carbonium ion should hinder such a process severely. It is possible for the oxygen function to migrate first to carbon one followed by the same process shown above. If this is the case then the migration shown must be the slow step. Alternatively the oxygen could undergo a 1,3-shift similar to a Claisen rearrangement. A study of these possibilities is contemplated.

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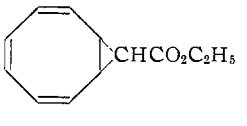
The Reaction between Diazoacetic Ester and Cycloöctatetraene

BY DONALD D. PHILLIPS

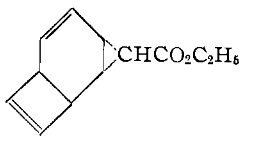
RECEIVED MAY 25, 1955

In continuation of our studies[1] in the field of diazoacetic ester (I) chemistry we have examined in some detail the product derived from I and cyclooctatetraene. Although our investigations on this interesting adduct are continuing, the recent communication of Akiyoshi and Matsuda[2] prompts us to record our observations at this time since they seem to be in essential agreement with those of the Japanese workers.

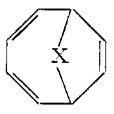
We considered from the outset that the adduct was the cyclopropane (II) although consideration had to be given to structure III in view of the well-established tendency of cycloöctatetraene to react through the intermediate bicyclo[4.2.0]system.[3] Furthermore IVa was considered a distinct possibility because of the recently proposed[4] structure for cycloöctatetraene oxide (IVb).[5] Structure III was readily eliminated by the experimental observation that the adduct absorbed three moles of hydrogen, each mole being taken up at a fairly constant rate.



II



III



IVa, X = $CHCO_2C_2H_5$
b, X = O

The ultraviolet absorption spectrum of the adduct (λ_{max} 245 mμ, log ε 3.51; λ_{min} 230 mμ, log ε 3.46) is quite similar to that of the oxide[4] (λ_{max} 240 mμ, log ε 3.60) and seemed too low for a cycloöctatriene such as II which should absorb[6] in the vicinity of 265 mμ. We have evidence, however, that there is a transannular interaction between the π-electrons of the carbonyl group in the ester and the triene chromophore because the corresponding alcohol (which still absorbs three moles of hydrogen) has λ_{max} 263 mμ, log ε 3.62. An inspection of models confirms the possibility of such an interaction since in two of the possible configurations that II may assume the carbonyl group is very close in space to the triene chromophore.[7] This anomalous behavior cannot be rationalized on the basis of IVa so that we favor II as the structure of the diazoacetic ester–cycloöctatetraene adduct.

Experimental[8]

Ethyl Bicyclo[6.1.0]nona-2,4,6-triene-9-carboxylate (II).—Diazoacetic ester (12.8 g., 0.11 mole) was added with stirring to 17 g. (0.16 mole) of cycloöctatetraene[9] containing 0.8 g. of copper powder. The initial temperature was 100° and at the end of the addition (1/2 hr.) was 115°. Nitrogen evolution was copious throughout the entire period. The product was filtered free of copper and distilled to give 11.0 g. of recovered cycloöctatetraene, b.p. 60–61° (48 mm.), about 1.0 g. of an intermediate fraction and 8.3 g. (40% based on diazoacetic ester) of ester II as a very pale yellow liquid, b.p. 102–104° (4.5 mm.), $n^{20}D$ 1.5110; d^{20}_4 1.056; MR_D (calcd.) 54.42,[10] MR_D (obsd.) 53.93.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.75; H, 7.42; sapon. equiv., 190.2. Found: C, 75.51; H, 7.46; sapon. equiv., 176.[11]

The **N-phenylmaleimide adduct** crystallized from benzene–petroleum ether as silky needles, m.p. 192–193.5°.

Anal. Calcd. for $C_{22}H_{21}O_4N$: C, 72.72; H, 5.83; N, 3.85. Found: C, 73.36; H, 5.93; N, 3.93.

The **N-(*p*-bromophenyl)-maleimide adduct** crystallized from methanol as a powdery solid, m.p. 156–158°.

Anal. Calcd. for $C_{22}H_{20}O_4NBr$: C, 59.74; H, 4.56; Br, 18.07. Found: C, 59.42; H, 4.44; Br, 17.91.

The **hydrazide** crystallized from dilute alcohol as long needles, m.p. 145–146°; λ_{max} 238–240 mμ (log ε 3.66).

Anal. Calcd. for $C_{10}H_{12}ON_2$: C, 68.16; H, 6.87; N, 15.90. Found: C, 68.45; H, 6.89; N, 15.69.

Catalytic Reduction of Ester II. In acetic acid over platinum black, 0.156 g. of ester II absorbed in six hours 46.0 ml. of hydrogen (93% of the theoretical for three moles). The reduced compound was characterized as the hydrazide which formed powdery crystals from ethyl acetate–isoöctane, m.p. 133–135°.

Anal. Calcd. for $C_{10}H_{18}ON_2$: C, 65.89; H, 9.95. Found: C, 66.06; H, 10.04.

9-Hydroxymethylbicyclo[6.1.0]nona-2,4,6-triene.—When the adduct II was reduced with lithium aluminum hydride in the usual fashion, the corresponding alcohol was obtained

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[1] D. D. Phillips, THIS JOURNAL, **76**, 5385 (1954).

[2] S. Akiyoshi and T. Matsuda, *ibid.*, **77**, 2476 (1955).

[3] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[4] O. H. Wheeler, THIS JOURNAL, **75**, 4858 (1953).

[5] Although no example of 1,4-addition has been reported for diazoacetic ester, it is stated that diazomethane reacts with dimethyl 2,3-dihydroterephthalate to give a bicyclic 1,4-addition product (P. C. Guha and G. D. Hazra, *J. Ind. Inst. Sci.*, **22A**, 263 (1939)).

[6] A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

[7] A similar phenomenon has recently been observed in the 3,5-cycloheptadienone spectrum which has a maximum at 213–214 mμ whereas cycloheptadiene absorbs at 248 mμ. See J. Meinwald, S. L. Emerman, N. C. Yang and G. Büchi, THIS JOURNAL, **77**, 4401 (1955). It is interesting to note that the Japanese workers[2] report that the acid corresponding to II has λ_{max} 244 mμ, log ε 3.56; λ_{min} 226 mμ, log ε 3.45 and that these figures favor the conclusion that the compound is a cycloöctatriene. This can hardly be so on the basis of Cope's work[6] and although we agree that the adduct is in fact a cycloöctatriene we feel that the ultraviolet evidence needs somewhat special interpretation to support the assigned structure.

[8] Melting points and boiling points are uncorrected. Ultraviolet absorption spectra were determined in 95% ethanol using a Beckman DU quartz spectrophotometer. Analyses are by Geller Labs., Hackensack, N. J. All the distillations were through a 30-inch Podbielniak column with partial reflux head.

[9] Obtained from the General Aniline Works, New York 14, N. Y.

[10] We used the values given in A. I. Vogel, "A Textbook of Practical Organic Chemistry," 2nd Ed., Longmans, Green and Co., New York, N. Y., 1951, p. 900, including that listed for the cyclopropane ring. See, however, V. A. Slabey, THIS JOURNAL, **76**, 3603 (1954).

[11] This is the average value of several determinations, none of which varied more than 1% from this figure. The Japanese workers[2] also report a low value for their saponification equivalent. No explanation is available for this anomalous result at the present time.

in 72% yield as a colorless liquid, b.p. 94–96° (2 mm.); $n^{20}{}_D$ 1.5425; $d^{20}{}_4$ 1.052; MR_D (calcd.)[10] 45.12, MR_D (obs.) 44.39; λ_{max} 263 mμ, log ϵ 3.62; λ_{min} 235 mμ, log ϵ 3.27.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.01; H, 8.16. Found: C, 80.74; H, 8.03.

The **N-(*p*-bromophenyl)-maleimide adduct** crystallized from methanol in colorless needles, m.p. 198–201°.

Anal. Calcd. for $C_{20}H_{16}O_3NBr$: C, 60.00; H, 4.53; N, 3.50. Found: C, 60.14; H, 4.54; N, 3.57.

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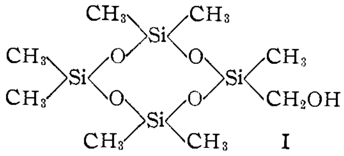
Hydroxyalkylcyclosiloxanes

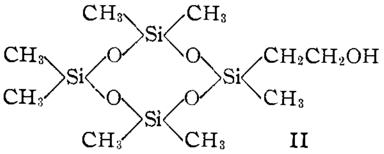
BY MAURICE PROBER

RECEIVED MAY 19, 1955

As part of a program on polar silicones, it was of interest to prepare cyclic tetramers containing hydroxyalkyl groups, notably hydroxymethylheptamethylcyclotetrasiloxane (I), and β-hydroxyethylheptamethylcyclotetrasiloxane (II).



I



II

Silicon compounds containing hydroxymethyl groups have been prepared by treating the chloromethyl compound with potassium acetate in acetic acid followed by methanolysis of the acetate.[1] With the chloromethyl cyclic tetramer, the reaction with potassium acetate–acetic acid led to ring opening and formation of polymeric siloxanes.[2] The preparation of I by neutral hydrolysis of the chloromethyl cyclic tetramer was unsuccessful.

Since the Grignard reagent of the chloromethyl cyclic tetramer has been described recently,[3] I was prepared by treating this reagent with oxygen; II was obtained by reaction with formaldehyde. The yields were low in both cases. Although improved yields are often obtained by coöxidizing a Grignard reagent in the presence of isopropylmagnesium bromide,[4] this technique did not increase the yield. Compound I is a crystalline solid, II a somewhat viscous liquid.

I and II were polymerized with ferric chloride and sulfuric acid and cross-linked gels were formed.[5]

Experimental

Hydroxymethylheptamethylcyclotetrasiloxane (I).—Grignard reagents were prepared from 92.1 g. (0.750 mole) of isopropyl bromide in 700 ml. of diethyl ether and 165.3 g. (0.500 mole) of chloromethylheptamethylcyclotetrasiloxane in 700 ml. of diethyl ether. The solutions were mixed and dry oxygen bubbled through the stirred solution for two hours. The solution was allowed to stand overnight and then poured into a 10% ammonium chloride solution containing a trace of sulfuric acid. The ether solution was washed with water, dried and distilled, yielding 78.4 g., b.p. 49–100° at 1.5 mm., with a 59.2-g. residue. Upon rectification of the distillate, there was obtained 24.7 g. of hydroxymethylheptamethylcyclotetrasiloxane, b.p. 55–58° at 0.5 mm., m.p. 52–56°, yield 16%. Recrystallized from Dry Ice-chilled pentane, m.p. 56–57°. Compound I (as a pure solid) exhibited a strong infrared absorption maximum for OH at 2.92 μ.

Anal. Calcd. for $C_8H_{24}O_5Si_4$: C, 30.73; H, 7.74. Found: C, 30.6; H, 7.7.

A 13% yield was obtained in the absence of isopropylmagnesium bromide.

β-Hydroxyethylheptamethylcyclotetrasiloxane (II).—The Grignard reagent was prepared from 264.6 (0.800 mole) of chloromethylheptamethylcyclotetrasiloxane in diethyl ether, the solution chilled to −30 to −40° and 21.0 g. (0.700 mole) of formaldehyde[6] was distilled in. The reaction mixture was stirred overnight, the temperature slowly rising to room temperature, followed by hydrolysis with dilute sulfuric acid. The ether solution was dried and distilled, yielding 190.7 g., b.p. 70–130° at 2.5 mm., and a 56.4-g. residue. Rectification of the distillate gave 28.5 g. of β-hydroxyethylheptamethylcyclotetrasiloxane, b.p. 112–114° at 9 mm., $n^{20}{}_D$ 1.4163, $d^{20}{}_4$ 1.020; MR_D (calcd.) 80.96,[7] MR_D (obsd.) 80.42; yield 13%. II (as a pure liquid) exhibited a strong infrared absorption maximum for OH at 2.98 μ.

Anal. Calcd. for $C_9H_{26}O_5Si_4$: C, 33.09; H, 8.02. Found: C, 33.2; H, 8.3.

Polymerization.—Anhydrous ferric chloride and concentrated sulfuric acid (0.5% by weight) were used as catalysts.[8] The polymerizations were carried out at 80° except for the room temperature reaction of II and sulfuric acid. The polymers were gels which swelled but did not dissolve in toluene.

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[1] J. L. Speier, B. F. Daubert and R. R. McGregor, THIS JOURNAL, **70**, 1400 (1948); **71**, 1474 (1949).

[2] J. L. Speier, U. S. Patent 2,550, 205 (August 24, 1951).

[3] M. Prober, THIS JOURNAL, **77**, 3224 (1955).

[4] M. S. Kharasch and W. B. Reynolds, *ibid.*, **65**, 50 (1943).

[5] The cross linking is due to etherification or the formation of trifunctional silicon. The latter could result from the interaction of acid and alcohol to form carbonium ions which undergo silicon–carbon bond cleavage: F. C. Whitmore, L. H. Sommer, J. R. Gould and R. E. Van Strien, *ibid.*, **69**, 1551 (1947); L. H. Sommer and F. J. Evans, *ibid.*, **76**, 1186 (1954).

(6) Monomeric formaldehyde was prepared according to J. F. Walker, "Formaldehyde," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1953, p. 14. Although an excess of formaldehyde had been prepared, less than the stoichiometric amount was distilled into the reaction flask because of polymerization in storage at −78°.

(7) A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 531 (1952); A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 177 (1954).

(8) J. Marsden and G. F. Roedel, U. S. Patent 2,469,883 (May 10, 1949).

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Studies on the Decarboxylation of Radioactive Glucuronolactone by *in vitro* Systems[1–3]

BY JOSEPH L. RABINOWITZ

RECEIVED MAY 14, 1955

A soluble enzyme system from various tissues of the rat has been obtained which is capable of decarboxylating C^{14}-glucuronolactone as well as C^{14}-glucuronic acid. The concentration of this enzyme appeared to be highest in liver and kidney (Table I). Kidney appeared to be more constant in activity than did comparable liver preparations. Active extracts of the enzyme were obtained by treatment of kidney tissues with phosphate buffer at *p*H 7

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(1) The radioactive materials were obtained on allocation from the United States Atomic Energy Commission.

(2) The C^{14}-glucuronolactone uniformly labeled was obtained through the generosity of the Corn Products Refining Company.

(3) Aided by a grant from the Muscular Dystrophy Association of America, Inc.