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THE SYNTHESES OF SOME BENZOBICYCLO(2.2.2)OCTENE DERIVATIVES, INCLUDING BENZOBICYCLO(2.2.2)OCTATRIENE[*1]

Keizo Kitahonoki and Yoshihiro Takano
Shionogi Research Laboratory, Shionogi & Co., Ltd.
Fukushima-ku, Osaka, Japan

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MILLER and Stiles reported the synthesis of benzobicyclo(2.2.2)octatriene (1), which is an interesting compound in view of the benzohomolog of barrelene (2), in the latest issue of the Journal of the American Chemical Society. Independently, we also had synthesized the above-mentioned compound from the β-naphthol-maleic anhydride adduct (3) by a different route. This paper describes the bis-decarboxylation reaction using lead tetraacetate, exploited by Grob et al. (4), of some diacids from the naphthalene-maleic anhydride adducts and the transformation of these reaction products into benzobicyclo(2.2.2)octatriene and some related compounds.

Decarboxylation of the keto-endo-dicarboxylic acid[*2] (I) (3) with lead tetraacetate in benzene containing pyridine at 40° gave the anticipated unsaturated ketone (II), m.p. 56.5-58° (10% yield), the mono-

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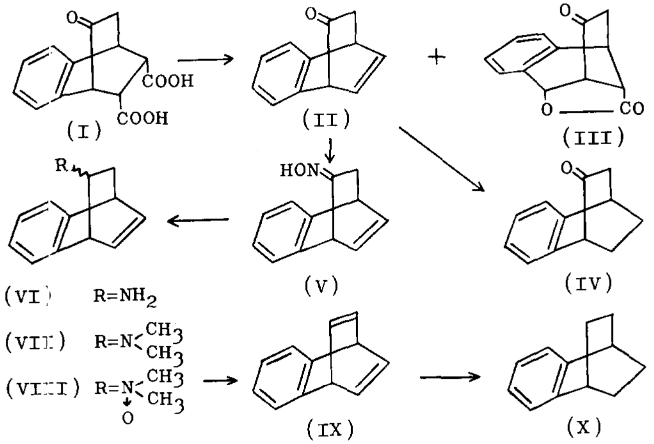
[*1] All melting points were determined in glass capillary tubes and are uncorrected. Satisfactory elemental analyses were obtained for all new compounds described.

[*2] The prefixes exo and endo are used in this report in the sense that substituents on the same side of the bicyclo(2.2.2)octene ring as the benzene ring are endo, those on the other side are exo. The definition of the prefixes was reversed in our earlier reports (9).

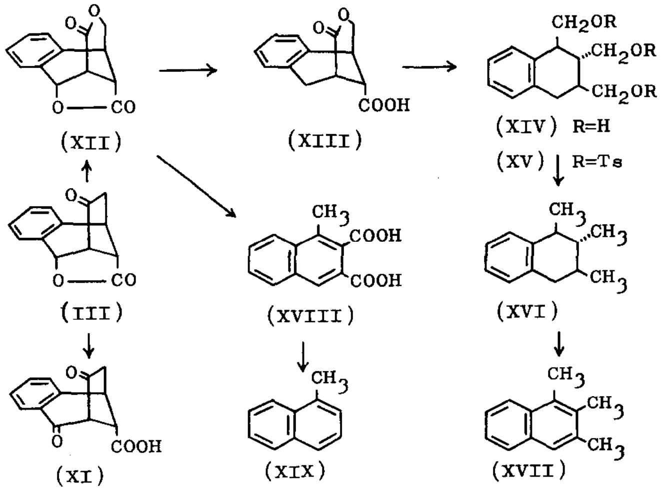
decarboxylated keto-lactone (III), m.p. 196-196.5° (14%), and a mixture of decarboxylated acetates of unknown structure (ca. 9%). The structure of the first product (II) was evidenced by the infrared (ν_{max}^{Nujol} 1728 (C=O), 690 cm^{-1} ($^{H}{>}C{=}C{<}^{H}$)), ultraviolet ($\lambda_{max}^{95\%EtOH}$ 296.5 mμ, ε 408 (homoconjugated C=O)) and NMR spectra. Catalytic reduction of II gave the saturated ketone (IV), m.p. 30-31°, (p-nitrophenylhydrazone, m.p. 183.5-184.5°).



From the unsaturated ketone (II) we succeeded in the synthesis of benzobicyclo(2.2.2)octatriene by the following way. The oxime (V), m.p. 154-156°, of II was reduced with sodium and ethanol to the amine (VI) (an oily mixture of stereoisomers), which was **transformed** to the dimethylamino derivative (VII) with formic acid and formaline. The N-oxide (VIII) prepared from VII by the action of hydrogen peroxide was subjected to the Cope reaction. Heating of VIII at 120-150° in vacuo (1-2 mmHg) gave an almost colorless distillate, which immediately solidified. Removal of naphthalene (ca. 10%, from (VII)) by chromatography on alumina and recrystallization of the later eluted crystals (40-49%, from (VII)) from petroleum ether gave the desired benzobicyclo-

(2.2.2)octatriene or "benzobarrelene" (IX), m.p. 65.5-66.5° (reported (1), m.p. 65.0-65.5°). The structure of this hydrocarbon was confirmed by the spectral data (IR, UV and NMR), which were in agreement with the reported values, and the conversion into the known saturated hydrocarbon (X) (5), m.p. 61-62°, by catalytic reduction. The hydrocarbon (IX) is thought to be thermally a little more stable than the reported bicyclo(2.2.2)octatriene (2), because heating of IX at 200° and 250° for 24 hours caused decomposition of only 5.7% and 31% respectively, as was shown by comparison of the relative area of the formed naphthalene and the unchanged IX on gas chromatography.

The infrared spectrum of another decarboxylated product (III) showed carbonyl bands at 1766 and 1738 cm^{-1} due to a γ-lactone and five-membered ring carbonyl, respectively. The structure of III was established by the following facts. On hydrolysis and subsequent oxidation with chromic anhydride, III gave the diketo-acid (XI), m.p. 167-170°, whose spectral data (IR ν_{max}^{Nujol} 1751, 1705, 1688, 1605 cm^{-1}; UV $\lambda_{max}^{95\%EtOH}$ 258.4 mμ, ε 11600, 294 mμ, ε 2030) showed the presence of



a carbonyl conjugated to the benzene ring. Oxidation of III with trifluoroperacetic acid afforded the dilactone (XII), m.p. 265-266.2°. XII was led into 1,2,3-trimethylnaphthalene (XVII) by the following steps: XII $\xrightarrow{\text{Pd-C, } H_2}$ lactone-acid (XIII), m.p. 247-249.5° $\xrightarrow{LiAlH_4}$ triol (XIV), m.p. 103-104°, (tritrityl ether, m.p. 227-228°) $\longrightarrow$ tritosylate (XV), oil $\xrightarrow{LiAlH_4}$ trimethyltetralin (XVI), oil (n_D^{20} 1.5192) $\xrightarrow{D.D.Q.}$ XVII. It was also found that XII was converted to the methylnaphthalene-dicarboxylic acid (XVIII), m.p. 240-241°, (anhydride, m.p. 241-242°), by the action of sodium ethoxide in refluxing ethanol. The dicarboxylic acid (XVIII) was decarboxylated with copper in quinoline to give 1-methylnaphthalene (XIX). The methylnaphthalenes, XVII and XIX, and their picrates were identified by direct comparison with authentic specimens. These facts confirmed the rearranged structure III.[*3]

Similar bisdecarboxylation of the trans-dicarboxylic acid (XX) (6) was also carried out. When XX was heated at 60-70° with lead tetraacetate in benzene containing pyridine for 25 hours, a hydrocarbon (24% yield) and a mixture of decarboxylated acetates of unknown structure (ca. 19%)[*4] were obtained after treatment of chromatography on alumina. Distillation of the hydrocarbon gave a pure sample

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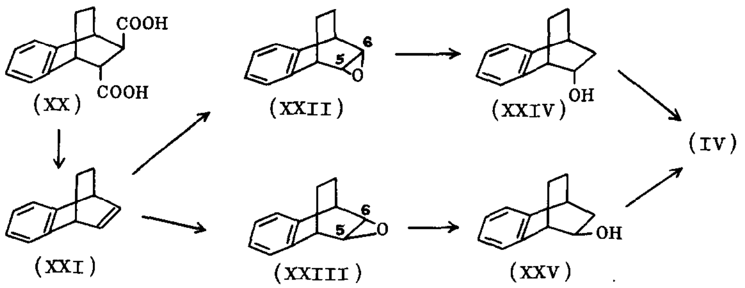
[*3] The formation of the keto-lactone (III) from I is interesting in connection with the recent reports on the formation of lactone from 1,3- or 1,4-dicarboxylic acids with lead tetraacetate. Cf. L. L. McCoy and A. Zagalo, J. Org. Chem. **25**, 824 (1960); L. R. C. Barclay, C. E. Milligan and N. D. Hall, Canad. J. Chem. **40**, 1664 (1962); W. R. Moore and H. Arzoumanian, J. Org. Chem. **27**, 4667 (1962). We favored the ionic mechanism involving intervention of a monodecarboxylated cationic species, which undergoes further decarboxylation to give II or rearrangement to a benzylic cation, forming the lactone in III with the carboxylate anion. Cf. E. J. Corey and J. Casanova, Jr., J. Amer. Chem. Soc. **85**, 165 (1963).

[*4] The structures of these acetates seem to have rearranged ring systems.

of benzobicyclo(2.2.2)octadiene (XXI), b.p.$_6$ 87-89°, (n_D^{20} 1.5711), which was identical with a sample prepared by cycloaddition of benzyne to cyclohexa-1,3-diene according to the procedure of Simmons (7). Catalytic hydrogenation of XXI gave the saturated hydrocarbon (X), m.p. 61-62° (5) identical with the sample obtained from benzobarrelene (IX). Heating of XXI at 200° for one hour caused 79% decomposition with the formation of naphthalene and ethylene (confirmed by gas chromatography). No decomposition of X was observed, when heated at 200° for 24 hours. Thus, the rates of thermal decomposition of the related hydrocarbons at 200° were estimated to increase in the following order: $X < IX <$ bicyclo(2.2.2)octatriene $<$ XXI.



Oxidation of XXI with perbenzoic acid in chloroform gave almost equal amounts of the *endo*-epoxide (XXII), m.p. 60.5-61°, (NMR C_5-, C_6-H, 6.62 τ in $CDCl_3$) and the *exo*-epoxide (XXIII), m.p. 65.5-66.5° (NMR C_5-, C_6-H, 6.70 τ, higher value than that of XXII due to the shielding effect of the benzene ring [*5]). Lithium aluminum hydride reduction of XXII and XXIII afforded the *endo*-alcohol (XXIV), m.p.

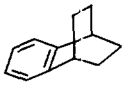
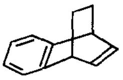
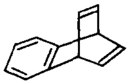
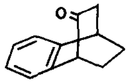
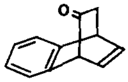
[*5] Analogous phenomena in the NMR spectra of some *endo*- and *exo*-isomers of bicyclo(2.2.2)octane compounds were discussed by us at the Second Symposium on Nuclear Magnetic Resonance held in Tokyo, November, 1962. The abstracts, p. 67. Cf. R. R. Fraser, *Canad. J. Chem.* **40**, 78 (1962).

103.5-104.5°, (IR $\nu_{max}^{CCl_4}$ 3586 cm^{-1} (OH)) and exo-alcohol (XXV), m.p. 99.5-101°, (IR $\nu_{max}^{CCl_4}$ 3620 cm^{-1} (OH)), respectively. Assignment of configuration of the epoxides and alcohols is based on the NMR spectrum and the presence of an internal interaction between the hydroxyl group

TABLE I.

UV Spectra of Benzobicyclo(2.2.2)octene Derivatives in n-Heptane

λ_{max} in mμ (ε in parentheses; sh, shoulder)

 (X)	 (XXI)	 (IX)	 (IV)	 (II)
191.5 (62500)	185.0 (42200)	174.9 (33100)	182.0 (32100)	174.5 (33300)
		187.7 (19700)		
		190.8 (19900)		
193.7 (61800)	198.7 (30600)	205.7 (28100)	197.6 (35200)	193.1 (37900)
209.8 (10300)			220.0^{sh} (6860)	213.1^{sh} (4300)
		230.8^{sh} (1200)	225.0 (5050)	
254.7 (361)	256.7 (301)	262.7 (498)	259.0^{sh} (347)	261.3^{sh} (380)
261.2 (542)	263.3 (423)	269.3 (688)	263.8 (446)	266.2 (458)
268.0 (748)	270.3 (431)	276.6 (768)	270.8 (445)	273.1 (414)
			287.8 (257)	285.6 (270)
			297.4 (313)	295.5 (367)
			307.8 (291)	306.2 (386)
			319.5 (153)	317.8 (234)

and the π-electrons of the benzene ring in the infrared spectrum of XXIV, which is absent in XXV. Both alcohols XXIV and XXV were oxidized to the same ketone (IV) with chromic anhydride and pyridine. This ketone was identical with the saturated ketone derived from the decarboxylated ketone (II).

The ultraviolet spectra of these benzobicyclo(2.2.2)octene derivatives are interesting in view of the homoconjugation of the double bond with the benzene ring and of that of the carbonyl (8) with the benzene ring, or the double bond, or both. The data of the ultraviolet spectra of the hydrocarbons (X), (XXI) and (IX) and of the ketones (IV) and (II) are summarized in Table I. Detailed discussions on the spectral data and electronic structures of these compounds will be reported later from this laboratory.

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(8) Cf. R. C. Cookson and J. Hudec, J. Chem. Soc. 1962, 429, and earlier papers.