11 by a retro-Diels–Alder process.

These discoveries help define the scope of triazolene photoreactivity and we intend to study the generality and utility of this process in related systems. Photochemical ketene formation of type 8 → 11 may have value in photoresist chemistry and photoaffinity labeling techniques.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer. IR spectra were obtained from either a Perkin-Elmer 137b or 298 spectrometer and UV spectra were obtained from a Perkin-Elmer 552 spectrometer. High-resolution mass measurements were performed at the University of California at Santa Barbara. Microanalyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI, and Galbraith Laboratories, Knoxville, TN.

4-[3-(Mesyloxy)propyl]-2,4,6-trimethyl-2,5-cyclohexadien-1-one (7b). The alcohol **7a** (0.22 g, 1.2 mmol) in dry methylene chloride (6 mL) was treated with triethylamine (0.25 mL, 1.8 mmol) and methanesulfonyl chloride (0.15 g, 1.3 mmol) at 0 °C for 15 min. Reaction workup as described by Crossland et al.[9] gave an oil (0.34 g) that was purified by flash chromatography (silica gel, 50% ether in hexane) to give mesylate **7b** (0.25 g, 78%): IR (film) 1670, 1640, 1355, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 3 H), 1.38–1.75 (m, 4 H), 1.81 (s, 6 H), 3.00 (s, 3 H), 4.16 (t, 2 H, J = 6 Hz), 6.52 (s, 2 H).

4-(3-Azidopropyl)-2,4,6-trimethyl-2,5-cyclohexadien-1-one (7c). To a solution of the mesylate **7b** (0.23 g, 0.86 mmol) in DMF (5 mL) was added sodium azide (0.07 g, 1.0 mmol) and the reaction mixture was stirred at room temperature for 50 h. After filtration of the reaction mixture, the filtrate was concentrated in vacuo and the residue was dissolved in ether. The ether layer was washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo to afford **7c** (0.19 g, 95%). ^1H NMR analysis (200 MHz) indicated that **7c** was of sufficient purity to be used directly; an analytical sample of **7c** was prepared by flash chromatography (silica gel; 18% ethyl acetate in hexane), but an acceptable analysis could not be obtained. **7c**: IR (film) 2100, 1668, 1632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (s, 3 H), 1.20–1.50 (m, 2 H), 1.60–1.80 (m, 2 H), 1.90 (s, 6 H), 3.32 (t, 2 H, J = 6.5 Hz), 6.51 (s, 2 H).

5,6,6a,9,9a,9b-Hexahydro-9-oxo-6a,8,9a-trimethyl-4*H*-1,2,3-triazolo[4,5,1-*ij*]quinoline (8). A solution of azide **7c** (0.19 g, 0.87 mmol) in benzene (5 mL) was refluxed for 36 h. Evaporation of solvent gave an oil (0.18 g); chromatography of a portion of the oil (41 mg) on silica gel (80% ether in hexane) gave triazoline **8** (R_f 0.3, 27 mg, 66%) and azide **7c** (R_f 0.6, 7 mg, 17%). The triazoline **8** was recrystallized from ether: mp 105–106 °C; IR (film) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16 (s, 3 H), 1.72 (s, 3 H), 1.81 (d, 3 H, J = 1.4 Hz), 1.37–1.96 (m, 4 H), 3.11 (d, 1 H, J = 2.4 Hz), 3.29 (br d, 1 H, J = 12 Hz), 4.31 (br d, 1 H, J = 12 Hz), 6.34 (dd, 1 H, J = 2.4, 1.4 Hz); ^{13}C NMR ($CDCl_3$) δ 16.92 (q), 22.81 (q), 23.05 (q), 29.29 (t), 34.12 (s), 37.81 (t), 46.27 (t), 68.09 (d), 83.22 (s), 138.76 (s), 149.79 (d), 190.41 (s); UV (MeOH) λ_{max} 204 nm (23.99 × 10^3), 236 (1.13 × 10^4), 2.80 (2.21 × 10^3), 3.50 (4.77 × 10^2).

Anal. Calcd for $C_{12}H_{16}N_3O$: C, 66.03; H, 7.39; N, 19.25. Found: C, 65.90; H, 7.78; N, 19.06.

Photolysis of Triazoline 8. A solution of triazoline **8** (16 mg, 0.07 mmol) in methanol (10 mL) was irradiated under an argon atmosphere for 65 min. A water-cooled Hanovia 679A36 450-W mercury arc lamp fitted with Corning color filters 0-52 and 7-54 was employed as the 366-nm light source. The solution was concentrated in vacuo to give an oil (19 mg) that was purified by flash chromatography (silica gel, ether) to give triazole **12a** (14 mg, 80%): bp, 140 °C (0.6 mm); exact mass m/e 251.1649 (calcd for $C_{13}H_{21}O_2N_2$ 251.1630); IR (film) 3120, 1732, 1555, 1210, 1170, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (d, 3 H, J = 7.1 Hz), 1.66 (d, 3 H, J = 0.9 Hz), 1.96–2.08 (m, 4 H), 2.36 (s, 3 H), 3.26–3.48 (m, 1 H), 3.68 (s, 3 H), 4.38–4.16 (m, 2 H), 5.22 (d, 1 H, J = 9.1 Hz), 7.27 (q, 1 H, J = 0.9 Hz); UV (MeOH) λ_{max} 207 nm (ϵ 5.24 × 10^3).

A degassed sample of **12a** in $CDCl_3$ solution was subjected to a ^1H NMR double-resonance experiment; pulse angle = 60°, delay time = 10 s, acquisition time = 3 s, decoupler mode = YYN (gated decoupler off during data acquisition irradiation centered at δ 1.66 (vinyl methyl group) resulted in a 21% enhancement of the intensity of the resonance due to H_c and only a 2% enhancement of H_a and 6% enhancement of H_b. Furthermore, irradiation centered at δ 2.03 (vinyl methylene group) resulted in a 19% enhancement of H_b, a 4% enhancement of H_a, and no effect on H_c.

Photolysis of Triazoline 8 in Benzene Solution. A solution of triazoline **8** (77 mg, 0.35 mmol) in dry, spectrophotometric grade benzene (20 mL) was irradiated under an argon atmosphere with Pyrex-filtered light for 30 min. Evaporation of solvent and flash chromatography (silica gel, 50% ethyl acetate in hexane to pure ethyl acetate) gave **12b** as an oil (27 mg, 28%): IR (film) 3700–2200, 3120, 1720, 1555, 1215, 1067 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (d, 3 H, J = 7 Hz), 1.70 (d, 3 H, J = 1 Hz), 1.96–2.20 (m, 4 H), 2.36 (s, 3 H), 3.20–3.74 (m, 1 H), 4.00–4.70 (m, 2 H), 5.23 (d, 1 H, J = 10 Hz), 7.27 (q, 1 H, J = 1.0 Hz). This oil was soluble in 1 N sodium hydroxide solution. Treatment of **12b** (27 mg) with excess diazomethane in ether gave triazole methyl ester **12a** (27 mg).

In a separate experiment, triazoline **8** (14 mg) was irradiated in benzene (4 mL) as previously described. The resulting light-yellow solution was concentrated to one-third the original volume and an IR spectrum was recorded; IR (benzene) 1800, 1743 cm^{-1}. To this solution was added methanol (2 mL) and the resulting solution was stirred for 8 h at room temperature. Evaporation of solvent and chromatography (silica gel, 50% ethyl acetate in hexane) gave triazole methyl ester **12a** (5 mg, 33%).

Acknowledgment. This work was supported by the National Institute of General Medical Science (GM 26568). Assistance in the acquisition of NMR data by Dr. Herbert M. Schwartz is gratefully acknowledged. NMR spectra were recorded on a Varian XL-200 instrument purchased with funds provided, in part, by a National Science Foundation department instrumentation grant.

Registry No. **7a**, 67471-86-7; **7b**, 86013-52-7; **7c**, 86013-53-8; **8**, 86013-54-9; **11**, 86013-55-0; **12a**, 86013-56-1; **12b**, 86013-57-2.

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Phosphoranylidenehydrazones as in Situ Sources of Diazo Compounds: A Facile Synthesis of Aryl-Substituted Benzoylcyclopropanes

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Diazo compounds are extremely important reagents in organic synthesis.[2] While a great variety of methods are currently available for the preparation of diazo compounds,[3] the instability of these materials and difficulties in handling them may limit their utility in a number of synthetic transformations. In the course of current synthetic work using acyl cyclopropanes as key intermediates we sought a method of generating diazo compounds in situ under neutral conditions. It appeared that one possible

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(2) Wulfman, D. S.; Linstrumelle, G.; Copper, C. F. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: London, 1968; pp 821–956 and references therein.

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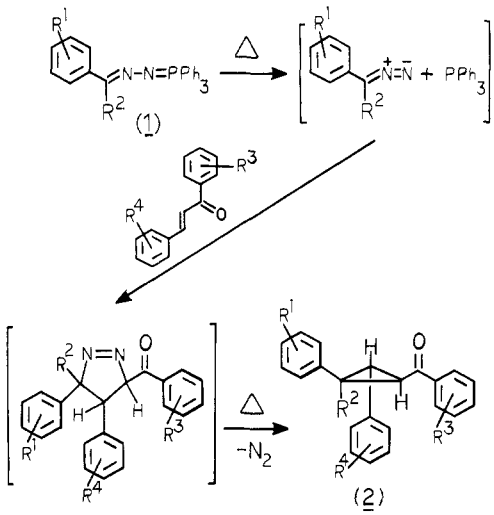
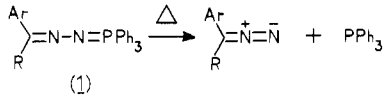
0022-3263/83/1948-2434$01.50/0

Scheme I



source of these materials might be triphenylphosphoranylidenehydrazones (phosphazines, 1). These



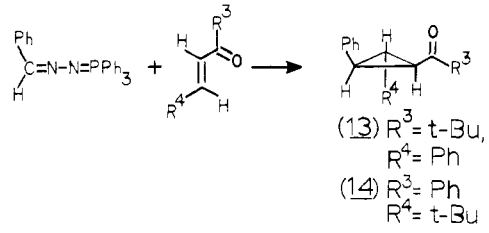
are typically stable crystalline compounds which can be easily prepared from the corresponding hydrazones[5] or carbonyl compounds[6] as well as from stable diazo compounds.[7]

While earlier work showed that pyrolysis of these phosphoranylidenehydrazones typically afforded nitrogen, the phosphine, and complex mixtures of products,[7,8] thermal decomposition of triphenylphosphoranylidenehydrazones has been recently used in the high yield preparations of selones and olefins.[9] The latter reaction has been shown to involve the intermediacy of a diazo compound. Accordingly, an investigation of the thermal reactions of triphenylphosphoranylidenehydrazones in the presence of enones, well-known acceptors of diazo compounds, was undertaken.

Thermolysis of mixtures of aryl triphenylphosphoranylidenehydrazones and chalcones, typically in refluxing *n*-butyl ether, leads to the expected 2,3-diaryl-1-benzoylcyclopropanes (2). Presumably, the reaction occurs through the typical dipolar addition of the in-situ-generated diazo component to the electrophilic double bond of the enone to give a thermally unstable Δ^1-pyrazoline which then extrudes nitrogen, affording the cyclopropane (Scheme I). While yields of cyclopropanes are typically low on using a 1:1 molar ratio of phosphoranylidenehydrazone to enone, more satisfactory yields may be obtained by increasing the number of equivalents of the phosphorus reagent (Table I). Yields are not increased by the addition of copper powder, zinc–copper couple, or copper bronze.

The stereochemistry of the benzoylcyclopropanes was determined by NMR analysis of unlabeled and deuterium-labeled cyclopropanes obtained from the corresponding labeled chalcones.[10] In each case the compounds were found to possess the *cis,trans*-2,3-diaryl stereochemistry expected from the stereospecific addition of a diazo compound to a *trans*-chalcone.

Thermolysis of the phosphoranylidenehydrazones (2 equiv) in the presence of the moderately hindered benzalpinacolone or its isomer gave the expected cyclopropanes **13** and **14** in yields of 32% and 27%, respectively.



In contrast, the thermolyses of phosphoranylidenehydrazones under the same conditions in the presence of relatively unsubstituted enones such as crotonophenone, phenyl vinyl ketone, or methyl vinyl ketone led to resinous materials containing triphenylphosphine but yielded no cyclopropanes. Similarly, no characterizable cyclized products were obtained from acrylonitrile, 2-butenolide, β-nitrostyrene, or ethyl cinnamate. It is likely that in some of these cases polymerization of the dipolarophile occurred at temperatures below that necessary for thermal generation of the diazo compound from the phosphoranylidenehydrazones.

While cyclopropanes may be prepared by the thermal reaction of a diazo compound with an enone, there are certain disadvantages to this method. Aside from the limited shelf stability of the diazo compounds, the room-temperature reaction of the aromatic diazo compound with an enone affords a Δ^2-pyrazoline, presumably by isomerization of the initially formed Δ^1-pyrazoline.[11] This is subsequently thermolyzed at a higher temperature, affording the cyclopropane in modest yield. Attempted direct reaction of the diazo compounds with chalcones at elevated temperatures led to complex mixtures with extensive azine formation, complicating isolation of the cyclopropane. In comparison, the phosphoranylidenehydrazones are typically easily prepared from the corresponding hydrazones[5] or carbonyl compounds,[6] are crystalline, and are shelf stable for months. The pyrolysis scheme directly affords the desired cyclopropane without requiring isolation of intermediates. While a direct com-

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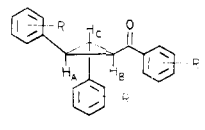
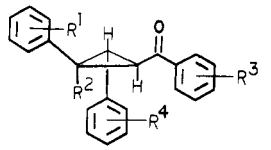
(10) Deuterium-labeled cyclopropanes were obtained from the corresponding specifically deuterated chalcones. This deuteration clearly allows asssignment of the cyclopropane protons, indicating that the proton furthest downfield is not that α to the carbonyl (H_B). Examination of models indicates that H_B should be significantly shielded by an aromatic substituent; similar results have been reported for other cyclopropane derivatives (Jackman, L. M.; Sternhill, S. "Applications of Nuclear Magnetic Resonance Spectroscopy of Organic Chemistry"; Pergamon Press, Ltd.: Oxford, 1969). The 270-MHz ^1H NMR spectra of the deuterated compounds was first order in splitting patterns. Typically the couplings observed were $J_{AB} \approx 9.2$–9.5 Hz, $J_{BC} \approx 4.6$–5.9 Hz, and $J_{AC} \approx 6.6$–7.4 Hz, consistent with the stereochemistry expected from a stereospecific addition and extrusion: cis, J = 8–10 Hz; trans, J = 4–6 Hz (Bothner-by, A. B. *Adv. Magn. Reson.* **1865**, *1*, 145). ^{13}C spectra were consistent with these assignments.



(11) Huisgen, R.; Grashey, R.; Sauer, J. In "The Chemistry of Alkenes"; Patai, S., Ed.; Wiley: London, 1964; pp 826–835 and references therein.

Table I

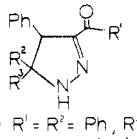


compd	R^1	R^2	R^3	R^4	time, h/ equiv of phosp[a]	yield,[b] %
3	H	H	H	H	12/3	66
4	H	H	4-CH_3	H	23/3	18
					12/1	11
5	H	H	H	4-CH_3	15/2	27
6	4-CH_3	H	H	H	12/3	55
					12/1	37
7	H	CH_3	H	H	15/3	61
8	H	H	4-Cl	H	12/1	13
9	H	H	4-Br	H	18/3	21
10	H	CH_3CH_2	H	H	23/4	65
					12/1	13
11	H	H	4-OCH_3	H	18/1	17
12	H	H	4-F	H	18/2	6

[a] Conditions not optimized. [b] Isolated yield of purified products.

parison of the two methods may not be realistic due to losses in isolation of intermediates, *cis*, *trans*-2,3-diphenyl-1-benzoylcyclopropane (**3**) was prepared in 66% yield from the phosphazine method vs. 16% via direct addition of the diazo compound. It appears that the phosphoranylidenehydrazone pyrolysis is the simplest method for the preparation of the title compounds.

In an attempt to discover whether a similar reaction would occur with the alkyl triphenylphosphoranylidenehydrazones, we heated 3-pentanone triphenylphosphoranylidenehydrazone in di-*n*-butyl ether in the presence of an equimolar amount of chalcone. Instead of the expected cyclopropane, the Δ^2-pyrazoline **16** was isolated in 24% yield. Similarly, modest yields of Δ^2-pyrazolines **17** and **18** were obtained from the reaction of this hydrazone with benzalacetone and from the reaction of the pinacolone triphenylphosphoranylidenehydrazone with chalcone. While none of the above reactions were optimized, it appears the alkyl-substituted phosphoranylidenehydrazones may also be useful precursors for the in situ generation of very unstable alkyl-substituted diazo compounds.



(15) $R^1 = R^2 = Ph$, $R^3 = H$
(16) $R^1 = Ph$, $R^2 = R^3 = Et$
(17) $R^1 = Me$, $R^2 = R^3 = Et$
(18) $R^1 = Ph$, $R^2 = t\text{-}Bu$, $R^3 = Me$

Experimental Section

Melting points were obtained by using a Fisher Melt-Temp apparatus and are uncorrected. Flash column and open column chromatographic separations utilized silica gel H (10–40 μm, Kensington Scientific Corp., No. 7736) and Baker silica gel (No. -3405, 60–200 mesh) with solvent systems of 90/10 and 80/20 hexane/ether or 90/10 and 80/20 hexane/tetrahydrofuran. With the same solvent systems, analytical thin-layer chromatographic separations utilized 90 × 15 mm sections of Eastman Chromagram sheets (No. 13181) and 50 × 20 mm Baker Si250F silica plates. Alumina open column chromatographic separations utilized Merck No. AX611 alumina (80–325 mesh) with solvent systems of 80/20 and 90/10 hexane/benzene. Di-*n*-butyl ether was predried over sodium metal and distilled from calcium hydride directly prior to use. Proton magnetic resonance spectra were recorded on Varian EM-360L and JEOL FX-270 spectrometers with deuteriochloroform or tetramethylsilane as an internal standard; ^{13}C magnetic resonance spectra were obtained by using a Bruker HX-270 instrument. Chemical-ionization (CI) and electron-impact (EI) mass spectra were recorded with a Finnigan 4021-B mass spectrometer. Infrared spectra were taken with a Perkin-Elmer 727-B instrument. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, and Guelph Chemical Laboratories, Ltd., Guelph, Ontario.

2,3-Diaryl-1-benzoylcyclopropanes. General Procedure. The phosphoranylidenehydrazone[5] (10 mmol) was added to a suspension of chalcone (3.3 mmol) in dry di-*n*-butyl ether (50 mL). The mixture was heated to reflux temperature via a heating mantle or oil bath whereupon all the components dissolved and the reaction mixture turned bright yellow-orange. Heating was continued for 18 h, and upon cooling, crystals of triphenylphosphine formed. The *n*-butyl ether was completely removed by using a rotary evaporator and then a vacuum pump. The resulting oily crystalline mass was treated with iodomethane (10–15 mmol) in dry diethyl ether (50 mL) at room temperature for 6 h, giving a precipitate of methyltriphenylphosphonium iodide. The salt was removed by vacuum filtration through a 100 mm × 15 mm Florisil column by using diethyl ether (200 mL) as a wash solvent. The ethereal filtrate was evaporated, giving a yellow oily crystalline residue which was chromatographed on silica (200 g) with a solvent system of 1:9 THF/hexane or 1:9 ether/hexane or on alumina (200 g) with a solvent system of 9:1 hexane/benzene. All the cyclopropanes were obtained as crystalline materials. The addition of commerical copper powder (1 equiv), copper bronze (1 equiv), or zinc–copper couple[12] (1 equiv) under identical conditions did not increase the yield of the cyclopropanes.

***cis*,*trans*-2,3-Diphenyl-1-benzoylcyclopropane (3, Table I).** Compound **3** was prepared according to the general procedure from benzaldehyde triphenylphosphoranylidenehydrazone[5] and chalcone. The crude oily crystalline mass was triturated with ethanol, yielding 0.47g (66%) of 2,3-diphenyl-1-benzoylcyclopropane as needles from ethanol: mp 153–154 °C (lit.[13] mp 156–157 °C); IR ($CHCl_3$) 1685 cm^{-1}; mass spectrum (70 eV), *m/e* 298 (m^+); ^1H NMR (270 MHz, $CDCl_3$) δ 3.27 (H_A, dd, J_{AB} = 9.56 Hz) 3.39 (H_B, dd, J_{AC} = 6.92 Hz) 3.62 (H_C, dd, J_{BC} = 4.61 Hz), 7.15–7.50 (m, 13 H, aromatic), 7.94 (2 H, m, *o*-benzoyl); ^{13}C NMR ($CDCl_3$) δ 37.8, 36.4, 29.9 (cyclopropane), 126.6–139.9 (10 signals, phenyl), 194.85 (carbonyl).

***cis*,*trans*-2,3-Diphenyl-1-(*p*-methylbenzoyl)cyclopropane (4):** mp 105–105.5 °C (ethanol); IR ($CHCl_3$) 1660 cm^{-1}; mass spectrum (70 eV), *m/e* 312 (M^+); ^1H NMR ($CDCl_3$) δ 2.38 (s, 3 H), 3.24 (dd, H_A, J_{AB} = 9.56 Hz), 3.35 (dd, H_B, J_{BC} = 5.27 Hz), 3.6 (dd, H_C, J_{AC} = 6.9 Hz), 7.14 (m, 12 H), 7.85 (m, 2 H). Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.14; H, 6.89.

***trans*-2-(*p*-Methylphenyl)-*cis*-3-phenyl-1-benzoylcyclopropane (5):** mp 105–107 °C (ethanol); IR ($CHCl_3$) 1667 cm^{-1}; mass spectrum (70 eV), *m/e* 312 (M^+); ^1H NMR ($CDCl_3$) δ 2.3 (s, 3 H) 3.25 (dd, H_A, J_{AB} = 9.55 Hz), 3.32 (dd, H_B, J_{BC} = 5.6 Hz), 3.6 (dd, H_C, J_{AC} = 6.92 Hz), 7.25 (m, 12 H), 7.92 (m, 2 H). Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.42; H, 6.39.

***cis*-2-(*p*-Methylphenyl)-*trans*-3-phenyl-1-benzoylcyclopropane (6):** mp 124–125 °C (ethanol); IR ($CHCl_3$) 1665 cm^{-1}; mass spectrum (70 eV), *m/e* 312 (M^+), ^1H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 3.25 (dd, H_A, J_{AB} = 9.4 Hz), 3.35 (dd, H_B, J_{BC} = 5.27 Hz), 3.6 (dd, H_C, J_{AC} = 6.9 Hz), 7.2 (m, 12 H), 7.93 (m, 2 H). Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.41; H, 6.46.

***cis*,*trans*-2,3-Diphenyl-*trans*-2-methyl-1-benzoylcyclopropane (7):** mp 147–148 °C (ethanol); IR ($CHCl_3$) 1670 cm^{-1}; mass spectrum (70 eV), *m/e* 312 (M^+); ^1H NMR ($CDCl_3$) δ 1.4 (s, 3 H), 3.3 (d, H_B, J_{BC} = 5.93 Hz), 3.8 (d, H_C), 7.3 (m, 13 H), 8.0 (m, 2 H). Anal. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45. Found: C, 88.33; H, 6.38.

(12) Fieser, L.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, p 1292, procedure 1.
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***cis,trans*-2,3-Diphenyl-1-(*p*-chlorobenzoyl)cyclopropane (8)**: mp 108–109 °C (hexane–benzene); IR ($CHCl_3$) 1670 cm^{-1}; mass spectrum (70 eV), *m/e* 332 (M^+); ^1H NMR ($CDCl_3$) δ 3.21 (dd, H_A, J_{AB} = 9.56 Hz), 3.32 (dd, H_B, J_{BC} = 5.27 Hz), 3.58 (dd, H_C, J_{AC} = 6.92 Hz), 7.3 (m, 12 H), 7.9 (m, 2 H). Anal. Calcd for $C_{22}H_{17}ClO$: C, 79.39; H, 5.14; Cl, 10.65. Found: C, 78.98; H, 5.23; Cl, 10.82.

***cis,trans*-2,3-Diphenyl-1-(*p*-bromobenzoyl)cyclopropane (9)**: mp 113–115 °C (hexane–benzene); IR ($CHCl_3$) 1670 cm^{-1}; mass spectrum (70 eV), *m/e* 376 (M^+); ^1H NMR ($CDCl_3$) δ 3.23 (d, 2 H), 3.56 (t, 1 H), 7.1–7.3 (m, 12 H), 7.63 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.1, 36.5, 38.0, 127.0, 127.1, 128.3, 128.8, 129.1, 129.7, 131.9, 194.0. Anal. Calcd for $C_{22}H_{17}BrO$: C, 70.04; H, 4.45. Found: C, 70.12; H, 4.27.

***cis,trans*-2,3-Diphenyl-*trans*-2-ethyl-1-benzoylcyclopropane (10)**: mp 135–137 °C (ethanol); IR ($CHCl_3$) 1670 cm^{-1}; mass spectrum (70 eV), *m/e* 326 (M^+); ^1H NMR ($CDCl_3$) δ 0.68 (t, 3 H), 1.65 (m, 2 H), 3.3 (d, H_B, J_{BC} = 5.93 Hz), 3.75 (d, H_C), 7.3 (m, 13 H), 8.0 (m, 2 H). Anal. Calcd for $C_{24}H_{22}O$: C, 88.17; H, 6.78. Found: C, 88.31; H, 6.90.

***cis,trans*-2,3-Diphenyl-1-(*p*-methoxybenzoyl)cyclopropane (11)**: mp 104–105 °C (ethanol); IR ($CHCl_3$) 1670 cm^{-1}; mass spectrum (70 eV), *m/e* 328 (M^+); ^1H NMR ($CDCl_3$) δ 3.85 (s, 3 H), 3.24 (dd, H_A, J_{AB} = 9.23 Hz), 3.32 (dd, H_B, J_{BC} = 5.94 Hz), 3.56 (dd, H_C, J_{AC} = 6.92 Hz), 7.2 (m, 12 H), 7.95 (m, 2 H). Anal. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14. Found: C, 83.99; H, 6.23.

***cis,trans*-2,3-Diphenyl-1-(*p*-fluorobenzoyl)cyclopropane (12)**: mp 101–102 °C (hexane); IR ($CHCl_3$) 1680 cm^{-1}; mass spectrum (70 eV), *m/e* 316 (M^+); ^1H NMR ($CDCl_3$) δ 3.2 (dd, H_A, J_{AB} = 9.56 Hz), 3.27 (dd, H_B, J_{BC} = 5.6 Hz), 3.54 (dd, H_C, J_{AC} = 6.59 Hz), 7.3 (m, 12 H), 7.9 (m, 2 H). Anal. Calcd for $C_{22}H_{17}FO$: C, 83.52; H, 5.41, F, 6.00. Found: C, 83.66; H, 5.60; F, 6.22.

***cis,trans*-2,3-Diphenyl-1-pivaloylcyclopropane (13)** was obtained by reaction of benzalpinacolone with 1 equiv of benzaldehyde phosphazine[5] for 16 h: 32% yield; mp 90–92 °C (pentane–benzene; IR ($CHCl_3$) 1690 cm^{-1}; mass spectrum (70 eV), *m/e* 278 (M^+); ^1H NMR ($CDCl_3$) δ 1.0 (s, 9 H), 2.92 (dd, H_B, J_{AB} = 9.23 Hz), 3.0 (dd, H_A, J_{AC} = 6.92 Hz), 3.36 (dd, H_C, J_{BC} = 5.27 Hz), 7.26 (m, 10 H). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.96. Found: C, 86.26; H, 8.07.

***cis*-2-Phenyl-*trans*-3-*tert*-butyl-1-benzoylcyclopropane (14)** was obtained by reaction of β-*tert*-butylchalcone with 2 equiv of benzaldehyde phosphazine[5] for 18 h: 27% yield; mp 112–114 °C (petroleum ether–benzene); IR ($CHCl_3$) 1665 cm^{-1}; mass spectrum (70 eV), *m/e* 278 (M^+); ^1H NMR ($CDCl_3$) δ 1.05 (s, 9 H) 2.45 (dd, H_C, J_{AC} = 7.45 Hz), 2.84 (dd, H_A, J_{AB} = 9.55 Hz), 2.97 (dd, H_B, J_{BC} = 5.93 Hz), 7.4 (m, 8 H), 7.9 (m, 2 H). Anal. Calcd for $C_{20}H_{22}O$: C, 86.29; H, 7.95. Found: C, 86.06; H, 7.87.

Cyclopropane (3) via Pyrazoline (15). Benzaldehyde hydrazone (6.5 g, 0.054 mol) in ether (20 mL) was added dropwise to a stirred cooled suspension of yellow mercuric oxide (23.3 g, 0.108 mol) in ether (100 mL). After the addition was complete (15 min), aqueous saturated sodium hydroxide solution (5.0 mL) was added. The suspension, which slowly turned wine red, was stirred (20 min) and gravity filtered through a fluted filter full of sodium sulfate (anhydrous). To the clear, wine-red solution of phenyldiazomethane was added chalcone (10 g, 0.048 mol) in ether (100 mL). The mixture was stirred for 4.5 h during which a slight amount of nitrogen evolution was observed and the mixture had decolorized. The solution was then concentrated to a light yellow oil and triturated with 95% ethanol (20 mL). The resulting white crystalline precipitate was collected by filtration, affording 4.2 g (26%) of **15**: mp 130–132 °C dec; IR ($CHCl_3$) 1660, 3450 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.5 (d, 1 H, J_{AB} = 5.9 Hz), 4.8 (d, 1 H), 6.8 (s, 1 H), 7.5 (m, 13 H), 8.2 (m, 2 H).

A suspension of **15** (0.250 g, 0.76 mmol) in dry *n*-butyl ether (10 mL) was heated to reflux (12 h) by using an oil bath. The *n*-butyl ether was removed from the yellow reaction mixture by a rotary evaporator and then a vacuum pump (room temperature). The residual oil was chromatographed on silica gel (hexane–ether, 8:2). The fractions which contained the cyclopropane were combined, concentrated, and then triturated with 95% ethanol, affording **3** as white crystalline needles: mp 153–154 °C; 0.14 g (62%). This product was identical with that obtained from the phosphoranylidenehydrazone reaction.

3-Benzoyl-4-phenyl-5,5-diethyl-Δ²-pyrazoline (16). 3-Pentanone triphenylphosphoranylidenehydrazone[5] (2.0 g, 5.5 mmol) was added to a suspension of chalcone (1.15 g, 5.5 mmol) in dry *n*-butyl ether (50 mL). The mixture was heated to reflux for 8.0 h, the reaction solvent removed via a rotary evaporator and then a vacuum pump, and treated with iodomethane (3 mL, 48 mmol) in ether (50 mL), affording a crystalline precipitate of methyltriphenylphosphonium iodide. The precipitate was removed by filtration through a 20 × 100 mm column of silica, and the filtrate was concentrated to an oil and triturated with 95% ethanol (20 mL). The resulting crystals were collected and recrystallized from hexane/benzene to yield 0.404 g (24%) of 3-benzoyl-4-phenyl-5,5-diethyl-Δ²-pyrazoline: mp 118–120 °C; ^1H NMR ($CDCl_3$) δ 0.5–1.9 (m, 10 H, *gem*-diethyl), 4.3 (s, 1 H, benzyl), 6.45 (br s, 1 H, NH), 7.0–7.5 (m, 8 H, phenyl), 8.1 (m, 2 H, *o*-benzoyl); IR ($CHCl_3$) 1655 cm^{-1}. Anal. Calcd for $C_{20}H_{22}N_2O$: C, 78.39; H, 7.23; N, 9.14. Found: C, 78.17; H, 7.27; N, 8.98.

Acylpyrazolines **17** and **18** could be prepared analogously. **17**: oil; 11% yield; ^1H NMR ($CDCl_3$) δ 0.5–1.8 (m, 10 H), 2.35 (s, 3 H), 4.0 (s, 1 H), 6.3 (s, 1 H), 7.3–7.8 (m, 5 H); IR ($CHCl_3$) 1655 cm^{-1}. **18**: oil; 5% yield; ^1H NMR ($CDCl_3$) δ 0.75 (s, 3 H), 0.90 (s, 9 H), 4.55 (s, 1 H), 6.7 (s, 1 H), 7.0–7.5 (m, 8 H), 7.58–8.15 (m, 2 H); IR ($CHCl_3$) 1650 cm^{-1}.

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Registry No. **1** (R^1, R^2 = H), 1103-87-3; **1** (R^1 = 4-CH_3; R^2 = H), 86118-52-7; **1** (R^1 = H; R^2 = CH_3), 2734-98-7; **1** (R^1 = H; R^2 = C_2H_5), 53813-64-2; **3**, 26597-09-1; **4**, 86118-53-8; **5**, 86161-60-6; **6**, 86161-61-7; **7**, 86118-54-9; **8**, 86118-55-0; **9**, 86118-56-1; **10**, 86118-57-2; **11**, 86118-58-3; **12**, 86118-59-4; **13**, 86118-60-7; **14**, 86118-61-8; **15**, 56445-39-7; **16**, 86118-62-9; **17**, 86118-63-0; **18**, 86118-64-1; (*E*)-PhCOCH=CHPh, 614-47-1; (*E*)-4-$CH_3C_6H_4COCH$=CHPh, 14802-30-3; (*E*)-PhCOCH=$CHC_6H_4CH_3$-4, 22252-14-8; (*E*)-4-ClC_6H_4COCH=CHPh, 22966-22-9; (*E*)-4-BrC_6H_4COCH=CHPh, 22966-23-0; (*E*)-4-$CH_3OC_6H_4COCH$=CHPh, 22966-19-4; (*E*)-4-FC_6H_4COCH=CHPh, 22966-25-2; (*E*)-*t*-BuCOCH=CHPh, 538-44-3; (*E*)-PhCOCH=CHBu-*t*, 29569-93-5; $PhCH{=}NNH_2$, 5281-18-5; PhCDO, 3592-47-0; 4-$CH_3C_6H_4CDO$, 13277-99-1; $PhCOCH_3$, 98-86-2; (*E*)-PhCOCH=CDPh, 32461-19-1; (*E*)-PhCOCH=$CDC_6H_4CH_3$-4, 86118-66-3; (*E*)-PhCOCD=CDPh, 23057-96-7; (*E*)-PhCOCD=$CDC_6H_4CH_3$-4, 86118-69-6; 3-pentanone triphenylphosphoranylidenehydrazone, 86118-65-2; 2-phenyl-1,3-dithiane, 5425-44-5; 2-*p*-tolyl-1,3-dithiane, 56637-44-6; *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane-*3-d*, 86118-67-4; *trans*-2-*p*-tolyl-*cis*-3-phenyl-1-benzoylcyclopropane-*2-d*, 86118-68-5; *cis,trans*-2,3-diphenyl-1-benzoylcyclopropane-*1,3-d_2*, 86118-70-9; *trans*-2-*p*-tolyl-*cis*-3-phenyl-1-benzoylcyclopropane-*1,2-d_2*, 86118-71-0.

Supplementary Material Available: Scheme showing stereochemistry with deuterium-labeled chalcones (2 pages). Ordering information is given on any current masthead page.

Aerosol Direct Fluorination: Syntheses of Perfluoro Ketones

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The aerosol direct fluorination method provides a continuous process for the production of perfluorocarbons from hydrocarbons with efficient fluorine utilization and minimal fragmentation.[1] The application of this process

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