removed under vacuum on a steam bath. The residual dark brown oil (950 g.) was then subjected to fractional distillation at reduced pressure. A forerun (207 g.) consisting essentially of 4-chloro-3-hydroxybutyronitrile and 4-hydroxycrotononitrile was collected from 90–115° at 0.4 mm. Pure 3-hydroxyglutaronitrile (723 g.) then distilled at 155–160° at the same pressure (yield 60%). A sample (12 g.) of the dinitrile was purified by fractional distillation through a 6-in. column and the portion boiling at 156° (0.22 mm.) collected (10 g.). $n^{23}D$ 1.4632 (Reported,[5] b.p. 202° (11 mm.) $n^{22}D$ 1.4805). The infrared spectrum of the material showed bands at 2.91 and 4.41 μ.

*Anal.* Calcd. for $C_5H_6N_2O$: C, 54.54; H, 5.49; N, 25.44. Found: C, 54.3; H, 5.5; N, 25.4.

**3-Hydroxy-3-methylglutaronitrile.**—Magnesium sulfate heptahydrate (112 g., 0.45 mole) and potassium cyanide (32.5 g., 0.5 mole) were dissolved in water (160 ml.). This solution was cooled to 5° and over a period of 1.25 hr. there was added 1-chloro-2,3-epoxy-2-methylpropane (26.6 g., 0.25 mole) dropwise. After 24 hr., the product was isolated as in the above experiment. The resulting dark brown liquid was distilled at 0.09 mm. and the main fraction (23 g.) consisting of almost pure 3-hydroxy-3-methylglutaronitrile, collected at 128–130°; yield 71%. A sample of this material redistilled for analysis boiled at 131° and 0.07 mm., $n^{25}D$ 1.4596.

*Anal.* Calcd. for $C_6H_8ON_2$: C, 58.05; H, 6.50; N, 22.57. Found: C, 58.0; H, 6.5; N, 22.3.

The infrared spectrum of the pure material showed bands at 2.91 and 4.41 μ characteristic of hydroxyl and saturated nitrile groups, respectively.

**3-Hydroxy-3-ethylglutaronitrile.**—This was prepared in exactly the same way as the methyl homolog. From 2-ethylepichlorohydrin (20.1 g., 0.167 mole) and a solution of potassium cyanide (2.17 g., 0.334 mole) and magnesium sulfate heptahydrate (73.8 g., 0.30 mole) there was obtained pure 3-hydroxy-3-ethylglutaronitrile (17.71 g., 77% yield) b.p. 134–137° (0.3 mm.), $n^{25}D$ 1.4658. A sample was redistilled for analysis b.p. 135° (0.35 mm.).

*Anal.* Calcd. for $C_7H_{10}N_2O$: C, 60.85; H, 7.3; N, 20.28. Found: C, 60.8; H, 7.4; N, 20.5.

**3-Hydroxy-3-phenylglutaronitrile.**—A solution of potassium cyanide (19.5 g., 0.3 mole), potassium carbonate (17 g.), and potassium bicarbonate (17 g.) in water (120 ml.) was stirred vigorously with 2-phenylepichlorohydrin (25 g., 0.15 mole) for 1 week at room temperature. The semisolid organic phase was then diluted with a small amount of a 50–50 mixture of ether and petroleum-ether (b.p. 30–60°) and the solid removed by filtration. The filtrate contained mainly unchanged epoxide. Recrystallization of the solid from ethanol gave almost pure 3-hydroxy-3-phenylglutaronitrile (7.8 g.) as feathery white needles, m.p. 117–118°. A sample recrystallized for analysis had m.p. 118–120°.

*Anal.* Calcd. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.05. Found: C, 70.9; H, 5.6; N, 15.1.

**Tris(cyanomethyl)carbinol.**—2-(Chloromethyl)epichlorohydrin (14.1 g., 0.1 mole) was added dropwise over a period of 15 min. to a cooled solution of potassium cyanide (20.4 g., 0.314 mole) and magnesium sulfate heptahydrate (74 g., 0.3 mole) in water (200 ml.). Isolation of the product in the usual way afforded a somewhat oily crystalline solid (10.5 g.). One recrystallization of this material from ethanol afforded tris(cyanomethyl)carbinol (8.0 g., yield 53.5%) m.p. 106–108°, raised to 109° from the same solvent. The infrared spectrum showed hydroxyl absorption at 2.99 μ and a split band at 4.37 and 4.41 μ for nitrile.

*Anal.* Calcd. for $C_7H_7N_3O$: C, 56.37; H, 4.73; N, 28.18. Found: C, 56.5; H, 4.8; N, 28.0.

**Acknowledgment.**—We are much indebted to Dr. C. K. Fitz who carried out all microanalyses.

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## Polycyclic Studies. II. The Ultraviolet Spectra of Some Diels-Alder Adducts[1]

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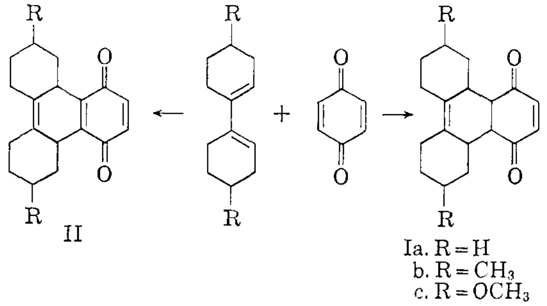
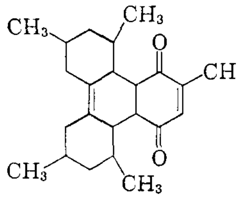
*Received November 28, 1961*

The bicyclohexenyl-*p*-benzoquinone Diels-Alder adducts I and II have been recently employed[1] as intermediates in the synthesis of triphenylenes.



Ia. R = H
b. R = $CH_3$
c. R = $OCH_3$

The difference in the ultraviolet absorption spectra between adducts I and II is one of the criteria[1] by which these two types of compounds can be distinguished. Whereas the quinones II show the expected maximum at 258–259 mμ (log ε 4.1–4.2), the adducts I do not show a definite maximum in the region 220–230 mμ, as would be expected from the data for enediones summarized in Table I. On the other hand, substituted enediones have been shown to exhibit an absorption maximum in the region 235–250 mμ (Table II). Indeed, of the compounds investigated by us, only one, 2,5,7,10,12 pentamethyl-$\Delta^{2,14}$-tetradecahydrotriphenylene-1,4-dione, III, showed such a maximum ($\lambda_{max}^{ethanol}$ 242 mμ, ε 11,500).



III

This apparent lack of a maximum has been observed also in other similar unsubstituted Diels-Alder adducts investigated in this laboratory.[3]

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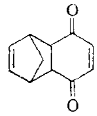
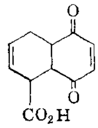
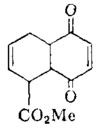
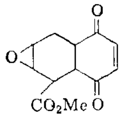
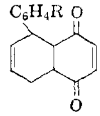
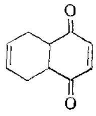
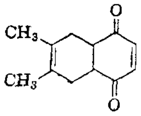
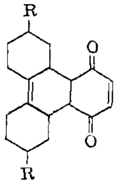
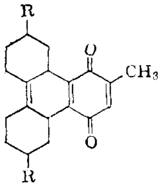
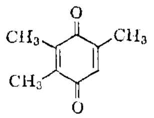
[1] Part I. A. Mandelbaum and Michael Cais, *J. Org. Chem.*, **26**, 2633 (1961).

[2] American Chemical Society–Petroleum Research Fund Fellow, 1959–1961.

[3] Yanina Altman and David Ginsburg, *J. Chem. Soc.*, 1498 (1961).

TABLE I

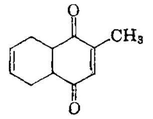
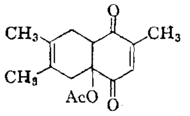
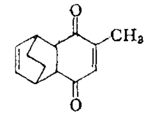
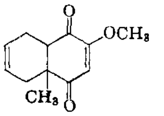
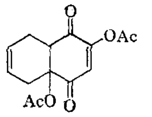
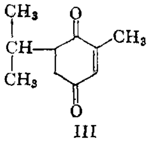
THE ULTRAVIOLET SPECTRA OF CYCLOHEXENE-1,4-DIONES AND SUBSTITUTED QUINONES

| Compound | | $\lambda_{max}$ mμ | $\epsilon^h$ |
|---|---|---|---|
|  | | 222[a] | 12,800 |
|  | | 224[b] | 11,300 |
|  | | 223[b] | 10,670 |
|  | | 221[b] | 10,380 |
|  | | 218–227[c] | 15,000–27,500[i] |
|  | | 224[d] | 12,000 |
|  | | 228 | 9,800 |
|  | Ia | 226[e] | 11,000 |
| | Ib | 226[e] | 11,100 |
| | Ic | 228[e] | 9,450 |
|  | R = H | 259[f] | 16,300 |
| | R = $CH_3$ | 258–259[f] | 12,700 |
|  | | 253, 260[g] | 19,800; 19,400 |

[a] H. Bastron, R. E. Davis, and L. W. Butz, *J. Org. Chem.*, 8, 515 (1943); [b] R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kirstead, *Tetrahedron*, 2, 1 (1958). [c] E. A. Braude, E. R. H. Jones, and E. S. Stern, *J. Chem. Soc.*, 1092 (1947). [d] Prepared according to O. Diels and K. Alder, *Ber.*, 62, 2361 (1929). M.p. 57–58° (lit., 58°) [e] Values obtained by subtraction, see Fig. 1. [f] See ref. 1 for synthesis. [g] E. A. Braude, *J. Chem. Soc.*, 493 (1945). [h] In ethanol solution, except where otherwise indicated. [i] In hexane solution.

TABLE II

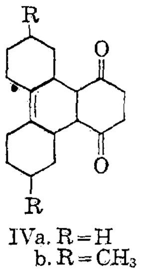
THE ULTRAVIOLET SPECTRA OF 2-SUBSTITUTED CYCLOHEX-2-ENE-1,4-DIONES

| Compound | $\lambda_{max}$ mμ | $\epsilon^f$ |
|---|---|---|
|  | 237[a] | 12,250 |
|  | 236[a] | 20,000 |
|  | 235[a] | 8,200 |
|  | 269[a] | 8,400 |
|  | 240[b] | 8,000 |
|  | 238[c] | 15,600[d] |
| III | 242[e] | 11,500 |

[a] H. Bastron, R. E. Davis, and L. W. Butz, *J. Org. Chem.*, 8, 515 (1943). [b] J. A. Barltrop and M. L. Burstall, *J. Chem. Soc.*, 2183 (1959). [c] O. Isler, H. Lindlar, M. Montavon, R. Rüegg, G. Saucy, and P. Zeller, *Helv. Chim. Acta*, 39, 2041 (1956). [d] Calculated from reported[c] value $\Sigma^{1\%}_{1\,cm}$ = 942, in petroleum ether solution. [e] See ref. 1 for synthesis. [f] In ethanol solution, except where otherwise indicated.

A comparison of I with the formulas of the compounds listed in Table I shows that in I the nonconjugated double bond 14:15 is tetrasubstituted and exocyclic to two fused six-membered rings. Such double bonds in the steroid series have been reported[4] to show a rather intense ultraviolet absorption in the region 210–225 mμ. For example $\Delta^{8(14)}$ and $\Delta^{9,10}$ are reported[4] to absorb in the range $\epsilon_{210\ m\mu}$ 6300–10,500 and $\epsilon_{220}$ 1900–7000.

The nonconjugated 14:15 double bond in the reduced adducts IV, which is similar to the 8:14 and 9:10 double bonds in steroids, shows a similar



IVa. R = H
b. R = $CH_3$

a. R = H
b. R = $CH_3$

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(4) P. Bladon, H. B. Henbest, and G. W. Wood, *J. Chem. Soc.*, 2737 (1952).

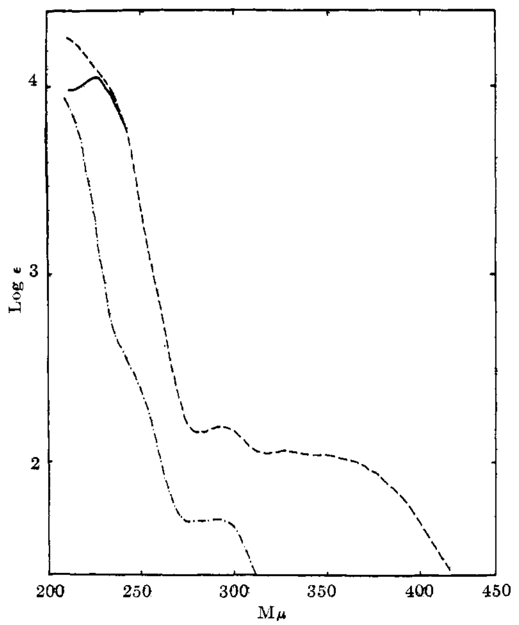

Fig. 1.—Evaluation of enedione chromophore absorption maximum in spectra of bicyclohexenyl-*p*-benzoquinone adducts
(– – – –) Spectrum of $\Delta^{2,14}$ tetradecahydrotriphenylene-1,4-dione (Ia) (in ethanol)
(- · – · –) Spectrum of $\Delta^{14}$ hexadecahydrotriphenylene-1,4-dione (IVa) (in ethanol)
(———) Curve obtained by subtracting IVa from Ia

high absorption in the 210–225 mμ region ($\epsilon_{210\ m\mu}$ 8700, $\epsilon_{220\ m\mu}$ 4400).

On the assumption that this high absorption of 14:15 double bond might mask the maximum due to the enedione chromophore, the intensity values of the reduced adducts IV in the 210–240-mμ region were subtracted from those of the adducts I. When the resulting intensity values were plotted against the respective wave lengths (Fig. 1), there was obtained for adducts Ia, Ib, and Ic the expected maximum of the enedione chromophore (Table I).

## Experimental

The absorption spectra were measured with a Unicam SP 500 spectrophotometer. Melting points were measured in a capillary and are uncorrected.

**6,7-Dimethyl-5,8,9,10-tetrahydronaphthoquinone (Table I).**—A mixture of 2,3-dimethylbutadiene (4 g., 0.049 mole) and *p*-benzoquinone (4 g., 0.037 mole) was kept for 1 week at room temperature. Trituration with ethanol (15 ml.) yielded yellow crystals (6.75 g., 96%), m.p. (from ethanol) 115–117° (lit.[5] m.p. 113–115°) $\nu_{C=O}^{CHCl_3}$ 1690 cm.$^{-1}$. $\lambda_{max}$ 228 mμ, ε 9800.

**6,11-Dimethyl-$\Delta^{14}$-hexadecahydrotriphenylene-1,4-dione (IVb).**—A solution of 6,11-dimethyl-$\Delta^{2,14}$-tetradecahydrotriphenylene-1,4-dione Ib (4.5 g.) in acetic acid (70 ml.) was shaken with powdered zinc (15 g.) for 15 min. The mixture was then filtered, and the filtrate was poured into cold water (1.5 l.), shaken for 15 min., and kept in the refrigerator overnight. A white precipitate was obtained which upon crystallization from methanol yielded white crystals 3.3 g.), m.p. 107–110°. Recrystallization from methanol gave the analytical sample, m.p. 133.5–135°.

*Anal.* Calcd. for $C_{20}H_{18}O_2$: C, 79.95; H, 9.39; O, 10.65. Found: C, 79.69; H, 9.39; O, 10.67.

**Acknowledgment.**—This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

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[5] L. F. Fieser, W. P. Campbell, and E. M. Fry, *J. Am. Chem. Soc.*, **61**, 2217 (1939).

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# A Method of Tritium Labeling

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The use of tritium as a tracer in reactions of various organic compounds is of growing interest. Much of the labeling is accomplished by the Wilzbach method which involves the exposure of such compounds to curie quantities of tritium gas for periods of hours or days.[1] In general, the labeling process is accompanied by the appearance of a number of labeled by-products often with specific activities 10–100 times greater than that of the desired material.[2] The presence of these by-products which arise from such processes as polymerization,[3] replacement of substituents,[4] isomerization,[3] and addition of tritium to unsaturated linkages[5] requires careful purification procedures. The times necessary for labeling by the Wilzbach method may be greatly reduced if an electric discharge is employed during the period of gas exposure.[6] Labeling in the presence of uranium hydride containing tritium has also been carried out with certain advantages over the usual procedure.[7]

It is well known that rapid exchange between deuterium gas and the active hydrogen in organic compounds such as acids and alcohols occurs in the presence of certain metal catalysts.[8] The same

[1] K. E. Wilzbach, *J. Am. Chem. Soc.*, **79**, 1013 (1957).

[2] K. E. Wilzbach, "Proceedings of the International Atomic Energy Agency Symposium on the Detection and Use of Tritium in the Physical and Biological Sciences," Vienna, Austria, 1961, paper 83.

[3] P. Riesz and K. E. Wilzbach, *J. Phys. Chem.*, **62**, 6 (1958).

[4] L. Dorfman and K. E. Wilzbach, *ibid.*, **63**, 799 (1959).

[5] H. J. Dutton, E. P. Jones, L. H. Mason, and R. F. Nystrom, *Chem. Ind.* (London), 1176 (1958).

[6] F. L. Jackson, G. W. Kittinger, and F. P. Krause, *Nucleonics*, **18**, 102 (1960).

[7] R. E. Felter and L. A. Currie, "Proceedings of the International Atomic Energy Agency Symposium on the Detection and Use of Tritium in the Physical and Biological Sciences," Vienna, Austria, 1961, paper 121.

[8] L. E. Line, Jr., B. Wyatt, and H. A. Smith, *J. Am. Chem. Soc.*, **74**, 1808 (1952); H. A. Smith and E. L. McDaniel, *ibid.*, **77**, 583 (1955); E. L. McDaniel and H. A. Smith in "Advances in Catalysis and Related Subjects," Vol. IX, Academic Press, Inc., New York, 1957, p. 76; H. A. Smith and B. B. Stewart, *J. Am. Chem. Soc.*, **82**, 3898 (1960).