"water soluble compounds cannot react" (or more accurately: can react but in a low yield) remains valid. In conclusion the polyalcohols not having the tetrahedral conformation fail to react because the rate of hydrolysis of the halide is faster than the rate of polyol alkoxide extraction in the organic phase. We are now in the process of extending the scope of this direct PTC etherification to most of the carbohydrates.[10]

Experimental Section

Gas chromatography was performed with a Delsi IGC 120 FL Model, the column used was 3% SP 2100 on 120–140 mesh, Chromosorb G, 1.50 m. Liquid chromatography was performed on silica gel 60 (Merck, 0.063–0.200 mm) on a 15 × 150 mm column. PE and TBAB (Fluka) D,L-threitol (Aldrich), and α-methyl glucoside (Janssen) were dried before use (60 °C under reduced pressure).

Preparation of ETM (2). The tetraalcohol **2** was prepared by the previously[4] described $S_{RN}1$ reaction of 2,2-dimethyl-5-(hydroxymethyl)-5-nitro-1,3-dioxane with 2,2-dimethyl-5,5-dinitro-1,3-dioxane under basic conditions, elimination of the two nitro groups by Na_2S, and cleavage of the two acetals by a sulfonic acid resin.

Alkylation of ETM (2). The tetraalcohol **2** (0.58 g, 3.90 mmol) was added to a freshly prepared solution of NaOH (12.56 g, 314 mmol) in H_2O (12.6 mL). The mixture was stirred at 80 °C for 1 h; TBAB (0.5 g, 1.57 mmol) and *n*-heptyl bromide (2.81 g, 15.7 mmol) were added. The reaction mixture was then stirred 8 h at 80 °C. Water (15 mL) and diethyl ether (20 mL) were added, and the diethyl ether layer was separated, washed with water (3 × 10 mL), and dried. Evaporation gave an oil from which di-*n*-heptyl ether was distilled (Kugelrohr, 90 °C, 0.6 mmHg). The residue was purified by LC (silica gel); elution with pentane (200 mL) made it possible to remove the last small amount of di-*n*-heptyl ether, and elution with pentane–ether (3:1) (250 mL) afforded 0.202 g of the tetraheptyl ether **3** as a pale yellow oil (yield 9.6%): IR (KBr) 3000–2850, 1480, 1100 cm^{-1}. Anal. Calcd for $C_{34}H_{68}O_4$: C, 75.50; H, 12.67. Found: C, 75.56; H, 12.60.

In a second experiment under the same experimental conditions, 2.81 g of *n*-$C_7H_{15}Br$ was added after 8 h and the reaction was continued for an additional 8 h: 0.587 g, 27.9%.

Alkylation of PE (1). PE (0.53 g, 3.90 mmol) was alkylated in the same way as **2** and afforded, after the same workup and LC, a mixture of tri- (45% GC) and tetraethers (55% GC) (1.185 g) (64%, isolated). An additional amount (2.8 g) of *n*-$C_7H_{15}Br$ after 8 h led to 1.410 g (yield 75.5%) of ethers (tri, 32%; tetra, 68%). GC-monitored experiments were carried out under the same experimental conditions as described above. Each aliquot was processed in the manner described previously.[1]

Alkylation of Glycerol. Glycerol (0.46 g, 5 mmol) was alkylated in the same way as **2** (NaOH, 12 g, 300 mmol; H_2O, 12 mL; TBAB, 0.5 g, 1.5 mmol; $C_7H_{15}Br$, 2.7 g, 15 mmol). After purification (LC) the triheptyl ether was obtained (0.36 g, 0.93 mmol): yield 20%. Anal. Calcd for $C_{24}H_{50}O_3$: C, 74.55; H, 13.03. Found: C, 74.61; H, 13.05.

Alkylation of D,L-Threitol. The above procedure was used (threitol, 0.61 g, 5 mmol; NaOH, 16 g, 400 mmol; H_2O, 16 mL; TBAB, 0.65 g, 20 mmol; *n*-$C_7H_{15}Br$, 3.6 g, 20 mmol). After 8 h, an additional 3.6 g of *n*-$C_7H_{15}Br$ was added. After purification, the tetraether (0.385 g, 0.75 mmol) was obtained: yield 15%. Anal. Calcd for $C_{32}H_{66}O_4$: C, 74.65; H, 12.92. Found: C, 74.71; H, 12.90.

Alkylation of α-methyl glucoside (α-methyl glucoside, 0.97 g, 5 mmol; tetraether, 0.415 g, 0.70 mmol): yield 14%. Anal. Calcd for $C_{35}H_{76}O_6$: C, 70.89; H, 12.92. Found: C, 70.96; H, 12.87.

Registry No. **1**, 115-77-5; **1** (triheptyl ether), 97431-23-7; **1** (tetraheptyl ether), 97431-24-8; **2**, 54902-90-8; **3**, 108451-65-6; glycerol, 56-81-5; D,L-threitol, 6968-16-7; α-methyl glucoside, 97-30-3; *n*-heptyl bromide, 629-04-9; glycerol triheptyl ether, 108418-30-0; D,L-threitol tetraheptyl ether, 108451-66-7; α-methyl glucoside tetraheptyl ether, 108451-67-8.

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Existence and Reactivity of Bicyclic Annulenones. 2. Bicyclo[3.3.0]octa-1(5),3,7-triene-2,6-dione

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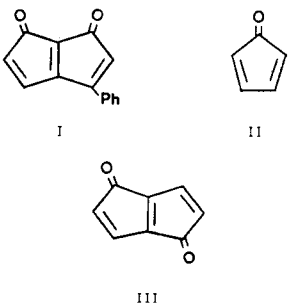
Evidence is presented that demonstrates the existence of free bicyclo[3.3.0]octa-1(5),3,7-triene-2,6-dione, which through an elimination process has been generated from an insoluble polymeric precursor. The diketone can act either as a diene or as a dienophile in pericyclic reactions.

A study of annulenones with fully unsaturated pentalenic structures was carried out by us, thus showing the existence and reactivity of 4-phenylbicyclo[3.3.0]octa-1-(5),3,6-triene-2,8-dione (I)[1] (Chart I). It was an elusive ketone with reactivity different from that of cyclopentadienone (II).[2] Since I was able to act as a diene, in Diels–Alder reactions, its behavior as a dienophile was never detected. Now we report the generation and reactivity of another unstable pentalenic diketone different from I in the relative position and orientation of its carbonyl groups: bicyclo[3.3.0]octa-1(5),3,7-triene-2,6-dione (III). For this purpose, we attempted first to prepare an adequate precursor able to yield III by an elimination reaction. This precursor was the polymeric sulfonate of 1-hydroxybicyclo[3.3.0]octa-4,7-diene-2,6-dione (VI, Scheme I).

Chart I



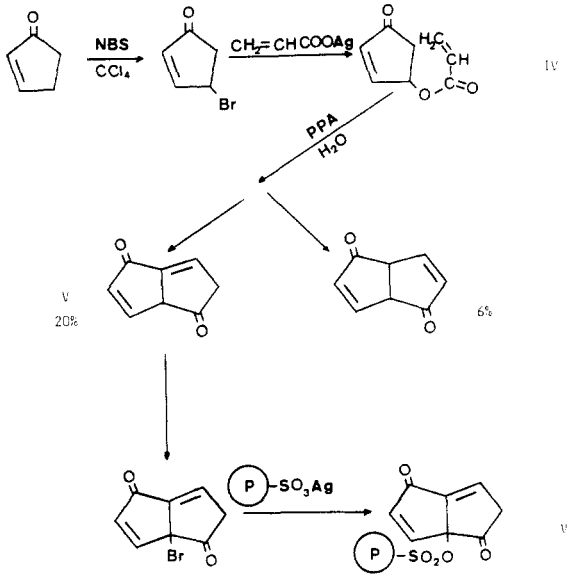
I II III

(1) Gaviña, F.; Costero, A. M.; Luis, S. V. *J. Org. Chem.* **1984**, *49* 4616–4618.

(2) Gaviña, F.; Costero, A. M.; Gil, P.; Luis, S. V. *J. Am. Chem. Soc.* **1984**, *106*, 2077–2080.

0022-3263/87/1952-2997$01.50/0

Scheme I



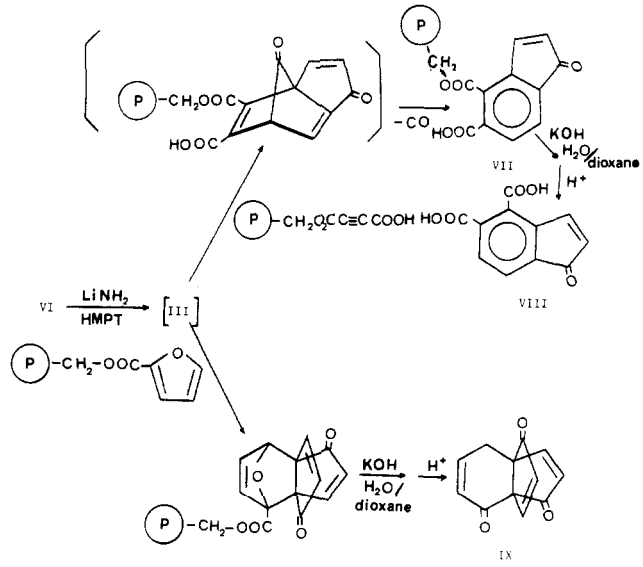
Methods and Results

Synthesis of Precursor VI. The synthesis of compound VI was carried out as outlined in Scheme I. Cyclopent-2-en-1-one was brominated by NBS, yielding the 4-bromo derivative, which reacted with the silver salt of acrylic acid to give the ketonic ester IV. Treatment of IV with polyphosphoric acid[3] yielded a mixture of products from which bicyclo[3.3.0]octa-4,7-diene-2,6-dione (V, 20%, IR 1720, 1703, 1651, 1595 cm^{-1}) and the known compound, bicyclo[3.3.0]octa-3,7-diene-2,6-dione[4] (6%, IR 1700, 1580 cm^{-1}) could be isolated. Reaction of V with NBS produced the 1-bromo derivative, from which VI (IR 1730, 1690, 1120, 1090 cm^{-1}) was then prepared by reaction with the silver salt of polymeric sulfonic acid.

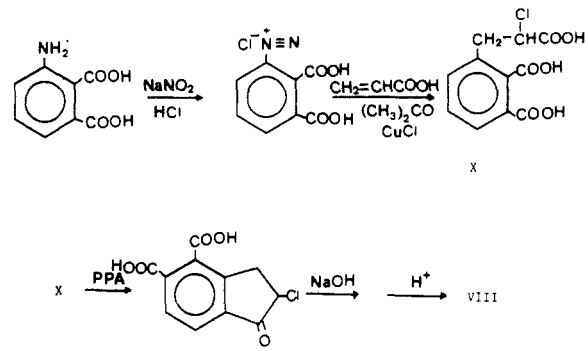
Three-Phase Tests. Attempts to isolate III in solution, from precursor VI, led to a mixture of carbonyl products. The same behavior has been observed in the cases of annulenones I and II, showing their instability facing polymerization or decarbonylation. Thus, the existence of bicyclo[3.3.0]octa-1(5),3,7-triene-2,6-dione was established by using the three-phase test.[5] As a dienophilic trapping agent, the polymeric monoester of acetylenedicarboxylic acid[6] was used (Scheme II). The solution of this polymer and VI in HMPT was treated at room temperature with $LiNH_2$. The resins were separated in the usual way.[1,2] The adduct resin VII was saponified to give a mixture of acetylenedicarboxylic acid and 4,5-dicarboxy-2-indenone (VIII), from which VIII could be isolated by preparative TLC. Resin VII came from initial polymeric adduct, probably via carbonyl extrusion and aromatization.[6]

The trapping of III by the polymeric monoester of acetylenedicarboxylic acid demonstrated its existence in solution and its ability to act as a diene in Diels–Alder reactions. The next step was to demonstrate that free bicyclo[3.3.0]octa-1(5),3,7-triene-2,6-dione, whose existence from resin VI was unambiguously proved, was likewise able to act as a dienophile in a Diels–Alder reaction. The polymeric ester of furoic acid[6] was used as a suitable dienic

Scheme II



Scheme III



trapping agent. Treatment of VI with $LiNH_2$/HMPT, in the presence of polymeric furoate (Scheme II), yielded the corresponding adduct, which was saponified and acidified which led to tricyclo[4.3.3.$0^{1,6}$]dodeca-3,8,11-triene-2,7,10-trione (IX) in solution.

Thus, annulenone III, like cyclopentadienone II, is able to react either as a diene or as a dienophile in pericyclic reactions. This behavior is partially different from the one of I, since this does not seem able to act as a dienophile. In the reaction between a diene and III, the process occurs through the central double bond C_1–C_5.

Reference Compounds. 4,5-Dicarboxy-2-indenone (VIII) was synthesized in a separate way by reacting the arenediazonium ion, corresponding to 3-aminophthalic acid, with acrylic acid, in a Meerwein arylation reaction,[7] to give X (Scheme III). Treatment of X with polyphosphoric acid yielded 2-chloro-4,5-dicarboxyindanone, from which VIII could be obtained by dehydrochlorination with aqueous sodium hydroxide and then acidification.

Tricyclo[4.3.3.$0^{1,6}$]dodeca-3,8,11-triene-2,7,10-trione (IX) has not been, until now, prepared in a different way. At any rate, spectroscopic and analytical data from the compound obtained in the reaction, shown in Scheme II, seem to correspond to the proposed structure.

Conclusions

The present trapping results support the conclusion that the pentalenic ketone bicyclo[3.3.0]octa-1(5),3,7-triene-2,6-dione (III) can exist in solution as a highly reactive species. Reactivity of this compound differs from the one

(3) (a) Dev, S. *J. Indian Chem. Soc.* **1955**, *32*, 255–264. (b) Dev, S.; *Ibid.* **1956**, *33*, 703–708. (c) Dev, S.; Rai, C. *Ibid.* **1957**, *34*, 266–274. (d) Dev, S. *Ibid.* **1957**, *34*, 169–177.

(4) Hagedorn, A. A., III; Farnum, D. G. *J. Org. Chem.* **1977**, *42*, 3765–3767.

(5) Rebek, J. Jr.; Gaviña, F. *J. Am. Chem. Soc.* **1974**, *96*, 7112–7114.

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of another pentalenic ketone, 4-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (I), since this does not seem able to act as a dienophile in such cases. This difference may be ascribed to the relative positions of carbonyl groups but, it may also be because of the influence of the phenyl group in I. Studies about related species with carbonyl groups in the 2,8 position (as in I) but without a phenyl substituent (as III) are in progress.

Experimental Section

Preparation of Ketonic Ester IV. A solution of 11.15 g of 4-bromocyclopentenone[8] and 14.0 g of freshly prepared silver acrylate in 50 mL of dioxane was heated under reflux for 24 h. After AgBr was filtered, the resulting yellow solution was evaporated to give IV (2.70 g, 25% yield) as an oil: IR 3000, 2990, 2920, 1720, 1680, 1600, 1260, 910 cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 7.9 (d, 1 H), 7.2 (dd, 1 H), 6.0 (t, 1 H), 5.5 (d, 1 H), 4.2 (d, 1 H), 3.3 (s, 2 H).

Bicyclo[3.3.0]octa-4,7-diene-2,6-dione (V). To 21.6 g of polyphosphoric acid at 100 °C was added 2.16 g of IV, and the resulting reaction mixture was heated at the above temperature for 24 h under stirring. Then, the mixture was treated with ice water saturated with ammonium chloride and extracted with ether. The organic phase was washed with aqueous solutions of $NaHCO_3$ (10%) and NaCl (saturated) and then dried (Na_2SO_4). V was obtained after a preparative TLC (CH_2Cl_2) in a yield of 20.7%: IR 1720, 1703, 1651, 1595, 1280, 1070, 720 cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 7.7 (d, 1 H), 7.3 (dd, 1 H), 6.8 (t, 1 H), 4.1 (m, 1 H), 3.6 (d, 2 H); mp 70.8 ± 0.20 °C. Anal. Calcd for $C_8H_6O_2$: C, 71.64; H, 4.47. Found: C, 71.89, H, 4.40. In the same TLC, the known compound bicyclo[3.3.0]octa-3,7-diene-2,6-dione[4] also could be isolated in a yield of 5.9%.

Synthesis of Polymeric Diketone VI. V (0.36 g), 0.42 g of NBS, and a catalytic amount of benzoyl peroxide were suspended in 150 mL of CCl_4 and heated on a steambath for 1 h. The solution was washed with 1:1 sodium thiosulfate/ice water and the organic phase was dried and evaporated to give 1-bromobicyclo[3.3.0]-octa-4,7-diene-2,6-dione in a yield of 60%: IR 3010, 2990, 2920, 1730, 1710, 1660, 1410, 1200, 1050, 1020, 820, 700, 610. To this product was added 1.5 g of polymeric sulfonic silver salt,[6] in a suspension of 60 mL dioxane, and the solution was then stirred for 67 h at 110–120 °C. After being washed with 5% aqueous KCN, water, dioxane, and ethanol, the resin VI (0.91 mequiv/g) was obtained: IR 1720, 1700, 1200, 1120, 1090, 1040, 820 cm^{-1}.

Reaction of III as a Diene. A suspension of VI (0.9 g) and the polymeric monoester of acetylene dicarboxylic acid[6] (0.6 g) in HMPT was stirred with 4 g of lithium amide, which was dissolved in 40 mL of HMPT and added dropwise at 30 °C. After 24 h at room temperature, washing and separation of the resins gave VII (IR 3010, 2910, 1730, 1700, 1680, 1600, 1450, 1110, 1010, 750, 705 cm^{-1}). Hydrolysis of VII with 0.5 M of KOH (dioxane–water, 1:1) under reflux for 20 h, followed by acidification and purification by preparative TLC, gave 0.048 g (27% yield) of a compound whose spectroscopic properties (IR, NMR, and MS) were identical with the ones of the reference compound VIII. Furthermore, comparative TLC corroborated the sameness of both compounds.

4,5-Dicarboxy-2-indenone (VIII). 3-Aminophthalic acid (45.0 g) was converted, in the usual way, into the corresponding diazonium salt. To this salt, in acetone/water, was added 105.0 mL of acrylic acid at 7 °C. Then the temperature was raised and a catalytic amount of CuCl was added at 15 °C. After the reaction mixture was stirred for 3 h at room temperature, the solution was filtered, the acetone was evaporated, and the aqueous residue was extracted with ethyl ether. The organic phase was dried and evaporated to give X[7] (IR 3000, 1730, 1690, 1600, 660 cm^{-1}); 30.0 g of X was added to 300.0 g of polyphosphoric acid at 90 °C and the resulting mixture, after 10 min of heating, was poured into iced water. The aqueous solution was extracted with ether and the organic phase, after being dried and evaporated, gave 9.8 g (33% yield) of 2-chloro-4,5-dicarboxyindanone (IR 3000, 1720, 1690, 1600, 1580, 1080, 660 cm^{-1}). To this product was added 190.0 mL of 1 N NaOH, and the mixture was heated under reflux, stirring for 8 h. The solution was acidified (dilute HCl) and extracted with ether. From the ether, after drying and evaporating, a yellow precipitate appeared. It was redissolved in ether/CH_2Cl_2 and after separation by TLC yielded 1.51 g (18%) of VIII as yellow needles, mp 135 °C dec: IR 3200, 1700–1715, 1650, 1630, 1400, 1275, 1010, 945, 825 cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 10.3 (s, 2 H), 8.7–8.4 (m, 3 H), 7.6 (d, 1 H); MS *m/e* 218, 217, 200, 190, 156, 132, 131, 102, 100, 91, 76, 72, 65, 63, 51, 45, 39. Anal. Calcd for $C_{11}H_6O_5$: C, 60.55; H, 2.75. Found: C, 60.50, H, 2.71.

Reaction of III as a Dienophile. A total of 1.6 g of the polymeric ester of furoic acid[6] and 1.12 g of VI were suspended in 130 mL of HMPT. Then 5.0 g of lithium amide in 70 mL of HMPT was added dropwise to the suspension. The mixture was allowed to stand at room temperature for 24 h. Then the resins were filtered, washed, and separated. Hydrolysis of trapping resin with 0.5 M NaOH (dioxane–water, 1:1) under reflux for 24 h, followed by acidification and purification by TLC (CH_2Cl_2), gave 0.050 g (25% yield) of IX as yellow crystals, mp 105 °C dec: IR 3020, 2920, 1705–1695, 1600, 1580, 1480, 1450, 1295, 1170, 1115, 1010, 820, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.5 (d, 2 H), 6.8 (m, 1 H), 6.3–6.1 (m, 3 H), 2.3 (d, 2 H); MS, *m/e* 200, 172, 146, 132, 68. Anal. Calcd for $C_{12}H_8O_3$: C, 72.00; H, 4.00. Found: C, 72.47, H, 4.11.

Acknowledgment. Financial support for this work was provided by Comisión Asesora de Investigación Científica y Técnica, del Ministerio de Educación y Ciencia., Project No 1470/82.

Registry No. III, 93887-76-4; IV, 108347-21-3; V, 108347-22-4; VI, 108347-23-5; VII, 108347-24-6; VIII, 108347-25-7; IX, 108347-27-9; X, 108347-27-9; CH_2=CHCOOAg, 5651-26-3; $CH_3O_2CC{\equiv}COOH$, 42507-71-1; cyclopent-2-en-1-one, 930-30-3; 4-bromocyclopentenone, 765-56-0; bicyclo[3.3.0]octa-3,7-diene-2,6-dione, 4945-71-5; 1-bromobicyclo[3.3.0]octa-4,7-diene-2,6-dione, 108347-28-0; methyl furoate, 611-13-2; methyl 1,10-dioxo-4,7-epoxy-7a,3a-propeno-1*H*-indene-4(7*H*)-carboxylate, 108347-29-1; 3-aminophthalic acid, 5434-20-8; 2,3-dicarboxybenzenediazonium chloride, 108347-30-4; 2-chloro-2,3-dihydro-1-oxo-4,5-indenedicarboxylic acid, 108347-31-5.

(8) DePuy, C. H.; Isaks, M.; Eilers, K. L.; Morris, G. F. *J. Org. Chem.* **1964**, *29*, 3503–3510.