Dehydrogenation of Octahydronaphthalenes with Bromine. 2,3,6,7-Naphthalenetetracarboxylic Dianhydride

O. W. WEBSTER AND W. H. SHARKEY

Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

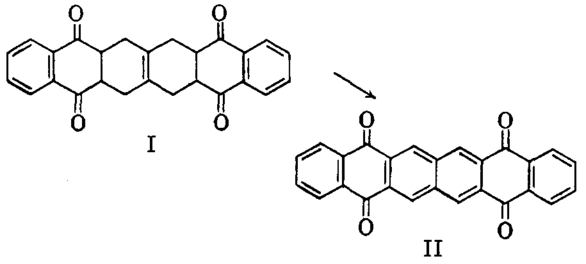
Received April 4, 1962

From the ease with which octahydronaphthalenes are synthesized from allene and dienophiles,[1,2] it would appear that these compounds should form the basis for a new synthetic route to substituted naphthalenes. This has not been the case heretofore because conditions vigorous enough to cause complete aromatization by usual catalytic methods also result in loss of functional groups.[1] We have found that bromine dehydrogenation is capable of aromatizing octahydronaphthalenes and have used this method to prepare 2,3,6,7-naphthalenetetracarboxylic dianhydride.

Reaction of 1,2,3,4,5,6,7,8 - octahydronaphthalene-2,3,6,7 - tetracarboxylic dianhydride, the 2:2 adduct from allene and maleic anhydride, with bromine in boiling trichlorobenzene has given good yields of 2,3,6,7-naphthalenetetracarboxylic dianhydride. The product isolated from the reaction mixture was free of bromine but did contain impurities not readily removed by recrystallizaton. Pure samples were obtained by recrystallization of the tetramethyl ester from methanol followed by reconversion to the dianhydride by hydrolysis and dehydration.

The spectral properties of the dianhydride confirmed its structural assignment. As expected for a naphthalene derivative, ultraviolet maxima occurred at 252, 285, and 346 mμ. Infrared absorption showed aromatic CH and cyclic anhydride. In addition, proton n.m.r.[3] of the tetramethyl ester of the dianhydride in deuterochloroform was composed of only two peaks—a methoxy hydrogen peak at −156 c.p.s. three times as intense as an aromatic CH peak at −333 c.p.s.

An additional example of the bromine dehydrogenation method is illustrated by aromatization of a complex polynuclear compound, 6,7,14,15,17,19,-22,24 - octahydro - 5,8,13,16 - hexacenetetrone (I). This compound, which can be obtained by reaction of naphthaquinone with 1,2-dimethylenecyclobutane,[4] was easily converted in high yields to the hexacenetetrone II by reaction with bromine.


I

II

II is a green-yellow solid that does not melt at temperatures up to 360°. It is reduced by sodium hydrosulfite to a soluble red-leuco form from which the original material can be recovered by air oxidation.

Experimental

Reaction of 1,2,3,4,5,6,7,8-Octahydro-2,3,6,7-naphthalenetetracarboxylic Dianhydride (I) with Bromine.—A suspension of 276 g. (1.00 mole) of 1,2,3,4,5,6,7,8-octahydro-2,3,6,7-naphthalene tetracarboxylic dianhydride in 2 l. of 1,2,4-trichlorobenzene was heated under reflux for 30 min. with 10 ml. of thionyl chloride. Bromine (660 g., 4.12 moles) was added dropwise to the stirred suspension over the course of 7 hr. During the addition, the temperature was maintained at 213°, which is slightly below the boiling point of trichlorobenzene. Hydrogen bromide evolution, though vigorous at the outset, almost completely ceased during the addition of the last 60 g. of bromine. After heating for an additional 3-hr. period, the reaction mixture was cooled to room temperature. The insoluble, crude 2,3,6,7-naphthalenetetracarboxylic anhydride,[5] 273 g., was collected on a filter and was used without further purification for conversion to its tetramethyl ester.

Tetramethyl 2,3,6,7-Naphthalenetetracarboxylate.—A mixture of 15 g. (0.056 mole) of crude 2,3,6,7-naphthalenetetracarboxylic dianhydride, 500 ml. of methanol, and 10 ml. of concentrated sulfuric acid was heated under reflux for 6 hr. As the solution cooled, 14 g. of tetramethyl 2,3,6,7-naphthalenetetracarboxylate separated. This product, after recrystallization from methanol, melted at 181–183°. Ultraviolet absorption in acetonitrile: λ_{max} 247 mμ (ϵ 6.44 $\times$ 10^4), 274 mμ (ϵ 7.32 $\times$ 10^3), 284 mμ (ϵ 6.28 $\times$ 10^3), 331 mμ (ϵ 1.91 $\times$ 10^3), and 343 mμ (ϵ 2.61 $\times$ 10^3). Infrared spectrum: 3035, 2985, and 1740 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{16}O_8$: C, 60.00; H, 4.20; sap. equiv., 90.1. Found: C, 59.83; H, 4.43; sap. equiv., 91.5.

2,3,6,7-Naphthalenetetracarboxylic Acid.[6]—A mixture of 1.2 g. (0.003 mole) of tetramethyl 2,3,6,7-naphthalenetetracarboxylate, 5 g. of potassium hydroxide, 100 ml. of ethanol, and 10 ml. of water was heated for approximately 1 hr. Additional water (50 ml.) was added and heating continued for 2 hr. The reaction mixture was concentrated to about 30 ml. and then acidified with hydrochloric acid. 2,3,6,7-Naphthalenetetracarboxylic acid (1.05 g., 100% yield) slowly crystallized. Approximately 1 g. of purified product was obtained by recrystallization several times from water. The tetracarboxylic acid does not melt below 300°.

Anal. Calcd. for $C_{14}H_4O$: C, 55.27; H, 2.65; neut. equiv., 76.0. Found: C, 55.35; H, 2.77; neut. equiv., 77.0.

---

[1] K. Alder and O. Ackermann, *Ber.*, **87**, 1567 (1954).

[2] H. N. Cripps, J. K. Williams, and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 2723 (1959).

[3] The n.m.r. spectrum was calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of tetramethylsilane. The spectrum was obtained on a high resolution n.m.r. apparatus manufactured by Varian Associates, Palo Alto, California, operating at 40 Mc. and approximately 10,000 gauss.

[4] H. N. Cripps, U.S. Patent 2,934,544, April 26, 1960.

[5] O. W. Webster, U.S. Patent 2,912,442, November 10, 1959.

[6] Further structural proof for 2,3,6,7-naphthalenetetracarboxylic acid is its ready conversion by SF_4 to 2,3,6,7-tetrakis(trifluoromethyl)-naphthalene, a substance also obtained by reaction of bis(trifluoromethyl)acetylene with benzene. C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **83**, 3432 (1961).

2,3,6,7-Naphthalenetetracarboxylic Dianhydride.—2,3-6,7-Naphthalenetetracarboxylic acid (0.50 g., 0.0017 mole) was dissolved in 100 ml. of acetic anhydride. The mixture was heated under reflux for 1 hr., and then most of the acetic anhydride was removed by evaporation. The solid that formed on cooling was recrystallized from acetic anhydride to give 0.12 g. of naphthalene dianhydride. The anhydride darkens on heating to 400° but does not melt.

Anal. Calcd. for $C_{14}H_4O_6$: C, 62.70; H, 1.50; neut. equiv., 67.1. Found: C, 63.21; H, 1.71; neut. equiv., 65.0.

Ultraviolet absorption of water solutions of the anhydride: λ_{max} 252 mμ (ϵ 6.56 $\times 10^4$), 285 mμ (ϵ 8.56 $\times 10^3$), 346 mμ (ϵ 2.41 $\times 10^3$). Infrared absorption: 3085 and 3040 cm.$^{-1}$ (aromatic CH), and multiple absorption at the 1820-cm.$^{-1}$ region (cyclic anhydride).

Reaction of 6,7,14,15,17,19,22,24-Octahydro-5,8,13,16-hexacenetetrone (I) with Bromine.—A mixture of the octahydronaphthalene[4] (3.3 g., 0.008 mole] in 75 ml. of 1,2,4-trichlorobenzene was heated under reflux (210–215°) and to it was added bromine (6 g., 0.037 mole) dropwise over a period of 1 hr. Hydrogen bromide evolved, and a brown precipitate formed in the reaction mixture. Heating was continued 2 hr. longer, and then the mixture was allowed to cool to room temperature. The yellow-brown product that separated weighed 3 g. It was insoluble in dimethylformamide, tetramethylene sulfone, acetone, and ethyl acetate. It was purified by trituration with hot trichlorobenzene.

Anal. Calcd. for $C_{26}H_{12}O_4$: C, 80.5; H, 3.06. Found: C, 79.98; H, 3.26.

Identity of this product as 5,8,13,16-hexacenetetrone (II) was confirmed by its infrared spectrum: 3080 (w) (aromatic CH), 1680 (s) (carbonyl), 1590 (s) (aromatic C=C), 1395 (s), 1320 (s), 1275 (vs), 1205 (m), 1165 (m), 1145 (m), 1125 (m), 953 (s), 715 cm.$^{-1}$ (s). For comparison, the infrared spectrum of I has bands at: 3060 (w), 2880 (m), 2840 (m), 1690 (s), 1590 (s), 1445 (m), 1365 (m), 1340 (m), 1280(s), 1245 (s), 1205 (m), 1070 (m), 993 (m), 944 (m), 806 (m), 780 (m), 739 (s), 712 (m), 690 cm.$^{-1}$ (m).

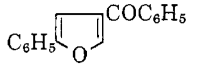
Addition of Phenylmagnesium Bromide to 2-Phenyl-4-benzoylfuran[1]

Reynold C. Fuson, H. Scott Killam,
and Wilburn S. Smith, Jr.[2]

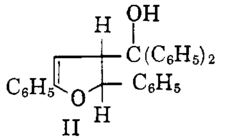
*Noyes Chemical Laboratory, University of Illinois,
Urbana, Illinois*

Received April 4, 1962

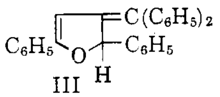
2-Phenyl-4-benzoylfuran (I) has been shown to be extremely susceptible to ring cleavage by alkaline reagents.[3] Treatment with dilute sodium hydroxide or with potassium carbonate led to ring opening. Ammonia or aniline converted the furan into the corresponding pyrrole. This behavior is predictable for a compound that is vinylogous with an ester of benzoic acid. Grignard reagents, therefore, might also be expected to cause opening of the ring. Experiments with phenylmagnesium bromide, however, led to unexpected results. The product was neither the open-chain compound nor the carbinol resulting from 1,2-addition to the carbonyl group; it corresponded, instead, to the compound to be expected from 1,4-addition followed by 1,2-addition. What appeared to be the primary product was the carbinol, II.



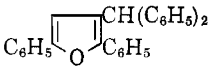
I



II



III



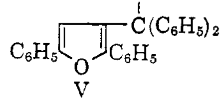
IV

The over-all change is similar to that observed when duryl phenyl ketone is condensed with benzyl- and *p*-chlorobenzylmagnesium chloride.[4] The alcohol was easily dehydrated to the olefin, III; in fact, in most experiments the alcohol was dehydrated during the work-up, and the olefin was isolated directly.

Isomerization of the olefin by transfer of the exocyclic double bond to the ring, although expected to occur readily, proved to be fairly difficult to effect. It was necessary to heat the olefin at reflux in ethanol with a small amount of hydrochloric acid to bring about this conversion. The product, 2,5-diphenyl-3-benzohydrylfuran (IV), was subsequently synthesized by an independent route. Cyclization of 1,4-diphenyl-1,4-butanedione with polyphosphoric acid gave 2,5-diphenylfuran in good yield; alkylation of this furan by means of benzohydrol and polyphosphoric acid yielded a compound that was identical in all respects to the furan obtained by isomerization of the olefin, III.

An attempt was made to form a benzoyl derivative by adding benzoyl chloride to the reaction mixture produced by condensation of phenylmagnesium bromide with ketone I; only furan IV was obtained. In a similar way the reaction mixture was treated with carbon dioxide, but no acid could be isolated; olefin III was formed in the usual yield. Attempts to prepare a mono-adduct by limiting the amount of Grignard reagent failed. The usual diaddition products were formed when at least 2.5 moles of the reagent were employed for each mole of ketone; when less than this amount of Grignard reagent was used, starting material was recovered.

3- Benzoyl - 2,5 - diphenylfuran reacted with



V

---

[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U.S. Army (Contract No. DA-11-022-ORD-874).

[2] California Research Corporation Fellow, 1958–1959.

[3] R. C. Fuson, C. L. Fleming, and R. Johnson, *J. Am. Chem. Soc.*, **60**, 1994 (1938).

[4] R. C. Fuson, J. P. Freeman, and J. J. Looker, *J. Org. Chem.*, **26**, 4217 (1961).