the main features of the spectrum are due to hyperfine interaction with protons on carbon atoms 1, 3, 6, 8 of II (each unpaired electron in II being effectively restricted to one-half of the molecule) while the additional splittings arise from the protons on 2, 4, 5, 7.

Ether solutions of the green form did not reveal any absorption at −77°. However, on warming to −46° a resonance was observed which disappeared as the color disappeared. Possibly some complexing occurs at the lower temperature leading to broadened lines which could not be detected.

A dark green solid may be obtained from I by sublimation onto a glass surface cooled by liquid nitrogen. At −197° this material exhibited a resonance (line width 14 gauss). After one hour at room temperature the material reverted to the yellow species which did not show e.s.r.[6]

The author is deeply grateful to Professors S. I. Weissman and J. Townsend for the availability of their e.s.r. apparatus.

(6) This e.s.r. examination was kindly performed by Dr. J. P. Gordon.

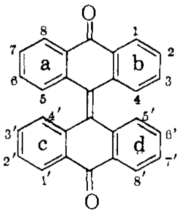
BELL TELEPHONE LABORATORIES
MURRAY HILL, N. J. EDEL WASSERMAN

RECEIVED JULY 30, 1959

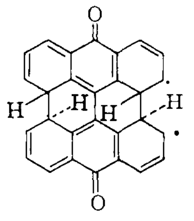
THE STRUCTURE OF THE THERMOCHROMIC FORM OF BIANTHRONE

Sir:

In solution, yellow $\Delta^{10,10'}$-bianthrone (I) exhibits a reversible thermochromism involving equilibration with a green form whose concentration increases with temperature.[1] The same green species is obtained by irradiation of the solution at −77° and by the application of pressure to the solid.[1,2] We propose that the green form is a diradical of which II is one of the resonance structures



I



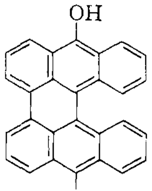
II

In support of II we note that the green form is magnetic.[3]

We may exclude the possibility that the magnetic species is a diradical in which two planar "anthrone halves" are twisted about a single bond. Harnik and Schmidt's X-ray analysis of I demonstrates that rings **a** and **b** are above the plane of the paper, and rings **c** and **d** below.[4] Consequently, a twisted diradical would be stabilized by substituents in the 4 and 4′ positions. However, Hirshberg and Fischer's data indicate that the introduction of such groups renders the green form *less* stable.[5] The increased lability of II is attributable to steric interactions between the substituents and the **d** and **a** rings.

The absence of a betaine structure is demonstrated by the kinetics of the disappearance of the green form at −50°. The rate in ethanol is greater than that in isoöctane by a factor of two.

In neutral solvents, I yields the green form (absorption maximum 6800 Å.) under ultraviolet irradiation at low temperatures. However, pyridine solutions produce a green color with an absorption maximum at 6270 Å. and a shoulder at 5750 Å. which are sensitive to both oxygen and excess I. This is the same band that Brockmann and coworkers have assigned to III, an isomer of II.[6]



III

Solutions of I react with sodium *t*-butoxide in the absence of light, to yield a red anion. Upon acidification (even methanol is a suitable acid) at −77°, the green form is produced. The formation of the thermodynamically less stable isomer finds precedence in the neutralization of other mesomeric anions.[7]

The piezochromism implies that the green species has a smaller volume than I.

The above data appear to be most compatible with structure II for the green form.

---

(1) G. Kortüm, *Angew. Chem.*, **70**, 14 (1958), and references cited therein.

(2) E. Wasserman and R. E. Davis, *J. Chem. Phys.*, **30**, 1367 (1959).

(3) E. Wasserman, THIS JOURNAL, **81**, 5006 (1959).

(4) E. Harnik and G. M. J. Schmidt, *J. Chem. Soc.*, 3295 (1954).

(5) Y. Hirshberg and E. Fischer, *ibid.*, 629 (1953). Data given in Figure 4. The authors do not comment on this effect of substituents.

(6) H. Brockmann, F. Pohl, K. Maier and M. N. Haschad, *Ann.*, **553**, 1 (1942); H. Brockmann and R. Mühlmann, *Chem. Ber.*, **82**, 348 (1949).

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 565.

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY R. B. WOODWARD
CAMBRIDGE, MASSACHUSETTS
BELL TELEPHONE LABORATORIES
MURRAY HILL, NEW JERSEY EDEL WASSERMAN

RECEIVED JULY 30, 1959

STRUCTURE OF STERCULIC ACID POLYMER. A CYCLOPROPENE REARRANGEMENT

Sir:

Sterculic acid (I)[1] is unstable at room temperature[2-4] and polymerizes with apparent destruction of the cyclopropene group.[3,4a] We now have established that this polymerization proceeds with ring opening to give the polymeric mixture of compounds IIa–d (where R′ and R″ are sterculic acid residues).

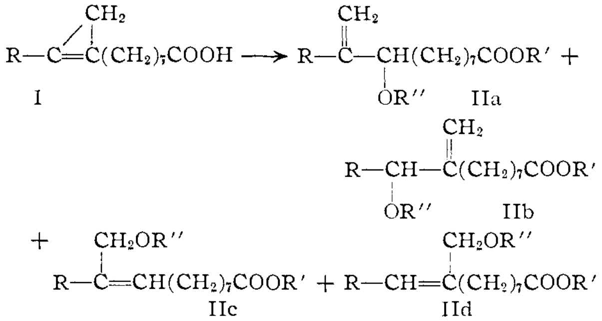
---

(1) For leading references, *cf.* K. L. Rinehart, Jr., W. A. Nilsson and H. A. Whaley, THIS JOURNAL, **80**, 503 (1958).

(2) J. R. Nunn, *J. Chem. Soc.*, 313 (1952).

(3) P. K. Faure and J. C. Smith, *ibid.*, 1818 (1956).

(4) (a) W. A. Nilsson, B.S. Thesis, University of Illinois, 1957; (b) H. A. Whaley, B.S. Thesis, University of Illinois, 1956.


I → IIa + IIb + IIc + IId

I, IIa-d, R = $CH_3(CH_2)_7$-

The polymer [*Anal.* Found: C, 77.63; H, 11.62] formed slowly at room temperature,[2,3,4b] rapidly at elevated temperature, gave no color with the Halphen reagent,[5,6] was insoluble in hot methanol. It showed no infrared absorption (CCl_4) at 1869 and 1010 cm.$^{-1}$ (cyclopropene)[3] but had bands at 1737 and 1169 cm.$^{-1}$ (ester),[7] 1712 and 960 cm.$^{-1}$ (end-group carboxyl),[7] 1648 and 901 cm.$^{-1}$ (*unsym.* disubstituted olefin).[7] The polymer was saponified to a mixture of the corresponding unsaturated hydroxy acids (IIa–d, R′ and R″ = H) [*Anal.* Found: C, 73.57; H, 11.57; N. eq., 318], infrared bands (CCl_4) at 3615 and 1281 cm.$^{-1}$ (hydroxyl),[7] 1707 and 935 cm.$^{-1}$, 1645 and 900 cm.$^{-1}$, which were acetylated to give the unsaturated acetoxy acids IIa–d (R′ = H; R″ = $COCH_3$)[8] [*Anal.* Found: C, 71.09; H, 10.91; N. eq., 354], with infrared bands (CCl_4) at 1735 and 1239 cm.$^{-1}$ (acetate),[7] 1707 and 945 cm.$^{-1}$, 1646 and 900 cm.$^{-1}$.

The unsaturated acetoxy acid mixture was oxidized by the periodate-permanganate procedure[9] to formaldehyde[10] (from IIa and IIb), determined with chromotropic acid,[9] together with the other products expected from structures IIa–d.

Pelargonic acid, m.p. 8–11°, (from IId) and azelaic acid, m.p. 105–107°, (from IIc) were identified by comparison with authentic samples, while 1-acetoxy-2-decanone, m.p. 55° [*Anal.* Found: C, 67.25; H, 10.23] (from IIc, R′ = H, R″ = $COCH_3$), was identical with a sample[11] prepared from nonanoyl chloride and diazomethane and subsequent acetolysis.[12]

The mixture of oxidation products from structures IIa and IIb (R′ = H, R″ = $COCH_3$), 9,10- and 10,9-acetoxyketoöctadecanoic acids [*Anal.* Found: C, 67.42; H, 10.42; N. eq., 352],[13] was saponified to a crude mixture of 9,10- and 10,9-hydroxyketoöctadecanoic acids,[13,14] melting 30–50°. The hydroxy keto acid mixture was further identified by chromic acid oxidation to 9,10-diketoöctadecanoic acid,[13,16] m.p. 82–83° (m.p. of authentic sample[14] 83–84°, lit.[16] m.p. 85–86°). The 2,4-dinitrophenylosazone,[15] prepared from the hydroxyketo acid mixture, had m.p. 147–147.5°, undepressed by mixture with an authentic sample, m.p. 148.5–149.5° (lit.[15] m.p. 146.5°), prepared from the oleic acid oxidation product.

The authors wish to express their appreciation for grants in support of this work to the University Research Board, Graduate College, University of Illinois, and to the Division of Research Grants, National Institutes of Health (No. RG-5883). They are also indebted to Mr. W. A. Nilsson[4a] for the results of preliminary experiments.

---

(5) G. Dijkstra and H. J. Duin, *Nature*, **176**, 71 (1955).

(6) P. K. Faure, *ibid.*, **178**, 372 (1956).

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd. ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

(8) This mixture (identical infrared spectrum) was prepared more simply by heating in acetic acid the acids isolated from saponification of *Sterculia foetida* seed oil, then isolating the unsaturated acetoxy acids (unadducted) by urea adduction and chromatography.

(9) R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710 (1955).

(10) The yield of formaldehyde (43%) compares favorably with the 50% yield reported by Lemieux and von Rudloff[9] from the oxidation of allyl acetate under similar conditions and suggests that the major products of the polymerization-rearrangement are IIa and IIb.

(11) Prepared by D. A. Teets.

(12) The second oxidation product from structure IId (R′ = H, R″ = $COCH_3$), 10-acetoxy-9-ketodecanoic acid, has not yet been isolated from the chromatographed products.

(13) The infrared spectra of these compounds were identical with those of authentic samples prepared *via* permanganate oxidation of oleic acid.[15,16]

(14) Authentic samples prepared by D. A. Davenport.

(15) G. King, *J. Chem. Soc.*, 1788 (1936).

(16) R. T. Holman, W. O. Lundberg, W. M. Lauer and G. O. Burr, THIS JOURNAL, **67**, 1285 (1945).

DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING
UNIVERSITY OF ILLINOIS
URBANA, ILL.

KENNETH L. RINEHART, JR.
CUTHBERT L. TARIMU
TOWNLEY P. CULBERTSON

RECEIVED JULY 14, 1959

REACTIONS OF ALKYLLITHIUMS WITH POLYHALIDES

Sir:

We wish to report the reaction of alkyllithiums with polyhalogen compounds and olefins to produce cyclopropanes. Our results support the conclusion that methylenes or carbenes are formed as reaction intermediates.

In attempting the preparation of trifluoromethyllithium from trifluoromethyl iodide by halogen–metal interconversion with methyllithium at −45°, Pierce, McBee and Judd observed the formation of tetrafluoroethylene in 43% yield. No evidence for the presence of the desired trifluoromethyllithium was obtained by hydrolysis of the reaction mixture.[1] This result suggests a possible intermediate formation of difluorocarbene by decomposition of trifluoromethyllithium[2] and has led us to investigate the reactions of alkyllithiums with polyhalogen compounds.

We find that when a variety of polyhalogenated methanes[5] are treated with methyl- or *n*-butyllithium in the presence of excess cyclohexene in ether solution at from −60° to room temperature olefin–carbene addition products are formed. Immediate precipitation of lithium halide takes place and

---

(1) O. R. Pierce, E. T. McBee and G. F. Judd, THIS JOURNAL, **76**, 474 (1954).

(2) This interpretation was first made in connection with unsuccessful attempts to prepare halofluoromethylzinc iodides.[3] We also note the possible formation of methylene by decomposition of iodomethylzinc iodide, although recent evidence appears to favor the direct reaction of iodomethylzinc iodide with olefins to form cyclopropanes.[4]

(3) W. T. Miller, Jr., E. Bergman and A. H. Fainberg, THIS JOURNAL, **79**, 4159 (1957).

(4) H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958); Abstracts of Papers, 120th Meeting, Amer. Chem. Soc., Boston, Mass., April, 1959, p. 51-O.

(5) Methane derivatives of the type RCX_2R' in which the R's may be organic groups as well as hydrogen or halogen are considered of possible application.