS JOURNAL, **76**, 1595 (1954)] for the autoxidation of 2-nitropropane in water or in alcohol under alkaline conditions. Evidence for this mechanism is based mainly on the occurrence of autocatalysis and of catalysis or inhibition by certain additives. These features are not present in the oxidations studied here. Addition of ferric chloride, picric acid, quinone, manganese dioxide and arsenic trioxide did not have any effect on the rate of oxidation of fluorene and 9-benzylfluorene. According to Russell ferric chloride was an efficient catalyst in the oxidation of 2-nitropropane, while arsenic trioxide inhibited the reaction completely.

[6] N. Kornblum and H. E. DeLaMare, THIS JOURNAL, **73**, 880 (1951).

[7] H. Hock, S. Lang and G. Knauel (*Chem. Ber.*, **83**, 227 (1950)), who had prepared this hydroperoxide by light-catalyzed autoxidation of fluorene, describe it as a colorless, crystalline compound melting at 93° and of poor stability in the presence of air and light. Following the instructions given, the author could only isolate a (stable) substance in yellow crystals, melting at 91–93° and corresponding in composition and properties to a 1:1 molecular compound of 9-fluoryl hydroperoxide and fluorenone. Details on the isolation and properties of this compound will be given elsewhere.

[8] For autoxidations of oxygen compounds (quinols, ketones and esters) under alkaline conditions, see, *e.g.*, W. Manchot, *Ann.*, **314**, 177 (1900); C. Dufraisse and S. Ecary, *Compt. rend.*, **223**, 1143 (1946); J. Rigaudy, *ibid.*, **228**, 253 (1949); W. von E. Doering and R. M. Haines, THIS JOURNAL, **76**, 482 (1954); C. Dufraisse, A. Etienne et J. Rigaudy, *Bull. soc. chim. France*, [5] **15**, 804 (1948). The latter

TABLE I

OXIDATION OF FLUORENES TO FLUORENONES[u]

Substituent	Mole	Reaction time, min.	O_2 absorbed, ml.	Melting point, °C. Crude	Recrystd.	Lit.	Yield of recrystd. product, %
None	0.200	40	4940	79–82.5	84–85	83.5–84.5[l]	90
2-Methyl[a]	.010	46	255	89–90.5	91.5–92.5	92[m]	88
1,2,3,4-Dibenzo[b]	.005	75	117	175–177	187.5–188.5	186–187[n]	75
2-Bromo[c]	.020	35	507	145–147	148–149.5	149[o]	91
2,7-Dibromo[d]	.010	67	254	202–204	205.5–207	202[p]	86
2-Acetyl[e]	.020	98	485	154–158	160–161.5	162–163[q]	73
2-Acetamino[f]	.020	304	460	218–224	231–232	227–228[r]	65
2-Hydroxy[g]	.010	83	262[j]	210–212	213.5–214.5	211[s]	85
4-Carboxy[h]	.005	40	116[k]	228–230	229.5–230.5	227 cor.[t]	90
2-Nitro[i]	.010	85	252	203–215	217–219	222–223 cor.[s]	45

[a] L. Mascarelli and B. Longo, *C. A.*, **32**, 4564 (1938). [b] E. Bergmann and F. Bergmann, THIS JOURNAL, **60**, 1805 (1938). [c] J. T. Thurston and R. L. Shriner, *ibid.*, **57**, 2163 (1935). [d] A. Sieglitz, *Ber.*, **53**, 1232 (1920). [e] F. E. Ray and G. Rieveschl, Jr., "Organic Syntheses," Coll., Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 448. [f] O. Diels, E. Schill and S. Tolson. *Ber.*, **35**, 3284 (1902). [g] C. Ruiz, *Chem. Zentr.*, 101, II, 1074 (1930). [h] W. E. Bachmann and J. C. Sheehan, THIS JOURNAL, **62**, 2687 (1940). [i] W. E. Kuhn, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 447. [j] Thirty ml. of pyridine and 5 ml. of Triton B were used, and the water of neutralization was removed by distilling off 10 ml. of solvent *in vacuo*. [k] Fifteen ml. of pyridine and 2.5 ml. of Triton B were used, and 5 ml. of solvent was distilled as in *j*. The actual volume of oxygen absorbed is probably higher owing to absorption during the distillation. [l] E. H. Huntress, E. B. Hershberg and J. S. Cliff, THIS JOURNAL, **53**, 2720 (1931). [m] O. Kruber, *Ber.*, **65**, 1382 (1932). [n] C. F. Koelsch, THIS JOURNAL, **56**, 480 (1934). [o] M. Gomberg and J. C. Pernert, *ibid.*, 48, 1372 (1926). [p] A. Werner and A. Egger, *Ber.*, **37**, 3026 (1904). [q] Elsevier's "Encyclopedia of Organic Chemistry," Vol. 13, Series III, 1946, p. 91. [r] O. Gerhardt, *Monatsh.*, **41**, 199 (1920). [s] O. Diels, *Ber.*, **34**, 1758 (1901). [t] Ref. *q*, p.108. [u] Ten ml. of pyridine and 0.25 ml. of a 40% pyridine solution of Triton B were used per 0.01 mole of the fluorene; temp. 25°.

convenient method for the preparation of fluorenone and related compounds, as well as for that of tertiary 9-fluoryl hydroperoxides and the corresponding fluorenols.[9,10]

In the oxidation of fluorenes to fluorenones (Table I), the volume of oxygen absorbed, in most cases, closely approached the calculated value (approximately 250 ml. per 0.01 mole) and, with the exception of 2-nitrofluorene, the melting point of the crude product was close to that of the pure product, indicating that side reactions were unimportant. The crude fluorenone produced from 2-nitrofluorene contained an appreciable amount of impurities the nature of which was not investigated. In the three experiments where the volume of gas absorbed was somewhat lower than the theoretical, the melting point of the crude product was appreciably lower than that of the pure ketone.[11]

In the low temperature oxidation of 9-alkylfluorenes to the corresponding hydroperoxides (Table II), the reaction was carried to complete absorption of oxygen. In most experiments the volume absorbed was close to the calculated value (500 ml.), indicating that little carbinol was formed. The absorption of the last portion of gas was usually very slow, as may be inferred from comparison of the time of total absorption to the time required for the absorption of the first 450 ml. of gas. It might be suspected that the marked decrease in rate was due to reaction 3 being polymolecular with regard to the hydrocarbon. This possibility was ruled out by an experiment in which 9-benzylfluorene was oxidized in a tenfold diluted solution under conditions otherwise equal to those employed in the experiments of Table II. The oxidation was complete within 25 minutes. It consequently was inferred that the reaction must be hampered by the gradually increasing concentration of the reaction product. In order to check this conclusion, a solution prepared from 9-benzylfluorene and 9-hydroperoxy-9-benzylfluorene in a 1:9 molar ratio of hydrocarbon to peroxide was oxidized under the standard conditions. As expected, the absorption of oxygen proceeded at the same slow rate as that of the last tenth part of the volume of gas absorbed in the experiment (Table II) in which 9-benzylfluorene alone was used as the starting material.

TABLE II

OXIDATION OF 9-ALKYLFLUORENES TO 9-HYDROPEROXY-9-ALKYLFLUORENES[a]

9-Substituent	Temp., °C.	Total O_2 absorption	Time of total absorption, min.	Time of absorption of 450 ml., min.
Methyl	−15	467	440	185
Ethyl	−15	496	430	198
Benzyl	−15	495	460	250
p-Methoxybenzyl	−30	499	675	426
Phenyl	−40	475	207	156

[a] There were used 0.02 mole of the fluorene and 0.20 ml. of a 40% solution of Triton B in 30 ml. of pyridine.

While in most cases the formation of hydroperoxide, as judged by the volume of oxygen absorbed, was almost quantitative at −15°, the time required for complete oxidation (Table II) was exceedingly long unless fairly high dilutions were used. It has been found, however, that moderate

---

work reports the formation of 10-hydroperoxy-10-phenylanthrone from 10-phenyl-9-anthrol. It is of interest to note that while an ionic mechanism has been proposed for this reaction, the reaction proceeds readily in ether solution in the absence of a basic catalyst. The formation of 1,2,7,8-dibenzofluorenone (see footnote 3) appears to represent the only instance where an oxygen compound has been isolated from a hydroxide (or alkoxide) ion-catalyzed autoxidation of a hydrocarbon.

(9) 9-Alkylfluorenes recently have become relatively accessible, as they can be obtained by alkylation of fluorene with alcohols in the presence of the corresponding sodium alkoxides [K. L. Schoen and E. I. Becker, THIS JOURNAL, **77**, 6030 (1955); D. N. Matthews and E. I. Becker, *ibid.*, **78**, 1317 (1956)]. See also reference *c* of Table III.

(10) Experiments with air in place of oxygen gave equally good results (see Experimental).

(11) When the substituent in fluorene is a carboxyl or phenolic hydroxyl group, Triton B must be added, in order for oxidation to take place, in excess of the amount required for complete neutralization.

TABLE III

OXIDATION OF 9-ALKYLFLUORENES TO 9-HYDROPEROXY-9-ALKYLFLUORENES[p] (REVERSE METHOD)

9-Substituent	Time of addition, min.	O_2 absorbed, ml.	Yield of recrstd. prod., %	M.p., °C.	Formula	Analyses, % Calcd. C	H	N	[O]	Found C	H	N	[O]
CH_3[a]	120	490	81	150 dec.[g]	$C_{14}H_{12}O_2$	79.22	5.70	..	7.5	79.20	5.55	..	7.5
C_2H_5[b]	72	503	83	108–109[h,i]	$C_{15}H_{14}O_2$	79.62	6.24	..	7.1	79.81	6.15	..	7.1
C_4H_9[b,c]	75	497	81	56–58[j]	$C_{17}H_{18}O_2$	80.28	7.13	..	6.3	80.73	7.30	..	6.0
$C_6H_5CH_2$[d]	70	497	72	70–72[h]	$C_{20}H_{16}O_2$	83.31	5.59	..	5.5	83.15	5.42	..	5.1
p-$CH_3C_6H_4CH_2$[d]	104	502	79[f]	76–77[k]	$C_{26}H_{33}O_2N$	81.88	6.04	3.67	4.2	81.92	6.27	3.58	4.1
p-$CH_3C_6H_4CH_2$	..	..	..	94–95[h,l]	$C_{21}H_{18}O_2$	83.44	5.96	..	5.3	83.13	5.78	..	5.2
p-$CH_3OC_6H_4CH_2$[d]	104	475	85[f]	82–92 d.[m]	$C_{26}H_{23}O_3N$	78.57	5.83	3.52	4.0	78.36	5.98	3.46	3.9
p-$CH_3OC_6H_4CH_2$	..	..	..	104–105[n,h]	$C_{21}H_{18}O_3$	79.24	5.66	..	5.0	79.20	5.76	..	4.9
C_6H_5[e]	82	492	81[f]	90–91[m]	$C_{24}H_{19}O_2N$	81.59	5.38	3.96	4.5	81.61	5.42	3.8	4.3
C_6H_5	..	..	..	67–69[h,l,o]	$C_{19}H_{14}O_2$	83.20	5.15	..	5.8	82.90	4.95	..	5.8

[a] Ref. 9. [b] Obtained by hydrogenation of the corresponding fulvene in alcohol solution and in the presence of palladium-on-charcoal. [c] M.p. 29–30°. This compound has been described as an oil (ref.9). [d] Y. Sprinzak, THIS JOURNAL, **78**, 466 (1956). [e] A. Kliegl, *Ber.*, **38**, 284 (1905). [f] A 1:1 molecular compound with pyridine. [g] From benzene. [h] From benzene–heptane, 1:2. [i] Lit. 106.5–107.5°; E. J. Greenhow, E. N. White and D. McNeil, *J. Chem. Soc.*, 2848 (1951). [j] From benzene–heptane, 1:3. [k] From benzene–heptane, 1:3, and a little pyridine. [l] Obtained from the pyridine complex by washing its ethereal solution with dilute hydrochloric acid. [m] From benzene–heptane 1:2 and a little pyridine. [n] Preheated block. [o] Lit. 53–55° [M. Bassey, E. Buncel and A. O. Davis, *ibid.*, 2550 (1955)]. [p] The hydrocarbon (0.02 mole), dissolved in pyridine (65 ml.), was run into pyridine (5 ml.) containing Triton B (0.2 ml. of a 40% pyridine solution) and kept at 0°.

dilutions can be employed at the higher (and more convenient) temperature of 0° without lowering the yield, provided that the hydrocarbon (dissolved in pyridine) is introduced gradually into the reaction flask containing pyridine and Triton B (Table III). A possible explanation of the restriction of carbinol formation under these conditions may be sought along the lines suggested by Walling and Buckler,[12] who used a similar procedure in the analogous low temperature oxidation of Grignard reagents in ether solution (eq. 5 and 6). These

$$RMgX + O_2 \longrightarrow ROOMgX \qquad (5)$$

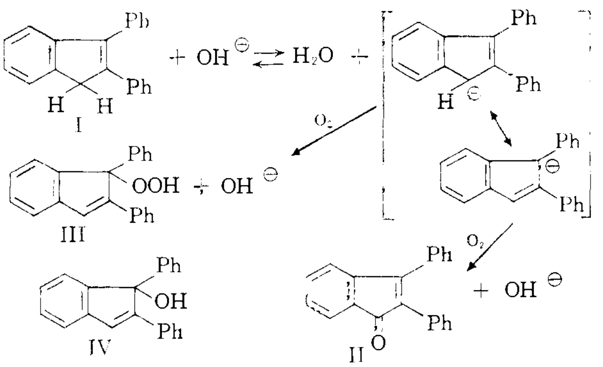
$$ROOMgX + RMgX \longrightarrow 2ROMgX \qquad (6)$$

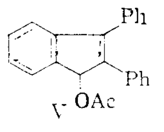
authors surmise that the favorable effect on the yield of hydroperoxide of slower addition of the Grignard solution may result from the maintenance of a higher ratio of dissolved oxygen to hydroperoxide or to reaction 6 being polymolecular in respect to the Grignard compound.

As already stated, in the oxidation of 9-alkylfluorenes to 9-alkylfluorenols the product is usually accompanied by the corresponding hydroperoxide, the amount of which depends on the rate of agitation. The formation of peroxide may eventually be minimized by using a very slow agitation or, alternatively, a uniform product can be secured by flushing the reaction flask with nitrogen after termination of the oxidation and introducing an additional quantity of hydrocarbon, corresponding to the amount of peroxide present as computed from the volume of oxygen absorbed. It has been found more convenient, however, to use moderate agitations and, rather than supplement the reaction mixture with hydrocarbon, to treat it with a sodium bisulfite solution in order to reduce the hydroperoxide to the carbinol. High yields of 9-alkylfluorenols (Table IV) were obtained by this procedure.

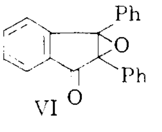
Indene undergoes destructive oxidation under the conditions of the present method, yielding an amorphous substance of a complex nature. The volume of oxygen absorbed depends on the amount of Triton B added, as the latter is rapidly neutralized by the acidic product of oxidation.

On the other hand, oxidation of 2,3-diphenylindene (I) at −40° proceeded smoothly with absorption of one mole of oxygen per mole of hydrocarbon. The product consisted of about equal quantities of 2,3-diphenylindone (II) and a tertiary hydroperoxide, identified as 1-hydroperoxy-1,2-diphenylindene (III). While the formation of II is analogous to that of fluorenone from fluorene, III apparently results from attack of the oxygen molecule at the γ-carbon of the mesomeric anion[13]





V



VI

Structure III for the hydroperoxide is suggested by its stability under alkaline conditions. It was further established in the following way: reduction of

---

[12] C. Walling and S. A. Buckler, THIS JOURNAL, **77**, 6039 (1955).

[13] The eventual existence of a parallel mechanism which does not involve the free carbanion must not be overlooked. It is conceivable that simultaneous attack by the hydroxide ion and oxygen at the α-carbon and γ-carbon, respectively, may lead to the hydroperoxide directly.

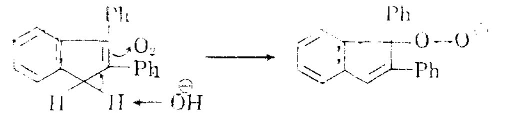


TABLE IV

OXIDATION OF 9-ALKYLFLUORENES TO 9-ALKYLFLUORENOLS

9-Substituent	Yield, %	M.p., °C.
CH_3	82[a]	174–175[d]
C_2H_5	81[b]	103–104[e]
C_4H_9	78[b]	131–133[f]
$C_6H_5CH_2$	94[c]	144–145[g]
p-$CH_3C_6H_4CH_2$	90[c]	147–149[h]
p-$CH_3OC_6H_4CH_2$	83[c]	110–111.5[i]
C_6H_5	84[b]	111.5–112.5[j]

[a] From benzene. [b] From benzene–heptane, 1:2. [c] From benzene–heptane, 1:1. [d] Lit. 174.5° [F. Ullmann and R. von Wurstemberger, *Ber.*, **38**, 4105 (1905]. [e] Lit. 102° [P. Ramart-Lucas and J. Hoch, *Bull. soc. chim. France*, [5] **2**, 1376 (1935)]. [f] Lit. 129° [W. Schlenk, Jr., *Ber.*, **64**, 739 (1931)]. [g] Lit. 139°, ref. *d*. [h] *Anal.* Calcd. for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 88.36; H, 6.34. [i] *Anal.* Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.30; H, 5.86. [j] Lit. 108–109° [W. E. Bachmann, THIS JOURNAL, **52**, 3287 (1930)]. This product was occasionally obtained in crystals of m.p. 85° [*cf.* C. L. Arcus and M. M. Coombs, *J. Chem. Soc.*, 3977 (1954), and reference *o* of Table III].

III by means of potassium iodide in acetic acid afforded a diphenylindenol to which formula IV must be assigned, as its acetate was not identical with the isomeric acetate V which was obtained by NBS bromination of I, followed by interaction of the resulting bromoindene with silver acetate in acetic acid.[14]

Oxidation of 2,3-diphenylindene (I) at room temperature afforded 2,3-diphenylindone (II), along with carbinol IV and the epoxide of 2,3-diphenylindone (VI). While the carbinol evidently arises from reduction of the intermediate hydroperoxide III, the epoxide probably results from oxidation of 2,3-diphenylindone by the same hydroperoxide, a reaction analogous to the formation of the epoxide from the indone and hydrogen peroxide under alkaline conditions.[15] In keeping with this assumption, the peroxide was obtained readily when 2,3-diphenylindone was treated with 9-hydroperoxy-9-benzylfluorene in pyridine solution and in the presence of Triton B.

Experimental[16]

Materials.—The pyridine was of "practical" grade. It was dried over potassium hydroxide and distilled.[17] A 40% Triton B solution in pyridine was prepared by evaporating under reduced pressure a mixture of 100 ml. of a 40% methanolic solution of the hydroxide and 100 ml. of pyridine to a volume of about 85 ml. and bringing to 100 ml. with pyridine.

Apparatus and Procedure.—All the oxidation experiments were carried out in a flask equipped with a stirrer passing through a rubber seal. One side-opening of the flask was connected to a two-way 100-ml. graduated buret by means of rubber tubing, with a calcium chloride drying tube as part of the line. In experiments performed below 0°, a thermometer was inserted through the second side-opening of the flask. The lower end of the buret was connected to a 500-ml. bulb filled with a nearly saturated sodium chloride solution. Dry oxygen from a cylinder, after passing through a mercury safety valve and a bubbling flask containing sulfuric acid, was introduced into the buret.

After introduction of the substance to be oxidized and pyridine, the flask was flushed several times with oxygen, and the Triton B solution was pipeted through the thermometer side-opening during the last flushing. The apparatus was brought to atmospheric pressure and stirring was started. The pressure in the system was equalized from time to time by means of the bulb.

A Dry Ice–acetone-bath was used in the low temperature experiments. Small portions of Dry Ice were occasionally added to the bath to keep the temperature in the flask constant. In experiments at or above 0°, a water-bath, kept at the appropriate temperature, was used.

Fluorenones.—The results of the oxidation experiments of fluorenes to fluorenones are recorded in Table I. While in some cases, including that of fluorene, 10 ml. of pyridine was used per 0.01 mole of substance, higher dilutions were employed in other cases in consideration of solubility or effect on the yield of the product.

After termination of the oxygen absorption, the reaction mixture was acidified with a few drops of acetic acid in pyridine, and the product was precipitated by pouring into a sevenfold volume of water. In the case of 2-hydroxy- and 9-carboxyfluorene, the product was precipitated by adding the requisite quantity of acetic acid to the homogeneous mixture formed on pouring the product into water. Addition of 1 or 2 ml. of acetic acid to the aqueous mixture facilitated agglomeration of the precipitate. The crystals were filtered, washed well with water and recrystallized from the appropriate solvent. The identity of the products was confirmed by a mixed melting point determination with an authentic sample or by elementary analysis. All analyses checked well with the calculated values.

9-Hydroperoxy-9-alkylfluorenes.—In the "direct" procedure experiments recorded in Table II, the product was worked up and yields were as good as in the "reverse" procedure experiments (Table III).

The reverse procedure consisted in running a pyridine solution of the 9-alkylfluorene into the reaction flask containing pyridine and Triton B, the addition being so regulated as to keep pace with the absorption of oxygen.

After termination of the reaction, the mixture was acidified with a little acetic acid and poured into a sevenfold volume of water. Three of the hydroperoxides (see Table III) crystallized as pyridine complexes containing 1 molecule of pyridine per molecule of peroxide. They were filtered, washed with water, dried *in vacuo* at room temperature and recrystallized from a benzene–heptane mixture containing a little pyridine. The pyridine-free compounds were obtained by washing the solvates, in ethereal solution, with 5% hydrochloric acid.

The other hydroperoxides formed an oily layer. They were extracted with ether, the ethereal solution was freed of pyridine by washing with water and 5% hydrochloric acid, then washed with a sodium bicarbonate solution, dried over sodium sulfate and evaporated at room temperature. The residue crystallized either spontaneously or on trituration with petroleum ether.

Active oxygen was determined iodometrically by the procedure of Wibaut, Van Leeuwen and Van der Wal,[18] except that the 0.02 *N* solution of sodium thiosulfate was replaced by a 0.1 *N* solution.

9-Alkylfluorenols.—In the oxidation of 9-alkylfluorenes at the ordinary temperature (25°) performed with the aim of obtaining the corresponding fluorenols (Table IV), the volume of oxygen absorbed usually appreciably exceeded the value calculated for carbinol formation exclusively. Thus, in the experiment with 9-ethylfluorene (0.01 mole), the volume absorbed (38 min.) amounted to 146 ml., indicating the formation of approximately 83% of carbinol and 17% of hydroperoxide. In the (exceptional) case of 9-phenylfluorene (0.02 mole), 246 ml. of oxygen was absorbed (in 11 min.), indicating that hardly any hydroperoxide was produced. The mixture was invariably treated with bisulfite. The recorded yields refer to the pure product, obtained by washing the crude product with petroleum ether and recrystallizing it from a benzene–heptane mixture. In all cases the melting point of the petroleum ether-washed product lay within two degrees of that of the recrystallized product. The identity of the products was checked by a mixed melting point determination with authentic samples or by elementary analysis.

The procedure is illustrated by the following example: A solution of 9-butylfluorene (4.44 g., 0.02 mole) and Triton B

---

(14) J. Thiele and P. Ruggli, *Chem. Zentr.*, **83**, II, 1771 (1912).

(15) E. Weitz and A. Scheffer, *Ber.*, **54**, 2327 (1921).

(16) All melting points are corrected.

(17) A. J. Vogel, "Practical Organic Chemistry," Longmans, Green & Co., London, 1948, p. 173.

(18) J. P. Wibaut, M. B. Van Leeuwen and B. Van der Wal, *Rec. trav. chim.*, **73**, 1033 (1954).

(0.1 ml.) in pyridine (30 ml.) was oxidized at 25° with moderate stirring. The absorption of oxygen was complete within 15 min., the volume absorbed amounting to 321 ml. The mixture was treated with sodium bisulfite (2 g.) dissolved in water (5 ml.), and stirring was continued for 60 minutes. The product was precipitated by pouring into a sevenfold volume of water, filtered, washed with water, dried and washed with petroleum ether 60–90°, to afford 3.90 g. of **9-butylfluorenol**, m.p. 129–132.5°. Recrystallization from benzene–heptane, 1:2, gave 3.65 g. (yield 78%), m.p. 131–133°.

Oxidation with Air. (a) **Fluorenone.**—A solution of fluorene (33.2 g., 0.20 mole) and Triton B (5 ml.) in pyridine (200 ml.) was oxidized with vigorous stirring and while a stream of air was passed over the stirred liquid through the side openings. Oxidation was complete within 90 min., as was judged by ascertaining that under-pressure was no longer created in the flask on closing and connecting it with a water buret. After acidifying with acetic acid, 150 ml. of solvent was distilled from the reaction mixture under reduced pressure and the residue was poured into water (500 ml.). There was obtained 36.5 g. of crude product, m.p. 77–82°. Recrystallization from alcohol (37 ml.) afforded 30.5 g. (yield 85%) of pure fluorenone, m.p. 84–85°.

Oxidation proceeded much more slowly when, rather than passing a stream of air through the flask, the side openings were just left open to air.

(b) A solution of 9-benzylfluorene (5.12 g., 0.02 mole) and Triton B (0.1 ml.) in pyridine (30 ml.) was oxidized as in (a). Oxidation was complete within 22 minutes. After reducing with sodium bisulfite and working up as in the general procedure, there was obtained 5.10 g. (yield 94%) of 9-benzylfluorenol, m.p. 142.5–144.5°.

Interaction of 9-Benzylfluorene and 9-Hydroperoxy-9-benzylfluorene.—A solution of the hydroperoxide (1.50 g., 0.0052 mole) in pyridine (15 ml.) was run during 10 minutes into a stirred solution of 9-benzylfluorene (1.28 g., 0.0050 mole) and Triton B (0.2 ml.) in the same solvent (10 ml.) kept at 50° in an atmosphere of nitrogen. Stirring was continued for another 10 minutes, after which the solution was acidified with a little acetic acid and poured into water (200 ml.). The product precipitated as an oil which soon solidified. After filtering, drying and washing with petroleum ether (8 ml.) on a suction funnel, there was obtained 2.48 g. (yield 91%) of 9-benzylfluorenol, m.p. and mixed m.p. 142.5–144°.

Conversion of 9-Fluorylhydroperoxide to Fluorenone.—A solution of the complexed hydroperoxide[7] (0.765 g.) in pyridine (9 ml.) was cooled to −40° and treated with a droplet of Triton B. After 4 minutes the solution was acidified with acetic acid and poured into water. The precipitated product was filtered, washed with water and dried. It consisted of pure fluorenone (0.695 g., yield 95%), m.p. and mixed m.p. 83–84°.

Oxidation of Indene.—A solution of indene (2.32 g., 0.02 mole) in pyridine (30 ml.) was oxidized at 0°. Several drops of Triton B were added from time to time to maintain the oxidation; 715 ml. of oxygen was absorbed in 195 minutes (627 ml. was absorbed during the first 80 minutes), the consumption of Triton B being about 6 ml. The dark solution was poured into water (300 ml.) whereupon the product precipitated as a dark-brown solid. After acidification with acetic acid (6 ml.) to precipitate a minor alkali-soluble fraction, the solid was filtered, washed with water and dried; yield 1.40 g., melting range 120–160°, completely soluble in pyridine and insoluble in benzene, partly (8%) soluble in aqueous sodium carbonate. The remainder was insoluble in aqueous sodium hydroxide and soluble in acetone to the extent of 75% of the total. The latter fraction was analyzed. Found: C, 77.64; H, 5.26.

Oxidation of 2,3-Diphenylindene. (a) **At −40°.**—A solution of 2,3-diphenylindene[19] (8.04 g., 0.03 mole) and Triton B (0.3 ml.) in pyridine (150 ml.) was oxidized at −40° (750 ml. of oxygen absorbed in 45 minutes). The solution was poured into water (1200 ml.) containing acetic acid (5 ml.). The product gradually solidified. It was filtered, washed with water and dissolved in ether. The ethereal solution was washed with 5% hydrochloric acid, water and a sodium bicarbonate solution, dried over sodium sulfate and evaporated. The solid residue (8.6 g.) contained 54% of hydroperoxide III, as determined by iodometric titration. The peroxide was extracted with cold alcohol (120 ml.), leaving behind 2,3-diphenylindone (II, 2.87 g., yield 34%), m.p. and mixed m.p. 154–155°.[20] The alcoholic extract was poured into water and the precipitated product filtered, washed with water and dried in a vacuum desiccator. It was then heated to boiling with petroleum ether 60–90° (100 ml.) and filtered after standing overnight (4.33 g., m.p. 127–129°). Recrystallization from benzene–heptane, 1:3, afforded 3.26 g. (yield 35%) of **1-hydroperoxy-1,2-diphenylindene** (III) in the form of slightly yellow needles. The compound melts with decomposition on heating for a short time above 130°. Its instantaneous melting point lies above 140°.

Anal. Calcd. for $C_{21}H_{16}O_2$: C, 84.00; H, 5.33; [O], 5.3; mol. wt., 300. Found: C, 84.12; H, 5.38; [O], 5.2; mol. wt. (benzene), 295.

(b) **At 25°.**—A solution of 2,3-diphenylindene (5.36 g., 0.02 mole) and Triton B (0.2 ml.) in pyridine (50 ml.) was oxidized at 25° (470 ml. of oxygen absorbed in 37 minutes, 460 ml. absorbed in the first 20 minutes). After working up as in (a), the solid crude product (5.9 g.) was extracted with hot alcohol (50 ml.), leaving behind red crystals of 2,3-diphenylindone (1.76 g.), m.p. 148–153°. The crystals deposited in the alcoholic extract after cooling contained a considerable quantity of the indone. The latter (1.13 g.) was separated by washing the crystal mixture with ether (20 ml.). Evaporation of the ether and three recrystallizations of the residue from benzene–heptane, 1:2, afforded 0.25 g. (yield 4%) of 2,3-diphenylindone epoxide (VI), m.p. and mixed m.p. 143.5–144.5°.[15]

The residue obtained from the evaporation of the alcoholic mother liquors afforded, after 2 recrystallizations from benzene–heptane, 1:2, 0.53 g. (yield 9%) of **1-hydroxy-1,2-diphenylindene (IV)**, m.p. 138.7–139.5°, identical with the carbinol obtained by reduction of hydroperoxide III with potassium iodide in acetic acid.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.73; H, 5.63. Found: C, 88.70; H, 5.52.

The combined two portions of crude diphenylindone (2.84 g.) were recrystallized from a 1:1 alcohol–ethyl acetate mixture (35 ml.) to give 2.45 g. (yield 43%) of the pure ketone II, m.p. 155–156.5°.

1-Acetoxy-1,2-diphenylindene was prepared by refluxing carbinol IV with an excess of acetyl chloride for 2 hours; m.p. 189–190° (from benzene–heptane, 1:3).

Anal. Calcd. for $C_{23}H_{18}O_2$: C, 84.66; H, 5.52. Found: C, 84.50; H, 5.64.

1-Bromo-2,3-diphenylindene.—A mixture of 2,3-diphenylindene (2.14 g.), N-bromosuccinimide (1.04 g.), carbon tetrachloride (20 ml.) and a pinch of benzoyl peroxide was refluxed for 4 hours. The solvent was evaporated and the residue treated with water, filtered, dried and recrystallized twice from benzene–heptane 1:1 to afford 1.45 g. of the bromide, m.p. 163.5–164.5° dec., lit.[14] 158°.

Anal. Calcd. for $C_{21}H_{15}Br$: Br, 23.05. Found: Br, 22.93.

1-Acetoxy-2,3-diphenylindene (V) was obtained according to Thiele and Ruggli[14] by heating the bromide with silver acetate in acetic acid; m.p. 170–171° (from benzene–heptane 1:5), lit.[14] 166–167°.

This acetate and the isomeric 1-acetoxy-1,2-diphenylindene (see above) showed very similar absorptions in the infrared region, with strong bands at 1740 and 1225 cm.$^{-1}$.

Hydrolysis of V afforded a ketone isomeric with the expected carbinol[21]: the acetate (0.16 g.) was refluxed with potassium hydroxide (0.2 g.) in alcohol (2 ml.) for 60 minutes in an atmosphere of nitrogen. On treatment with water the product precipitated as a stocky mass which soon solidified on addition of a little petroleum ether. Two recrystallizations from heptane afforded 0.10 g. of the pure product, presumably 2,3-diphenylindanone, m.p. 101–102°, lit.[22] 100–101°. The compound showed the characteristic absorption of the carbonyl group at 1715 cm.$^{-1}$.

---

[19] C. F. Koelsch and P. R. Johnson, *J. Org. Chem.*, **6**, 534 (1941).

[20] C. F. H. Allen, J. W. Gates, Jr., and J. A. VanAllan, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 353.

[21] The author was unable to reproduce the results of A. Garcia Banus and F. Boqué [*Chem. Zentr.*, **106**, II, 3770 (1935)], who report the isolation of a carbinol of this structure from the reduction of 2,3-diphenylindone with zinc dust and acetic acid.

[22] W. Schlenk and E. Bergmann, *Ann.*, **463**, 98 (1928).

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.73; H, 5.63. Found: C, 88.72; H, 5.78.

Oxidation of 2,3-Diphenylindone with 9-Hydroperoxy-9-benzylfluorene.—A solution of the hydroperoxide (0.80 g., (0.0028 mole) in pyridine (5 ml.) was added to an ice-cooled solution of the indone (0.70 g., 0.0025 mole) and Triton B (0.1 ml.) in the same solvent (5 ml.), and the mixture was left at room temperature for 2 hours, acidified with acetic acid and poured into water. The precipitated product was filtered, dried, washed with cold alcohol (10 ml.) and recrystallized from the same solvent to afford 0.56 g. (yield 67%) of 2,3-diphenylindone epoxide, m.p. and mixed m.p.[15] 144.5–155.5°. Evaporation of the alcoholic solutions and recrystallization of the residue from benzene–heptane, 1:3, gave 0.60 g. (yield 88%) of 9-benzylfluorenol, m.p. 141–144°.

Acknowledgment.—The author is indebted to Mr. Abraham Deshe for his capable assistance in carrying out the oxidation experiments.

REHOVOTH, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO UNIVERSITY]

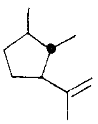
Reactions of Diolefins at High Temperatures. II. The Cyclization of 1,6-Octadiene and 7-Methyl-1,6-octadiene[1]

BY WILLIAM D. HUNTSMAN, VICTOR C. SOLOMON AND DONALD EROS

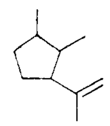
RECEIVED APRIL 18, 1958

1,6-Octadiene undergoes cyclization at 457° to give 1-methyl-*cis*-2-vinylcyclopentane, and under the same conditions 7-methyl-1,6-octadiene furnishes 1-methyl-*cis*-2-isopropenylcyclopentane. 1,6-Heptadiene fails to cyclize even at 500°. These results lend support to the intramolecular mechanism previously proposed for the thermal cyclization of 1,6-diolefins.

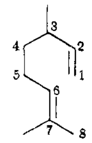
At elevated temperatures, properly substituted 1,6-diolefins undergo cyclization to give substituted cyclopentanes. For example, 1-*trans*-2-dimethyl-*cis*-3-isopropenylcyclopentane (I) and 1-*cis*-2-dimethyl-*cis*-3-isopropenylcyclopentane (II) are formed from 3,7-dimethyl-1,6-octadiene (III) at 400-500°.[2] Evidence was presented recently which indicates that the cyclization of III proceeds by an intramolecular mechanism involving hydrogen transfer from position 8 to position 1 simultaneously with bond formation between positions 2 and 6.[3] According to this scheme a hydrogen-bearing group at position 8 is a requisite for thermal cyclization; consequently it was anticipated that 1,6-octadiene (IV) would cyclize, but 1,6-heptadiene (V) would not.



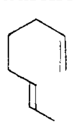
I



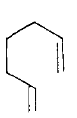
II



III



IV



V

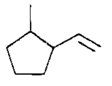
Results

1,6-Heptadiene failed to cyclize at 450 or 500°. The infrared spectra of the pyrolysis products were identical with the spectrum of V and, upon quantitative hydrogenation, the hydrogen consumption corresponded to two double bonds per molecule.

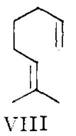
A cyclic olefin (A) was formed in approximately 35% yield when IV was pyrolyzed at 457° with a contact time of 56 seconds. The separation of A from unreacted IV was accomplished by chromatography over silica gel at 0°. Strong absorption bands at 10.00 and 10.99 μ in the infrared spectrum of A indicated the presence of a monosubstituted double bond,[4] $RCH{=}CH_2$, and the spectrum of the product obtained by hydrogenation of A was identical with the recorded spectrum of 1-methyl-*cis*-2-ethylcyclopentane.[5] These results provide strong evidence that A is 1-methyl-*cis*-2-vinylcyclopentane (VI); this was confirmed by comparison with a sample of VI obtained by an independent synthesis. Analysis of the pyrolysate by careful fractional distillation and vapor–liquid partition chromatography showed that 1-methyl-*trans*-2-vinylcyclopentane (VII) was absent.

The 1,6-octadiene used in this study was apparently a mixture of the *cis* and *trans* isomers as evidenced by infrared absorption bands at 14.38 and 10.35 μ.[4] Evidently both isomers underwent cyclization since the ratio of the intensities of these bands was essentially the same for the pyrolysate as for the starting diolefin. Models reveal that both isomers should be able to assume the proper conformation for cyclization with nearly equal facility.

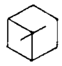
A cyclic olefin (B), b.p. 147.5-148.5°, n^{25}_D 1.4480, was obtained by the pyrolysis of 7-methyl-1,6-octadiene (VIII) at 457°. These properties, as well as the infrared spectrum, are in agreement with those reported (b.p. 149-150°, n^{20}_D 1.4496) for a cyclic olefin (C) obtained by the pyrolysis of 6,6-



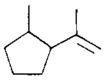
VI *cis*
VII *trans*



VIII



IX



X *cis*
XI *trans*

---

[1] This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command under contract No. AF18(600)546.

[2] H. Pines, N. E. Hoffman and V. N. Ipatieff, THIS JOURNAL, **76**, 4412 (1954).

[3] W. D. Huntsman and T. H. Curry, *ibid.*, **80**, 2252 (1958).

[4] H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

[5] Catalog of Infrared Spectral Data, Serial No. 534, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1946.