to the thio ester R′C(O)SMe which is assumed to be formed in the photolytic process, while we have already mentioned that the direct addition of silyl radicals to this substrate is rather difficult and leads to weak EPR spectra.[26] Furthermore, reaction sequences 4 and 5 would take some time to build up a significant concentration of the byproduct R′C(O)SMe, hence one should expect that the EPR signal of radical **6** required an elapse of time to appear. This is contrary to the observation that the spectra are detectable almost immediately after irradiation of the samples begins.

It is also worthwhile noting that attempts of generating radical **6a** (R = Me) in the presence of *trans*-piperylene were unsuccessful; this, however, is far from constituting evidence of the occurrence of reaction sequence 6 as *trans*-piperylene, known[27] to be an effective "carbene trap", can also act as a scavenger for both silyl and thiyl radicals.

A choice between the different reaction sequences would thus be only speculative at this stage and it appears advisable to delay it until additional and more complete experimental data become available.

Experimental Section

The compounds used in the present work were commercially available, with the exception of benzoyltrimethylsilane,[28] acetyltrimethylsilane,[29] pivaloyltrimethylsilane,[29] and *S*-methyl thiobenzoate,[30] which were prepared according to the literature.

Samples for the EPR measurements were prepared under vacuum by the freeze–thaw technique in Suprasil quartz tubes. The spectra were run either on a Varian E-104 or on a Bruker ER-200 spectrometer equipped with a NMR gaussmeter (field calibration) and a frequency counter. A 500- or 1000-W high-pressure Hg lamp was used as UV light source.

Kinetic measurements were carried out with the rotating sector technique, and the decay curves were accumulated by means of an Aspect 2000 computer.

Acknowledgment. L.G. and L.L. thank the Ministry of Public Education (Rome) for financial assistance.

Registry No. **2a**, 92284-54-3; **2b**, 92284-55-4; **3**, 75195-55-0; **5a**, 92284-56-5; **5b**, 92284-57-6; **6a** (R = Me), 92284-58-7; **6a** (R = *n*-Bu), 92284-59-8; **6b** (R = Me), 92284-60-1; **6b** (R = *n*-Bu), 92284-61-2; **6b** (R = CF_3), 92284-62-3; **6c** (R = Me), 92284-63-4; **6c** (R = CF_3), 92284-64-5; **7**, 92284-65-6; DTBQ, 719-22-2; PhC(O)$SiMe_3$, 5908-41-8; MeC(O)$SiMe_3$, 13411-48-8; *t*-BuC(O)$SiMe_3$, 13411-49-9; MeSSMe, 624-92-0; *n*-BuSSBu-*n*, 629-45-8; CF_3SSCF_3, 372-64-5.

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[26] Addition to the C═O double bond of *S*-alkyl thio esters is actually a difficult process. For instance, we found that the radicals $Ph_3\dot{S}i$, $Ph_3\dot{G}e$, and $Ph_3\dot{S}n$ (produced by H-atom abstraction with *t*-BuOOBu-*t* from the corresponding hydrides) do not add to PhC(O)SMe to give the adducts $Ph\dot{C}(OMPh_3)SMe$ (M = Si, Ge, Sn, respectively) but rather yield adducts of structure[25] $Ph\dot{C}(OMPh_3)MPh_3$, where the SMe fragment has been replaced by MPh_3 (M = Si, Ge, Sn).

[27] Grasse, P. B.; Bauer, B. E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6883.

[28] Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 95.

[29] Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434.

[30] *J. Prakt. Chem.* **1885**, *31*, 462.

[31] Upon prolonged irradiation a second signal becomes evident, superimposed on the original spectrum of **6b**, R = CF_3, and exhibiting couplings of the unpaired electron with two different sets of three fluorine atoms (a_{3F} = 3.0 G, a_{3F} = 4.08 G) and with a single hydrogen (a_H = 19.7 G); the *g* factor is 2.0028. We believe that this adventitious spectrum can be assigned to the radical $(CF_3S)_2\dot{C}HC(OSiR_3)SCF_3$ (**7**), where the SCF_3 group α to the radical center is responsible for the larger quartet splitting, and one of the two β-SCF_3 lies close to the nodal plane of the α-carbon and hence is characterized by a negligibly small splitting. Radical **7** may originate through a sequence of disproportionation and addition reactions undergone by the original adduct **6b**, R = CF_3.

Existence and Reactivity of Bicyclic Annulenones. 4-Phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione

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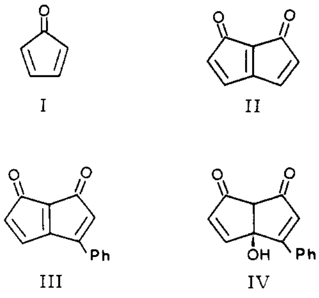
The elusive ketone 4-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione has been generated from an insoluble polymeric precursor which was synthetized from chlorosulfonated macromolecular resin and 5-hydroxy-4-phenylbicyclo[3.3.0]octa-3,6-diene-2,8-dione. The liberated diketone can act as a diene but not as a dienophile in the assayed pericyclic reactions.

After studying the existence of cyclopentadienone (I) and its reactivity as a diene and dienophile,[1,2] we started the study of some related species, particularly the ones with fully unsaturated pentalenic structures as II. The presence of the second condensed ring of cyclopentadienone may remarkably affect the stability of such species and their reactivity in Diels–Alder processes. The study of such species has received no attention up to now, although partially saturated structures similar to II have shown to be very useful synthons for the synthesis of natural products and other compounds of theoretical interest.[3]

Chart I



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[1] Gaviña, F.; Costero, A. M.; Gil, P.; Palazón, B.; Luis, S. V. *J. Am. Chem. Soc.* **1981**, *103*, 1797–1798.

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

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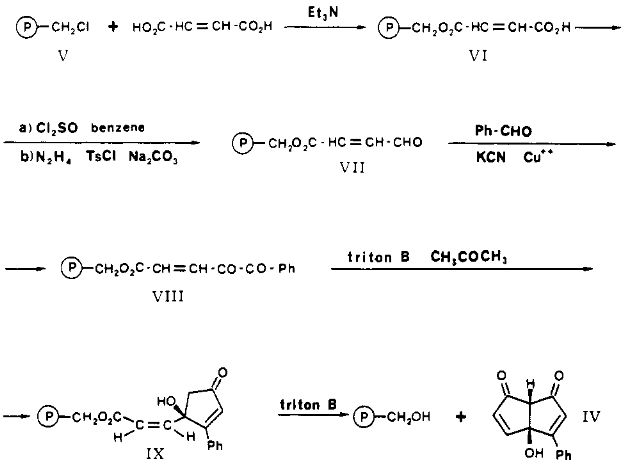
Scheme I



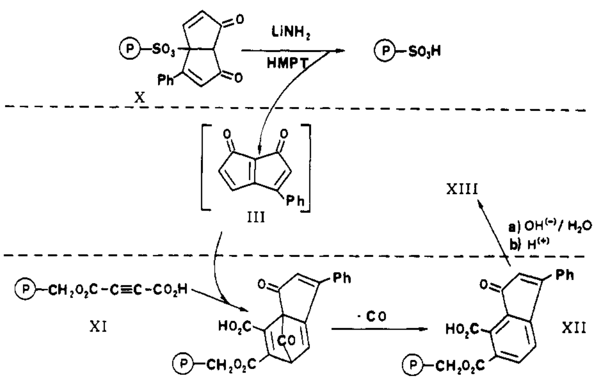
The first compound of this class, which we attempted to study, was 4-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (III). Theoretical calculations on the stability of III predict a high reactivity for this species.[4] Thus, the first step in our work was the synthesis of an adequate precursor from which III could be easily obtained. This precursor was 5-hydroxy-4-phenylbicyclo[3.3.0]octa-3,6-diene-2,8-dione (IV) which can generate III via an elimination process.

Methods and Results

Synthesis of Precursor IV. The synthesis of compound IV was carried out as shown in Scheme I by using techniques of synthesis on solid supports.[5] These techniques present the advantage of an easier separation between the principal and side products, which can be very useful in processes with a high number of steps.

The initial resin was a chloromethylated (3.5 mequiv of Cl/g), 2 % crosslinked polystyrene–divinylbenzene polymer. This Merrifield's resin (V) was treated with an excess of maleic acid and triethylamine to give the polymeric monoester of maleic acid (VI) (IR C=O bands at 1700–1730 cm^{-1}, functionalization degree, 2.53 mequiv/g). The free acidic groups of resin VI were then reduced to aldehydic ones via a McFadyen–Stevens reaction[6] by treatment of acid chloride of VI with hydrazine to obtain the polymeric hydrazide (IR showed the characteristic C=O band below 1700 cm^{-1} and N–H bands at ca. 3400 cm^{-1}). Reaction of this resin with *p*-toluenesulfonyl chloride afforded the double hydrazide, which when treated with sodium carbonate and ethylene glycol gave the aldehydic polymer VII. Compound VII was condensed with benzaldehyde in the presence of potassium cyanide and then with copper(II) acetate and ammonium nitrate to yield the diketonic compound VIII, whose IR presented three carbonyl bands at 1735, 1710, and 1680 cm^{-1}. From VIII, the next step was the condensation with acetone by using triton B as a base to afford IX. Longer treatment of the polymer in these conditions gave the diketonic alcohol IV, which must be the racemic pair corresponding to a cis compound.[7,8] The overall yield from V to IV was about 12%.

Scheme II



Attempts to isolate the annulenone III in solution always led to a complex mixture of carbonylic products. This behavior closely corresponds to that observed for the parent compound cyclopentadienone,[9-11] the stability of which is so small that it can only be isolated as its dimer or as its decarbonylation products.

Three-Phase Test. The existence and reactivity of 4-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (III) was established by using the three-phase test.[12] A suitable polymeric precursor for III was prepared by reaction of chlorosulfonated macromolecular resin[13] with the alcohol IV to yield the polymeric tosylate X (Scheme II).

A dienophilic reagent, the polymeric monoester of acetylenedicarboxylic acid[1] (XI), was first used as a polymeric trapping agent for the three-phase test. Treatment of X with $\mathrm{LiNH_2}$/HMPT at room temperature in the presence of XI yielded the polymeric adduct XII, probably via carbonyl extrusion and aromatization of the initial adduct.[1] Saponification of XII followed by acidification led to the reference compound 3-phenyl-6,7-dicarboxy-2-indenone (XIII) in solution.

The reference compound XIII was synthesized by reacting cinnamoyl chloride with phthalic anhydride via a Friedel–Crafts reaction to give 3-phenyl-6,7-dicarboxyindanone (XIV) in low yields (ca. 5%). Treatment of XIV with NBS in carbon tetrachloride followed by triethylamine gave the indenone XIII, which was identical with the sample obtained through the three-phase test.

Thermal treatment of X in $\mathrm{Me_2SO}$ did not liberate the intermediate III, unlike the case of cyclopentadienone, even in more drastic conditions; the unchanged polymer X was always obtained. This greater difficulty with the elimination reaction can be explained by the relative cis position of leaving groups in X.

The trapping of III by the polymer XI demonstrated its existence as a free species in solution and its ability to act as a diene in Diels–Alder reactions. Until now, the only regioisomer detected for this process has been that produced by the reaction of double bonds from the less substituted ring. Two facts may account for this result: first, the stabilizating effect of the phenyl group on the ring to which it is attached; second, that the reactive sites of III close to the reactive sites of polymer XI will be favored when attack occurs from the less substituted ring. This must be related to the steric effects of the polymeric bulk

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(3) Hanna, E. R.; Finley, K. T.; Saunder, W. H., Jr.; Boekelheide, V. *J. Am. Chem. Soc.* **1960**, *82*, 6342–6347.

(4) Costero, A. M., unpublished results.

(5) Mathur, N. K.; Narang, C. K.; Williams, R. E. "Polymers as aids in Organic Chemistry"; Academic Press: New York, 1980.

(6) Dudman, C. C.; Grice, P.; Reese, C. B. *Tetrahedron Lett.* **1980**, *21*, 4645–4648.

(7) Clark; T. J. *J. Org. Chem.* **1973**, *38*, 1749–1751.

(8) Quesada, M. L.; Schlessinger, R. H.; Parsons, W. H. *J. Org. Chem.* **1978**, *43*, 3968–3970.

(9) Allen, C. F. H.; Van Allan, J. A. *J. Am. Chem. Soc.* **1950**, *72*, 5165–5167.

(10) Alder, K.; Flock, F. H.; *Chem. Ber.* **1954**, *87*, 1916–1922.

(11) De Puy, C. H.; Isaks, M.; Eilers, K. L., Morris, G. F. *J. Org. Chem.* **1964**, *29*, 3503–3507.

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

(13) Roush, W.; Feitler, D.; Rebek, J. *Tetrahedron Lett.* **1974**, 1391–1392.

itself.[2,14] The two feasible stereoisomers obtained by addition to the dienic system of the unsubstituted ring are converted into the same compound after the hydrolysis.

Trapping of the intermediate III as a dienophile was attempted by using some polymers functionalized with dienic groups of varying electron density, such as the polymeric ester of 2-furoic acid and the buta-1,3-dien-1-ol polymeric ester, which have been especially good trapping agents for the parent compound cyclopentadienone.[1,2] Under the same experimental conditions for which the trapping of III by XI was done, both dienic polymers were recovered unchanged, and a mixture of carbonylic compounds was found in the solution. Here, we must notice that in the reaction between a diene and III, the process through the central double bond (C_1–C_5) will be more favorable because the reaction through the other double bonds will give structures with an unstable cyclopentadienone ring. However, the nearness of the central double bond and the reactive sites may again be hindered by important steric factors.

Conclusions

For the first time, we have demonstrated the possibility of the existence in solution, as highly reactive species, of compounds with structures of bicyclo[3.3.0]octatrienedione, which formally can be considered as constituted of two condensed structures of cyclopentadienone.

The first species of this class, the existence of which has been demonstrated by the three-phase test, has been the 4-phenylbicyclo[3.3.0]octa-1(5),3,6-triene-2,8-dione (III). The reactivity of this ketone seems to be partially different from the reactivity of cyclopentadienone itself, since III is able to act as a diene in Diels–Alder reactions but its behavior as a dienophile has never been detected. This fact seems likely to depend on steric and electronic factors. The reaction of III as a diene shows a very high degree of regioselectivity and that may be ascribed to the influence of the phenyl group and to steric factors, which again may be very important for Diels–Alder processes using polymeric reagents.[2,14]

The study of other related species will permit us to determine the influence of the substituents and the second cyclopentenone ring on stability and reactivity of these species. Such studies are underway.

Experimental Section

Preparation of the Polymeric Monoester of Maleic Acid (VI). Maleic acid (1.22 g) and triethylamine (10 mL) were dissolved in 50 mL of xylene, then Merrifield's resin (chloromethylated polystyrene, 3.5 mequiv of Cl/g) was added, and the mixture was stirred for 70 h at 110–120 °C. The resin was filtered and washed with dioxane, acetone, and ether: IR 3300, 1730–1700, 1260, 1160 cm^{-1}; functionalization (by saponification) 2.53 mequiv/g; yield, 92.7%.

Preparation of Polymeric Aldehyde VII. VI (1 g) was treated with an excess of thionyl chloride in 50 mL of benzene for 5 h at 75 °C. Filtering and washing with benzene gave the acyl chloride: IR 1730, 1710, 1510, 1260 cm^{-1}. This polymer was stirred with 15 mL of benzene and 1.5 mL of 99% hydrazine at room temperature for 19 h. The filtered and washed resin (IR 3200, 1700–1650, 1600, 1500, 1150, 1010 cm^{-1}) was suspended in 25 mL of pyridine containing 1.85 g of *p*-toluenesulfonyl chloride and allowed to stand at room temperature for 40 h. After washing with dioxane, methanol, acetone, and ether, the resin showed IR 1700, 1640, 1220, 1180, 1120, 1030, 1010 cm^{-1}. This resin was suspended in 50 mL of ethylene glycol and heated at 165 °C, and then 3 g of Na_2CO_3 were added. After heating at 165 °C for 48 h, the polymer was filtered, washed with dioxane–water, dioxane, acetone, and ether, and dried to give VII: IR 1720, 1700, 1490, 1450, 1210 cm^{-1}.

Benzoin Condensation. VII (1 g) was suspended in 50 mL of dioxane–water (1:1) with 0.1 g of KCN and 2 mL of benzaldehyde. The suspension was heated under reflux for 5 h, filtered, and washed with ethanol, acetone, and ether: IR 3400, 1720, 1700, 1600, 1380, 1100, 1050 cm^{-1}. Afterward, the resin was treated with 4 g of ammonium nitrate and 0.1 g of copper(II) acetate under reflux for 16 h. After washing with acetic acid, water, dioxane, ethanol, acetone, and ether, the polymer showed IR 3400, 1710, 1670, 1650, 1600, 1450, 1380, 1080 cm^{-1} (VIII).

Reaction of VIII with Acetone. VIII (1 g) was suspended in 10 mL of triethylene glycol with 1 mL of triton B and 2.5 g of acetone at 100 °C for 20 h. The resin was filtered and washed with dioxane–water, methanol, acetone, and ether to give IX: IR 3420, 1710, 1670, 1635, 1600, 1490, 1450 cm^{-1}.

Preparation of 5-Hydroxy-4-phenylbicyclo[3.3.0]octa-3,6-diene-2,8-dione (IV). IX (1 g) was suspended in 25 mL of benzene with 25 mL of 40% triton B in methanol and was heated under reflux for 3 days. IV was obtained after a preparative TLC in a yield of 12%: IR 3410, 1705, 1600, 1200, 1100, 750, 700 cm^{-1}; ^{1}H NMR ((CD_3)$_2$CO) δ 3.3 (s, 1 H), 4.3 (s, 1 H), 7.1 (d, 1 H), 6.9–7.6 (m, 7 H); MS 226, 122, 110, 91, 77. Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.42. Found: C, 74.60; H, 4.41.

Synthesis of the Polymeric Diketone X. Polymeric tosyl chloride (0.5 g) was stirred with IV (0.3 g) in 10 mL of dioxane for 72 h. After the reaction was filtered and washed with HCl–water, dioxane, methanol, acetone, and ether, resin X was obtained: IR 1710, 1600, 1500, 1490, 1210, 1180, 1120 cm^{-1}.

Reaction of III as a Diene. X (0.3 g) and 0.2 g of the polymeric monoester of acetylenedicarboxylic acid (XI) were suspended in 25 mL of HMPT. Lithium amide (1.5 g in 15 mL of HMPT) was added dropwise at 30 °C. After the reaction was stirred for an additional 24 h at room temperature, washing and then separation of the resins gave XII. Hydrolysis of XII with 0.5 M NaOH (dioxane–water 1:1) under reflux for 16 h followed by acidification and purification by preparative TLC gave XIII.

3-Phenyl-6,7-dicarboxyindanone (XIV). A solution of 10 g of cinnamic acid and 16 g of thionyl chloride in 100 mL of cyclohexane was heated under reflux for 3 h. The solution was evaporated to give the acyl halide. Phthalic anhydride (8 g) and 3 g of $AlCl_3$ in 50 mL of decalin were heated at 114 °C and then acyl chloride in 50 mL of decalin was added for 2.5 h and stirred for an additional 14 h. The solution was dried and evaporated to give XIV, recrystallized in ether–hexane as white needles: IR 3000, 1720, 1690, 1600, 1580, 1280, 1250, 1110, 1080, 900 cm^{-1}; ^{1}H NMR ((CD_3)$_2$CO) δ 10.2 (s, 2 H), 7.8–7.6 (m, 7 H), 3.8 (d, 2 H), 2.8 (t, 1 H); MS 296, 210, 148, 91, 77, 28; mp 80.8 ± 0.2 °C. Anal. Calcd for $C_{17}H_{12}O_5$: C, 68.92; H, 4.05. Found: C, 68.81; H, 4.17.

3-Phenyl-6,7-dicarboxy-2-indenone (XIII). Indanone XIV (0.322 g), 0.187 g of NBS, and benzoyl peroxide in a catalytic amount were suspended in 50 mL of CCl_4 and heated on a steam bath for 1 h. The solution was washed with 1:1 sodium thiosulfate/ice water, and the organic phase was dried and evaporated to give the bromoindanone. To this product 10 mL of triethylamine and 25 mL of ether were added and the solution was stirred at room temperature for 7 h. The solution was dried and evaporated giving XIII as deep yellow needles: IR 3200, 1700, 1575, 1390, 1250, 1130 cm^{-1}; ^{1}H NMR ((CD_3)$_2$CO) δ 10.3 (s, 2 H), 7.9–7.6 (m, 7 H), 7.5 (s, 1 H); MS 294, 208, 207, 148, 147, 91, 45; mp 125 °C dec.

Behavior of III with Dienes. As an example, 0.15 g of X and 0.5 g of the polymeric ester of furoic acid were suspended in 20 mL of HMPT. Then, 1.5 g of lithium amide in 15 mL of HMPT was added dropwise. The solution was allowed to stand at room temperature for 24 h. Unchanged polymeric ester of furoic acid was then isolated.

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Registry No. III, 92241-94-6; XIII, 92241-98-0; XIV, 92241-99-1; benzaldehyde, 100-52-7; acetone, 67-64-1; cinnamic acid, 621-82-9; cinnamoyl chloride, 102-92-1; phthalic anhydride, 85-44-9.

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(14) Yedidia, V.; Leznoff, C. C. *Can. J. Chem.* **1980**, *58* 1148–1150.