moles) of *o*-bromotoluene illuminated by a mercury arc lamp. The mixture was stirred throughout the addition period and for one additional hour. Distillation yielded 492 g. (59%) of *o*-bromobenzyl bromide; b.p. 127–133° (15 mm.).

o,o'-**Dibromobibenzyl.**—Phenyllithium (890 ml. of a 1.06 *N* ether solution) was added slowly to a solution of 492 g. (1.97 moles) of *o*-bromobenzyl bromide in 500 ml. of ether. During the addition of the phenyllithium the ether refluxed spontaneously. The next day the pale yellow solution was hydrolyzed with 300 ml. of water, the resulting layers were separated and the ether layer washed, dried, and distilled. The bromo compound distilled at 193–200° at 5 mm. and solidified on cooling. After recrystallization from 125 ml. of ethanol it melted at 83°; weight 191 g. (60% yield). The reported melting point is 84.5°.[3]

5-(2-Aminoethoxy)-10,11-dihydrodibenzo[b.f]borepin (I).—A solution of 100.0 g. (0.294 mole) of *o,o'*-dibromobibenzyl in 600 ml. of ether was added slowly to 0.632 mole of butyllithium in 578 ml. of ether at 5°; then the mixture was refluxed for one hour. During this period a white precipitate separated from the solution. This mixture was transferred to a dropping funnel and slowly added to 67.5 g. (0.294 mole) of tributyl borate in 700 ml. of ether maintained at −70°. The next morning the mixture was hydrolyzed with 400 ml. of 2 *N* hydrochloric acid. Distillation of the ether layer with 700 ml. of toluene and 10 ml. of butyl alcohol gave the high boiling fractions shown in Table I. Fractions 1, 2 and 3, which contained the desired heterocyclic organoboron compound, then were distilled separately with ethanolamine and toluene. In each case, after the excess ethanolamine had been removed but before all of the toluene had distilled, the solution was allowed to cool. The weights of the resulting precipitates also are included in Table I. The total amount of aminoethoxydihydrodibenzoborepin thus obtained was 30.82 g. (42%). Recrystallization of 2.16 g. of this material from 30 ml. of ethanol and 20 ml. of water yielded 1.33 g. of the purified ester, m.p. 195–196°.

TABLE I

Fract.	B.p., °C., 2 mm.	Wt., g.	Aminoethyl ester, g.
1	131–157	7.07	0.00
2	157–166	41.23	19.52
3	166–200	18.30	10.30

Anal.[4] Calcd. for $C_{16}H_{15}ONB$: B, 4.308; N, 5.58; equiv. wt., 251. Found: B, 4.32; N, 5.72; equiv. wt. (by titration with hydrochloric acid), 245.

It is interesting that no precipitate formed when an ether solution of fraction 3 was saturated with ammonia. In the case of butyl diphenylborinate,[2] a solid ammonia complex separated under these conditions.

Anhydride of Hydroxydihydrodibenzoborepin (II).—The aminoethyl ester (0.500 g.) was dissolved in a mixture of 10 cc. of ethanol and 10 cc. of 6 *N* hydrochloric acid. On addition of 30 cc. of 1 *N* hydrochloric acid, a white solid separated. It was filtered and dried in a vacuum oven at 40° for two hours; weight 0.381 g. (96% yield), m.p. 145–146°. A portion (0.2337 g.) was dissolved in a solution of 15 cc. of ethanol, 15 cc. of water and 2 g. of mannitol; then titrated with standard sodium hydroxide with the aid of a Beckman *p*H meter; equivalent weight: found 199; calcd. for II, 199.

In another experiment, 6.11 g. of the aminoethyl ester was acidified, then extracted with ether and distilled with toluene (200 cc.). The anhydride distilled at 265–270° (2 mm.) and weighed 3.84 g. (79%). Apparently, some decomposition occurred for this material melted over a range from 131–136°; however, the neutralization equivalent found by titration (203) agreed fairly well with the value calculated for II (199).

The infrared spectra of the materials obtained by these two procedures were virtually identical. Both showed strong absorption in the region of 7–8 μ, characteristic of organoboron compounds, and a weak maximum at 2.7 μ. This latter peak is in the region characteristic of the hydroxyl group and suggests that the compound might be the borinic acid rather than the anhydride. However, it seems unlikely that the acid would distil under the conditions employed. Furthermore, diphenylborinic anhydride[2] showed a weak maximum at 2.7 μ; and Neu found that diphenylborinic acid also dehydrated very easily to yield the anhydride.[5]

Reactions of I. (a) Bromine.—To 0.400 g. of I in 30 ml. of acetic acid was added a solution of 5 ml. of bromine in 20 ml. of water which contained potassium bromide. After 10 minutes, the solution was diluted with 100 ml. of water and excess bromine was reduced with sodium bisulfite. The white precipitate was separated by filtration, and dried; weight 0.501 g. (92.5% yield), m.p. 78–81°. After recrystallization from alcohol and water, the sample (0.366 g. recovered) melted at 82–83°. The melting point was not depressed when the sample was mixed with *o,o'*-dibromobibenzyl prepared from *o*-bromobenzyl bromide.

(b) **Hydrogen Peroxide.**—Ten milliliters of a 30% hydrogen peroxide solution was added to a solution of 0.400 g. of I in 10 ml. of acetic acid and 5 ml. of water at room temperature. After five minutes the solution was diluted with 70 ml. of water and cooled in an ice-bath. White crystals of *o,o'*-dihydroxybibenzyl separated; weight 0.222 g. (65% yield), m.p. 114–115°. The melting point was unchanged after the substance had been recrystallized from water and alcohol. This material burned without any green coloration, showing that boron was absent. The melting point reported for *o,o'*-dihydroxybibenzyl is 115°.[6]

Reactions of II. (a) Palladium.—The anhydride II (0.6127 g.) was heated at 280–320° for two hours with 0.47 g. of 5% palladium-on-charcoal in a stream of carbon dioxide. The gas evolved, presumably hydrogen, amounted to 16.6 ml. During the heating period a white solid (0.142 g.) slowly collected on the condenser which was situated above the surface of the reaction mixture. This substance was shown to be bibenzyl by its melting point (49–50° after recrystallization from aqueous ethanol) and the melting point of its trinitrobenzene adduct (102°). When a sample of II was heated in the same apparatus under the same conditions in the absence of the palladium-charcoal catalyst, no biphenyl was formed.

The residue from the palladium reaction was taken up in hot alcohol and filtered. Evaporation of the ethanol left a residue which solidified when petroleum ether was added. This substance, after drying for 10 hours at 90°, weighed 0.1462 g. and softened at 260–270°. It gave a positive flame test for boron, was soluble in alcohol and in benzene, and could be sublimed in vacuum.

(b) **Zinc Chloride.**—A portion of the oxide (0.063 g.) was heated under reflux for four hours with 5 ml. of water and 0.36 g. of zinc chloride. After cooling, 20 ml. of water was added and the mixture extracted with ether. The residue after distillation of the ether gave, on warming with an ethanol solution of 1,3,5-trinitrobenzene, a precipitate which melted at 102° after recrystallization from ethanol. The melting point was not depressed when the sample was mixed with the compound obtained from trinitrobenzene and commercial bibenzyl.

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[3] J. Kenner and J. Wilson, *J. Chem. Soc.*, **1108** (1927).

[4] The boron analyses were made by J. Thoburn; the nitrogen analyses by V. Stryker.

[5] R. Neu, *Ber.*, **87**, 802 (1954).

[6] J. Thiele and O. Kolzinger, *Ann.*, **305**, 99 (1899).

CHEMISTRY DEPARTMENT
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

The Dienone–Phenol Rearrangement. IV. A New Example of the Abnormal Path[1]

BY ELLIOT N. MARVELL AND JOHN L. STEPHENSON

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The majority of the examples of the dienone–phenol rearrangement are encompassed by the Arnold mechanism.[2] However 2,2-dimethyl-1-oxo-

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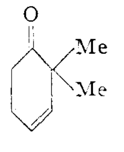
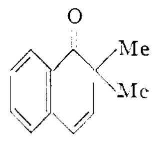
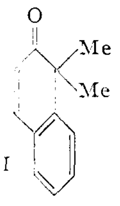
[1] Published with the approval of the Monographs Publications Committee, Oregon State College, as Research Paper No. 275, School of Science, Department of Chemistry. Taken from a thesis submitted by John Stephenson in partial fulfillment of the requirements for the Master of Science degree, Oregon State College, 1955.

[2] R. T. Arnold, J. S. Buckley and J. Richter, THIS JOURNAL, **69**, 2322 (1947).

1,2-dihydronaphthalene (II) and several related dienones have been shown[3] to react *via* an alternate path. The analogous dienone of the cyclohexane system I reacts, at least in part, in accord with the Arnold mechanism.[4] Since the incorporation of the 2,3-double bond of I into an aromatic ring altered the course of the reaction, it seemed desirable to study the compound III with the 4,5-double bond similarly incorporated.


I

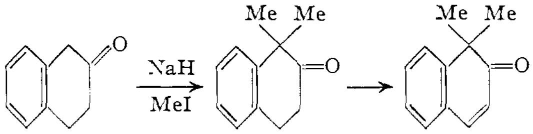

II


III

Results

The necessary compound III was prepared from β-tetralone as indicated. Alkylation was brought about by the procedure of Soffer, *et al.*[5] Robinson[6] has shown that monoalkylation of β-tetralone goes in the 1-position. Soffer, *et al.*,[5] have shown that dialkylation with methyl bromoacetate introduces both groups on carbon one. Our results prove that dimethylation follows the established pattern. The double bond was introduced by conventional means.[3] Addition of one mole of hydrogen to the dienone regenerated the 1,1-dimethyltetralone proving that no structural alteration had occurred during the dehydrohalogenation process. Unlike II which forms only an oxime, III gives rise to both a 2,4-dinitrophenylhydrazone and a semicarbazone.

The dienone III rearranges to give only a naphthyl acetate which appears to be a single compound. Formation of derivatives and mixed melting point tests with authentic samples identified this compound as 3,4-dimethyl-1-naphthyl acetate. This is an interesting result for both II and 4,4-dimethyl-1-oxo-1,4-dihydronaphthalene (IV)[2] give the same product. However, the rearrangement of III requires five days under conditions where five hours suffices for the reaction of II and IV.



Experimental

1,1-Dimethyl-2-oxo-1,2-dihydronaphthalene.—A solution containing 17.0 g. (0.1 mole) of 1,1-dimethyl-2-tetralone[5] in 30 ml. of carbon tetrachloride was treated dropwise with 16.0 g. (0.1 mole) of bromine in 100 ml. of the same solvent. After the addition the solvent was distilled and the residue heated for 30 minutes with 30 ml. (0.3 mole) of γ-collidine. The unsaturated ketone was isolated by distillation, b.p. 136–141° (16 mm.), as a pale yellow, light sensitive oil weighing 10.5 g. (62%), $n^{25}\text{D}$ 1.5843. The 2,4-dinitrophenylhydrazone melted at 224.5–225.5°.

Anal. Calcd. for $C_{18}H_{16}N_4O_4$: C, 61.36; H, 4.58. Found: C, 61.36; H, 4.60.

A semicarbazone was also prepared, m.p. 187–188°.

Anal. Calcd. for $C_{13}H_{15}N_3O$: C, 68.1; H, 6.55. Found: C, 67.4; H, 6.31.

Hydrogenation of 0.1597 g. of the dienone over platinum oxide at atmospheric pressure utilized 21.0 ml. of hydrogen (calcd. 20.8 ml.). The reduction product formed a 2,4-dinitrophenylhydrazone, m.p. 139.5–140.5°. The 2,4-dinitrophenylhydrazone of 1,1-dimethyl-2-tetralone melts at 140–141°.[5]

Rearrangement.—Two grams (0.012 mole) of 1,1-dimethyl-2-oxo-1,2-dihydronaphthalene was allowed to stand five days at room temperature with 30 ml. of acetic anhydride containing ten drops of sulfuric acid. The crude acetate, 2.37 g. (95%), was crystallized from benzene–petroleum ether until it melted at 87.5–88.5°. The acetate of 3,4-dimethylnaphthol melts at 88.5–89.5°.[2,3]

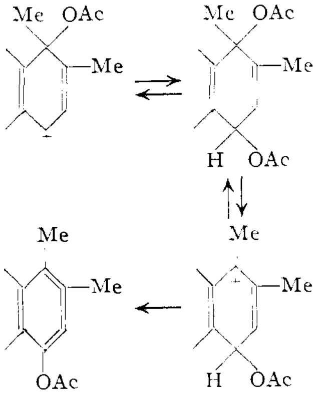
This acetate, 1.6 g. (0.0075 mole), was hydrolyzed[3] to a naphthol, m.p. 121.5–122.5° (reported[3] 120–122°). Bromination of the naphthol[2] gave the 2-bromo derivative, m.p. 98–99° (reported 99–101°[3]). The naphthol also was coupled with diazotized *p*-nitroaniline[2] giving a deep red azo compound, m.p. 241–243° (reported[2] 241–243°).

Discussion

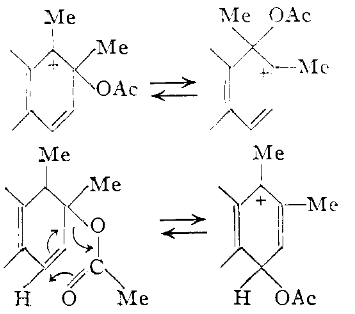
The results reported here combined with those noted earlier,[3] show that whenever the Arnold mechanism requires participation of a double bond that is also part of an aromatic ring the reaction follows an alternate course. There is no logical reason why that alternate should always follow the same pattern, but in all cases investigated so far, it involves the migration of the oxygen.

Little can be said at present about the manner of the oxygen migration, but the notable difference in rates of rearrangement between II and III is suggestive. It seems likely that the difference in rate must be due to the mode of that migration for the earlier steps are very similar and seem unlikely to account for that difference.

The 1,4-shift which occurs in the reaction of II seems best explained *via* a reaction with the solvent as shown.



The 1,3-shift occurring in III is probably not a simple allylic rearrangement since the neighboring



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[3] E. N. Marvell and A. O. Geiszler, This Journal, **74**, 1259 (1952); E. N. Marvell and E. Magoon, *ibid.*, **76**, 5118 (1954).

[4] E. N. Marvell and E. Magoon, *ibid.*, **77**, 2542 (1955).

[5] M. D. Soffer, R. A. Stewart, J. C. Cavagnol, H. E. Gellerson and E. A. Bowler, *ibid.*, **72**, 3704 (1950).

[6] J. W. Conforth, R. H. Conforth and R. Robinson, *J. Chem. Soc.*, 689 (1942).

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.

DEPARTMENT OF CHEMISTRY
OREGON STATE COLLEGE
CORVALLIS, OREGON

The Reaction between Diazoacetic Ester and Cycloöctatetraene

BY DONALD D. PHILLIPS

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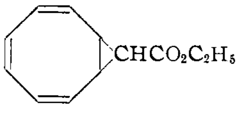
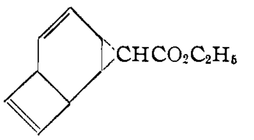
In continuation of our studies[1] in the field of diazoacetic ester (I) chemistry we have examined in some detail the product derived from I and cyclooctatetraene. Although our investigations on this interesting adduct are continuing, the recent communication of Akiyoshi and Matsuda[2] prompts us to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

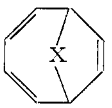
We considered from the outset that the adduct was the cyclopropane (II) although consideration had to be given to structure III in view of the well-established tendency of cycloöctatetraene to react through the intermediate bicyclo[4.2.0]system.[3] Furthermore IVa was considered a distinct possibility 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.