[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, N. J.]

Synthesis of Bridged Hydrofluorenes[1]

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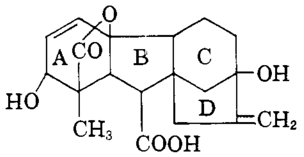
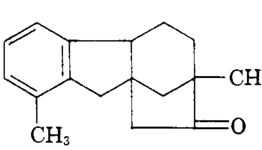
Itaconic acid and 5-phenyl-2,4-pentadienoic acid produced a Diels–Alder adduct III. The appropriate derivative of this adduct VIII underwent a Dieckmann followed by a Friedel–Crafts cyclization to give XI, a new tetracyclic, bridged ring system.

Gibberellic acid (I) from *Gibberella fujikuori*, has unique and striking effects on higher plants.[3] The structure of I was shown by degradation and an independent synthesis of the degradation products.[4] The stereochemistry recently has been elucidated.[5] Neither I nor its rearranged and degraded products resemble other known natural products; few synthetic hydrofluorenes are known. Gibberone II was selected as the degradation product most amenable to synthesis which retained the unknown bridged tetracyclic ring system and the reactions described here were designed as models for the synthesis of II

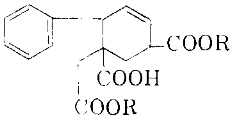


I

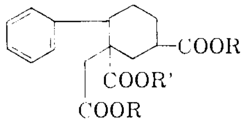


II

Itaconic acid condensed with 5-phenylpentadienoic acid; the product, in high yield, was a single crystalline anhydride III. Optimum conditions for the reaction were developed by following the disappearance of the strong, conjugated diene band at 308 mμ.[6] Because III was insoluble in common organic solvents it was partially esterified prior to catalytic reduction of the double bond. The rate of hydrogen absorbtion decreased slowly; no sudden change occurred near the 1 equivalent point. Addition of 1.1 equivalents of hydrogen gave high yields of VIII after esterification. A small sample of III absorbed 4 equivalents of hydrogen; the ultraviolet absorption spectrum showed evidence of ring reduction. In addition, the ultraviolet spectrum showed that isomerization of the double bond in III, IV or V to either of the adjacent, tertiary, conjugated positions where sluggish reduction might be expected did not occur. This resistance to hydrogenation, observed before,[7] may be rationalized as an association of the double bond and the carboxyl groups, one of which at least must be axial. There was no spectral evidence for lactonization. Furthermore, the bulk of the carboxyl groups might hinder a close approach of either catalyst or hydrogen to that side of the ring. These ideas also explain why IV and V did not decolorize permanganate solutions while III, where 2 of the carboxyl groups are held in positions away from the double bond, did. The olefinic compounds III, IV and V, had molar extinction coefficients at 220 mμ of 7,000–12,000; the range for VI, VII and VIII was 2300–4300. Ordinary esterification of acids IV and VI produced diesters V and VII, respectively, which were used for analysis since the triacids tended both to retain water and, when heated, to form anhydrides. Diazomethane and the oil isolated from hydrogenation furnished VIII, homogeneous to chromatography.

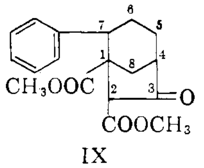


III, R = H, anhydride
IV, R = H
V, R = CH_3

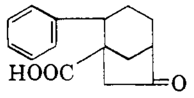


VI, R = R' = H
VII, R' = H; R = CH_3
VIII, R = R' = CH_3

Dieckmann cyclization of VIII produced oily diester ketone IX which gave a positive ferric chloride test and furnished a yellow 2,4-dinitrophenylhydrazone derivative. Crystalline X in 50% yield was obtained by acid-catalyzed hydrolysis and decarboxylation. Thionyl chloride furnished the acid chloride of X which with aluminum chloride in nitrobenzene was cyclized to the diketone XI in 68% yield. Both X and XI crystallized readily but melted over wide ranges and were difficult to purify. Both sublimed and exerted considerable vapor pressure below the melting point. These properties are all typical of bicyclic compounds. The absorption at 5.7 μ (1750 cm.$^{-1}$) in



IX



X

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[1] (a) A Frederick Gardner Cottrell grant from the Research Corporation, New York, N. Y., supported this investigation. (b) Presented at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

[2] Nopco Chemical Co., Harrison, N. J.

[3] For a comprehensive review see B. B. Stowe and T. Yamaki, *Ann. Rev. Plant Physiol.*, **8**, 181 (1957).

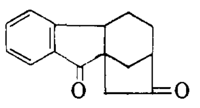
[4] (a) B. E. Cross, J. F. Grove, J. MacMillan and T. P. C. Mulholland, *Chemistry & Industry*, 954 (1956); (b) B. E. Cross, J. F. Grove, J. MacMillan and T. P. C. Mulholland, *J. Chem. Soc.*, 2520 (1958); A. Morrison and T. P. C. Mulholland, *ibid.*, 2536 (1958); (c) B. E. Cross, J. F. Grove, J. MacMillan, J. S. Moffatt, T. P. C. Mulholland and J. C. Seaton, *Proc. Chem. Soc.*, 302 (1959).

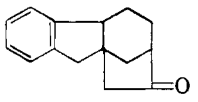
[5] G. Stork and H. Newman, THIS JOURNAL, **81**, 3168, 5518 (1959); B. E. Cross, J. F. Grove, P. McCloskey, T. P. C. Mulholland and W. Klyne, *Chemistry & Industry*, 1345 (1959).

[6] Itaconic anhydride rearranges to citraconic anhydride at 200–215° (R. L. Shriner, S. G. Ford and L. J. Roll in A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 140) and adducts from the rearranged dienophile are known [D. E. A. Rivett, *J. Appl. Chem.* (*London*), 337 (1951)], but itaconic acid was recovered unchanged from a control run. Furthermore neither the adduct from citraconic acid nor the isomeric one from itaconic acid (in which the carboxyl groups are *ortho*) would undergo the subsequent steps.

[7] N. N. Gerber, Dissertation, Rutgers University, 1957, pp. 93–96.

X and XI is characteristic of an unconjugated carbonyl group in a five-membered ring and is observed in gibberellic acid degradation products.[4a] The conjugated carbonyl group in XI must be hindered since it was unaffected by 2,4-dinitrophenylhydrazine. Ethylene glycol selectively blocked the unhindered ketone as the ketal. Wolff-Kishner reduction followed by acid hydrolysis produced 35% of XII as an oil, but the 2,4-dinitrophenylhydrazone derivative analyzed correctly. Lengthy treatment with ethylene glycol and acid apparently gave some diketal since a mixture of XI and XII mono-2,4-dinitrophenylhydrazones was obtained from the hydrolysis mixture.


XI


XII

The bicyclo[3,2.1]system is uncommon relative to the [2.2.1] or [2.2.2] system; it is, however, quite stable and has been prepared from the latter by rearrangements.[8] The new general route described here has the additional advantage of supplying a reactive group at a bridgehead position (in IX). A variety of substituents might be placed at carbons 5,6 and 7 according to the diene used and the carbonyl group at 3 is capable of useful transformations.

Experimental[9]

5-Phenyl-2,4-pentadienoic Acid.—We were unable to prepare this acid from cinnamaldehyde and malonic acid in quantitative yield as published[10]. The following procedure gave a 60% yield. Pure cinnamylidenemalonic acid was prepared in 87% yield[11] and washed with cold benzene. A mixture of it (1 g.), acetic anhydride (5 ml.) and acetic acid (3 ml.) was refluxed 1 hour then poured into water (100 ml.) and after 3 hours the precipitate (0.8 g.) filtered off. This crude material in chloroform (20 ml.) was allowed to stand 5 hours in daylight with a crystal of iodine.[12] The residue from the chloroform solution, crystallized from benzene, furnished 0.55 g. (69%) of the pure acid, m.p. 160–164° (lit. m.p. 161–165°[10]), λ_{max} 308 mμ (log ϵ 4.5).

1,5-Dicarboxy-2-phenyl-3-cyclohexeneacetic Acid (IV).—An intimate mixture of powdered 5-phenylpentadienoic acid (10 g.) and itaconic acid (15 g.) in a flask fitted with an air condenser was heated (bath 160°) for 8 hours. Itaconic acid alone at 160° for 8 hours was recovered unchanged. The semi-solid mass was stirred occasionally and after 5 hours the condenser was removed. At least 12 hours later the mixture was ground in a mortar with benzene (30 ml.), then the slurry was heated 5 minutes on the steam-bath with swirling and filtered with suction. Another hot washing with benzene (30 ml.) produced 11.8 g. (72%) of III, m.p. 240–245°; λ_{max} 252, 258, 265 mμ (log ϵ 3.0, 2.9, 2.8); ϵ_{220} 12,500; infrared λ_{max} 5.5, 5.6 μ.

Adduct III (1 g.) and potassium hydroxide (1 g.) in water (10 ml.) were refluxed 1 hour. Dilution with water (2 ml.) and hydrochloric acid (3 ml.) furnished 1.0 g. of crystalline IV, m.p. about 210°; λ_{max} 253, 259, 265, 269 mμ (log ϵ 2.6, 2.5, 2.4, 2.3); ϵ_{220} 7710; infrared λ_{max} 5.8–6.0 μ.

Triacid IV (0.4 g.) and sulfuric acid (0.4 g.) in dry methanol (6 ml.) were refluxed 18 hours. The methanol was removed under vacuum and the residue washed with three 10-ml. portions of ice-water. Recrystallization of the crude product from methanol–water then benzene–isoöctane yielded V, m.p. 159–161°; λ_{max} 253, 259, 266, 269 mμ (log ϵ 2.5, 2.5, 2.3, 2.1); ϵ_{220} 10,800; infrared λ_{max} 2.9 μ.

Anal. Calcd. for $C_{18}H_{20}O_6$: C, 65.05; H, 6.07. Found: C, 64.63; H, 6.34.

1,5-Dicarboxy-2-phenylcyclohexaneacetic Acid (VI).—A mixture of III (10 g.), dry methanol (100 ml.) and hydrochloric acid (10 drops) was swirled and warmed occasionally until homogeneous (*ca.* 1 day). Freshly prepared platinic oxide (0.1 g.) was added and the magnetically stirred mixture hydrogenated at atmospheric pressure until 1.1 equivalents of hydrogen had been absorbed (*ca.* 1 1., 8–12 hours). Reduction did not occur in very dilute solution or when the catalyst was reduced before III was added. Removal of the catalyst and solvent left an oil. Saponification of it as for III gave crystalline triacid VI, m.p. 188–198°; λ_{max} 245, 252, 257, 264, 268 mμ (log ϵ 2.3, 2.3, 2.3, 2.2, 2.0); ϵ_{220} 3600.

The dimethylester derivative VII was prepared from VI as for IV. Crystallization from methanol–water then from benzene–isoöctane furnished VII, m.p. 138–140°; λ_{max} 241, 246, 251, 257, 263, 266 mμ (log ϵ 2.2, 2.2, 2.3, 2.4, 2.2, 2.0); ϵ_{220} 3200; infrared λ_{max} 2.9 μ.

Anal. Calcd. for $C_{18}H_{22}O_6$: C, 64.65; H, 6.63. Found: C, 64.57; H, 6.70.

Excess diazomethane in ether was added to a solution of the oil from hydrogenation (*ca.* 10 g.) in ether (20 ml.). After 3 hours acetic acid (4 g.) was added and the solvent removed. The residual oil in benzene (50 ml.) was washed with dilute bicarbonate solution and water then dried and chromatographed on neutral activated alumina (50 g.). Elution with benzene (200 ml.) then chloroform was continued until a dark yellow band began to move off the column. The colorless or pale yellow residues from each 125-ml. fraction had identical infrared spectra, very similar ultraviolet spectra, ϵ_{220} 2300–4300. Even after additional chromatography VIII could not be crystallized. The combined residues weighed 9.7 g., (79% from III).

1-Carboxy-3-keto-7-phenylbicyclo[3.2.1]octane (X).—To methanol-free sodium methoxide (from 0.35 g. of sodium) under nitrogen was added benzene (10 ml.) then VIII (2.5 g.) in benzene (40 ml.) during 0.5 hour. The mixture was refluxed 18 hours, cooled and added to cold 10% acetic acid (100 ml.). The aqueous solution was extracted with benzene, then the benzene solution washed with water. The residue was an oil, λ_{max} 242, 247, 254, 257, 263 mμ (log ϵ 2.4, 2.5, 2.5. 2.5, 2.4); infrared λ_{max} 5.8 μ.

The 2,4-dinitrophenylhydrazone derivative after recrystallization from ethanol–ethyl acetate and benzene–isoöctane melted at 228–230°.

Anal. Calcd. for $C_{24}H_{24}O_8N_4$: C, 58.06; H, 4.87; N, 11.29. Found: C, 58.18; H, 5.04; N, 11.28.

A mixture of IX (2.3 g.), acetic acid (40 ml.) and 50% sulfuric acid (50 ml.) was refluxed 20 hours. The cooled reaction mixture was brought to a *p*H of 2 with saturated bicarbonate solution, extracted with chloroform and the chloroform solution washed with water. The residue (1.45 g.) after solvent removal crystallized within 24 hours. One recrystallization from ethanol–water gave 0.8 g. (50% from VIII) of X pure enough for subsequent steps, m.p. 180–190°; λ_{max} 247, 252, 257, 263 mμ (log ϵ 2.6, 2.6, 2.6, 2.6); 1620; infrared λ_{max} 5.75, 5.85 μ. One recrystallization from benzene–isoöctane, then two from ethanol–water furnished the analytical sample, m.p. 190–191° (sealed capillary).

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.75; H, 6.72.

The 2,4-dinitrophenylhydrazone derivative melted at 245–247° after recrystallization from ethanol–water and chloroform–isoöctane.

Anal. Calcd. for $C_{21}H_{20}O_6N_4$: C, 59.43; H, 4.75; N, 13.20. Found: C, 59.35; H, 4.85; N, 13.30.

1,2-Benz-3,5-diketo-3a,6-methano-3,3a,4,5,6,7,8a-octahydroazulene (XI).—Thionyl chloride (20 g.) and X (6 g.) were refluxed together for 0.5 hour. Excess reagent was removed by heating in vacuum, then two 30-ml. portions

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[8] For a discussion and references see W. R. Vaughan and A. C. Schoenthaler, THIS JOURNAL, **80**, 1956 (1958).

[9] The analyses were performed by W. Manser, Zurich, Switzerland. The melting points were determined on a Kofler hot-stage unless otherwise noted.

[10] A. G. Anderson, Jr., and S. Y. Wang, *J. Org. Chem.*, **19**, 277 (1954).

[11] P. N. Kurian, K. C. Pandya and V. R. Surange, *J. Indian Chem. Soc.*, **11**, 823 (1934).

[12] This converts any lower melting, benzene-soluble, allo-styrylacrylic acid into the desired *trans-trans* form; see J. C. Ghosh and S. Gupta, *Quart. J. Indian Chem. Soc.*, **2**, 241 (1925).

of dry benzene were added and removed similarly. The residue was heated at 100° under vacuum for 0.5 hour, then in cold nitrobenzene (40 ml.) added dropwise to a stirred suspension of aluminum chloride (7 g.) in nitrobenzene (40 ml.) at 0°. With stirring the reaction mixture warmed to room temperature during 3 hours, stood 18 hours, then was poured into cold dilute hydrochloric acid and the mixture extracted with chloroform. The organic solution was washed with dilute hydrochloric acid and water, then steam distilled. The resulting residue was dissolved in chloroform and washed with sodium carbonate solution. Solvent removal left an oil (3.5 g., 68%) which crystallized within 24 hours, m.p. 90–110°; λ_{max} 288, 380 mμ (log ε 4.1, 3.4); infrared λ_{max} 5.7, 5.8 μ. Recrystallization from ethanol–water, from isoöctane, then twice from ethanol–water gave the analytical sample, m.p. 118–128°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.35. Found: C, 79.62; H, 6.24.

The 2,4-dinitrophenylhydrazone derivative melted at 285–290° after recrystallization from acetic acid–water and chloroform–isoöctane.

Anal. Calcd. for $C_{21}H_{18}O_5N_4$: N, 13.79. Found: N, 13.62.

1,2-Benz-5-keto-3a,6-methano-3,3a,4,5,6,7,8,8a-octahydroazulene (XII).—A mixture of XI (1 g.), ethylene glycol (8 ml.), *p*-toluenesulfonic acid (50 mg.) and benzene (50 ml.) was refluxed 8 hours with an azeotroper. A few drops of absolute ethanolic sodium ethoxide was added then the reaction mixture was diluted with chloroform and washed with dilute potassium carbonate solution. Removal of the solvent gave an oil (infrared λ_{max} 5.7 (weak), 5.8 (strong) μ) which was mixed with 85% hydrazine hydrate (5 ml.) and dimethylene glycol (20 ml.) and heated at 120° for 15 minutes. Potassium hydroxide (0.7 g.) was added and the mixture held at 170° for 17 hours then cooled, diluted with water and extracted with chloroform. The residue from the washed chloroform solution showed no carbonyl absorbtion in the infrared. Hydrolysis was accomplished with 75% acetic acid (13 ml.) at 100° for 1 hour. The acid mixture was neutralized with aqueous potassium carbonate, extracted with chloroform and the solvent removed. The residue, in benzene, was chromatographed on neutral alumina (30 g.). Benzene (75 ml.) eluted 0.3 g. (35%) of oil which could not be crystallized; infrared λ_{max} 5.7 μ.

The 2,4-dinitrophenylhydrazone derivative melted at 209–211° after recrystallization from ethanol–ethyl acetate.

Anal. Calcd. for $C_{21}H_{20}O_4N_4$: C, 64.27; H, 5.14; N, 14.28. Found: C, 64.13; H, 5.17; N, 14.33.

[CONTRIBUTION NO. 169 FROM THE CENTRAL RESEARCH LABORATORIES OF MINNESOTA MINING AND MANUFACTURING CO.,[1] ST. PAUL 9, MINN.]

The Chemistry of Xylylenes. VI. The Polymerization of *p*-Xylylene[2]

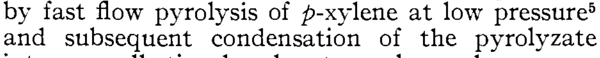
BY L. A. ERREDE, R. S. GREGORIAN AND JOHN M. HOYT

RECEIVED FEBRUARY 19, 1960

Polymerization of *p*-xylylene is initiated at −78° when a solution of the monomer is disturbed by momentary contact with a warm surface. This presumably creates diradical *n*-mers that continue to grow by successive addition of monomer units and/or by coupling. Apparently termination does not occur by chain transfer with solvent nor by interaction with atmospheric oxygen. Consequently propagation continues at −78° until all monomer is consumed or the free radical end groups are entrapped in the chain mesh affording a linear polymer whose molecular weight is greater than 2 × 10^5. The polymerization is first order with respect to monomer and second order with respect to free radical end groups. Low molecular weight cyclic products such as cyclo-tri-*p*-xylylene or cyclo-di-*p*-xylylene can be formed selectively by proper control of the reaction conditions.

Introduction

p-Xylylene is a diamagnetic compound and yet it is so reactive that it behaves chemically as if it were a diradical.[3] Thus it reacts readily at low temperature with monoradicals such as nitric oxide and diphenylpicrylhydrazyl to afford linear telomeric products and with diradicals such as oxygen to afford polymers.[4] In all instances, reaction occurs at the two terminal methylene groups.



Solutions of this unusual monomer were prepared by fast flow pyrolysis of *p*-xylene at low pressure[5] and subsequent condensation of the pyrolyzate into a well-stirred solvent, such as hexane or toluene kept at −78°.[6] The solvent serves to protect the accumulated monomer from the activating effect of incoming hot molecules. The resulting solutions obviously are not pure and, indeed, it was shown that the condensable portion of the pyrolyzate is a mixture of *p*-xylene, *p*-xylylene, toluene, *p*-ethyltoluene, styrene, 1,2-di-*p*-tolylethane, diphenylmethanes and anthracenes.[7] The proportion of each component is dependent upon the pyrolysis conditions. The concentration of *p*-xylylene in the mixture is determined iodometrically by the difference of its titer at −78° and that observed after it is warmed to room temperature.[6] Thus these solutions afforded a convenient medium in which to study the polymerization of *p*-xylylene.

Products of Polymerization.—*p*-Xylene is so reactive that polymerization occurs slowly even at temperatures as low as −78° and the reaction is not arrested even by large concentrations of the usual inhibitors. The polymerization is extremely rapid when solutions of the monomer are warmed to room temperature. When the degree of polymerization exceeds about 20, polymer molecules precipitate throughout the solution. The polymer is obtained in a highly swollen state whose bulk appears to fill the flask, and it can be removed easily by filtration. Once the polymer is dried, however, it cannot be made to swell again, let alone dissolve, in the usual solvents at room temperature. It does dissolve at

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(1) Most of this work was carried out in the laboratories of The M. W. Kellogg Co. The data were acquired by Minnesota Mining and Manufacturing Company with the purchase of the Chemical Manufacturing Division of The M. W. Kellogg Co. in March, 1957.

(2) Presented before the Gordon Conference on Polymers, A.A.A.S., New London, N. H., July, 1959.

(3) L. A. Errede and J. M. Hoyt, THIS JOURNAL, **82**, 436 (1960).

(4) L. A. Errede and S. L. Hopwood, Jr., *ibid.*, **79**, 6507 (1957).

(5) M. Szwarc, *J. Polymer Sci.*, **6**, 319 (1951).

(6) L. A. Errede and B. F. Landrum, THIS JOURNAL, **79**, 4952 (1957).

(7) L. A. Errede and J. P. Cassidy, *ibid.*, **82**, 3653 (1960).