(t, J = 7 Hz, 2 H), 3.77 (t, J = 4 Hz, 1 H), 5.95 (s, 1 H, CHN_2); ^{13}C NMR (1:1 D_2O–D_3COD, 0 °C) δ 27.0, 36.5, 55.0, 58.1, 174.4, 198.4.

Acknowledgment. We are grateful for support of this investigation by Grant CA 16049-05-07 awarded by the National Cancer Institute, DHW, Mrs. Mary Dell Pritzlaff, the Olin Foundation (Spencer T. and Ann W.), the Fannie E. Rippel Foundation, Mrs. Pearl Spear, and Mr. Robert B. Dalton.

Registry No. 1, 157-03-9; 2, 3705-42-8; 3, 71389-33-8; 4·DCHA, 53363-74-9; 5, 84332-53-6; 6, 1676-73-9; 7, 84369-01-7; 8·DCHA, 84344-29-6; 9, 1535-57-5; 10, 7589-24-4.

Oxidation of Acylphosphoranes with Sodium Hypochlorite. Substituted Carboxylic Acids through Charge-Directed Conjugate Addition Reactions

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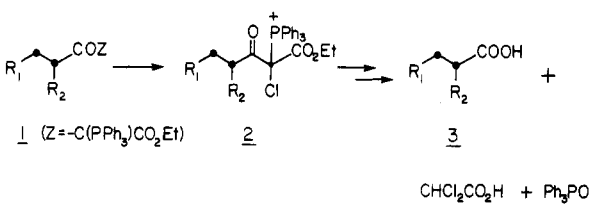
We have previously described a useful new approach to conjugate addition–alkylation reactions involving the charge-directed conjugate additions of a variety of nucleophiles to unsaturated acylcarbalkoxytriphenylphosphoranes with subsequent capture of intermediate ylide anions by electrophiles.[1] The resulting substituted ylides **1** may then be transformed into esters by acid catalyzed alcoholysis,[1a] into methyl ketones through decarbalkoxylation of *tert*-butyl ylide esters,[1c] and into highly substituted ketones by reduction of the ylide moiety and subsequent transformations of derived β-keto esters.[1d]

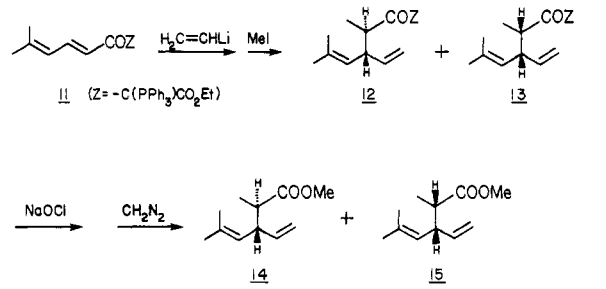
In the course of applying this new methodology to several natural product syntheses, we have found that the transformation to simple esters through the acid-catalyzed alcoholysis of the acyl ylide function is unsatisfactorily slow in cases where both C_α and C_β are highly substituted and that trisubstituted olefins undergo alcohol addition under the acidic reaction conditions.[2] We therefore required a mild method for the conversion of the ylide moiety to the carboxyl group and were led to investigate haloform-type oxidative cleavages,[3] in that, unlike acylphosphoranes,[1e] acylcarbalkoxyphosphoranes are not cleaved in neutral or alkaline media.[1f] We now report that phosphoranes such as **1** are readily cleaved by slightly more than 2 equiv of alkaline NaOCl (Scheme I) giving good yields of carboxylic acids.[3] Typical examples are shown in Table I. The reaction presumably occurs through chlorinated phosphonium intermediate **2**, which then undergoes either direct cleavage by hydroxide ion attack at the C-3 carbonyl group or through hydroxide ion displacement at phosphorous to give triphenylphosphine oxide and the chlorinated β-keto ester anion, which can then undergo a classical haloform reaction.[3]

Tetrahydrofuran (THF) and acetonitrile (AN) were found to be the best solvents for this reaction with somewhat faster rates being observed in acetonitrile. Lower yields were generally observed when MeOH was employed (see entry 5). The higher pH (≥10) required for the aqueous phase was difficult to maintain with EtOAc as the solvent though the previously reported acceleration in the rate of hypohalite reactions in this solvent was observed.[4] Triphenylphosphine oxide resulting from the reaction is readily removed by extraction prior to acidification of the aqueous phase, and extraction of the acidified mixture with pentane allows efficient separation of the desired carboxylic acid from an equal amount of water-soluble dichloroacetic acid, which is also formed.[5] In general, oxidations proceeded readily at 25 °C except in the case of entry **3**, which required somewhat more vigorous conditions owing to the presence of a less reactive carbonyl group. The more highly substituted ylides **8–10**, which undergo the acid-catalyzed alcoholysis process only very slowly, were also readily converted to the corresponding carboxylic acids. Equally noteworthy is the conversion shown in entry **4**, which demonstrates the compatability of the trisubstituted olefin moiety in **7** with these reaction conditions.

Scheme I



Scheme II



The utility of this conversion is demonstrated in a synthesis[6] of racemic methyl *epi*-santolinate[7] shown in Scheme II. In accordance with our previous finding that diene acyl ylides undergo 1,4-additions[1a] rather than the 1,6-additions common with Gilman reagents,[8] treatment of **11** with vinyllithium gave an intermediate ylide anion that upon alkylation with methyl iodide provided diastereomeric alkylated ylides **12** and **13** in 73% yield. The mixture was composed predominately of the 2R*,3R* isomer **12** (**12**:**13** = 9:1) as expected on the basis of steric considerations. Treatment of the mixture with NaOCl in acetonitrile gave the intermediate carboxylic acids (77%), which were esterified with CH_2N_2 giving esters **14** and **15** in 92% yield. The major component, **14** was identical with

(1) (a) Cooke, M. P., Jr.; Goswami, R. *J. Am. Chem. Soc.* **1977**, *99*, 642. (b) Cooke, M. P., Jr. *Tetrahedron Lett.* **1979**, *20*, 2199. (c) Cooke, M. P., Jr.; Burman, D. L. *J. Org. Chem.* **1982**, *47*, 4955. (d) Cooke, M. P., Jr. *Ibid.* **1982**, *47*, 4963. (e) Cooke, M. P., Jr. *Ibid.* **1973**, *38*, 4082. (f) Chopard, P. A.; Searle, R. J. G.; Devitt, F. H. *Ibid.* **1965**, *30*, 1015.

(2) Acidic methanolysis of **7** (1.7 equiv of HCl, 20 h at reflux) gives predominately methyl 5-methoxy-5-methoxy-5-methylhexanoate.

(3) Fuson, R. C.; Bull, B. A. *Chem. Rev.* **1934**, *15*, 275.

(4) Lee, G. A.; Freedman, H. H. *Tetrahedron Lett.* **1976**, 1641.

(5) Attempts to avoid the generation of dichloroacetic acid through the use of the corresponding *tert*-butyl ester ylide (**5**, Z = C(PPh$_3$)COO-*t*-Bu) were not successful. Hydrocinnamic acid was obtained in 87% yield after 8 h at 25 °C, however.

(6) A synthesis giving predominately methyl santolinate (**13**) has been reported: Boyd, J.; Epstein, W. *J. Chem. Soc., Chem. Commun.*, **1976**, 380.

(7) Noble, T. A.; Epstein, W. W. *Tetrahedron Lett.* **1977**, 3931.

(8) (a) Posner, G. H. *Org. React.* **1972**, *19*, 1. (b) Corey, E. J.; Chen, R. H. K. *Tetrahedron Lett.* **1973**, 1611. (c) Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1978**, *100*, 3240.

0022-3263/83/1948-0744$01.50/0

Table I. Carboxylic Acids from Acylphosphoranes

entry	phosphorane (Z = C(PPh$_3$)COOEt)	reaction solvent	reaction time, h	reaction temp, °C	yield of acid (Z = OH),[a] %
1	$CH_3(CH_2)_4COZ$ **4**	THF	4	25	92
2	$Ph(CH_2)_2COZ$ **5**	THF	17	25	94
		AN	4.5	25	96
3	PhCOZ **6**	THF	19.25	25-65[b]	74
4	$(CH_3)_2C{=}CH(CH_2)_2COZ$ **7**	AN	4.5	0-25[c]	78
5	 **8**	MeOH	10	25	60[d]
		THF	3.5	25	92[d]
6	$CH_3(CH_2)_3CH(C_2H_5)COZ$ **9**	THF	19	25	93
7	$PhCH(CH_3)CH(C_2H_5)COZ$ **10**	THF	40	25	88
		AN	21	25	81 (96)[e]

[a] Isolated yields. [b] 18 h at 25 °C, 1 h at 45 °C, 0.25 h at 65 °C. [c] 2.5 h at 0 °C, 2 h at 25 °C. [d] Yield determined by GLC. [e] Yield based on recovered starting material.

authentic methyl *epi*-santolinate[9] and represented 91% of the isomeric mixture by GLC analysis.

The functional group conversion described herein enables unsaturated acylcarbalkoxytriphenylphosphoranes to serve as useful precursors to a variety of substituted acrylate derivatives not usually available by conjugate addition–alkylation reactions with other Michael acceptors and Gilman reagents.[8c]

Experimental Section

^{1}H NMR spectra were recorded at 100 Mhz with a JEOL MH-100 spectrometer or at 90 Mhz with a JEOL FX-90Q spectrometer. ^{13}C NMR spectra were recorded at 22.5 Mhz with the JEOL FX-90Q spectrometer. Infrared spectra were recorded with a Beckman AccuLab 1 spectrometer. Preparative thick-layer chromatography (PTLC) was performed with 1–2-mm layers of Merck silica gel 60 PF-254. Bulb-to-bulb distillations of the Kugelrohr type were conducted at the air oven temperatures and pressures cited. Melting points are uncorrected. Analyses were performed by Galbraith Laboratories, Inc.

Tetrahydrofuran was distilled from sodium benzophenone ketyl prior to use. Sodium hypochlorite was obtained as commercial bleach and was titrated[10] prior to use.

Acylcarbethoxytriphenylphosphoranes. Ylides **4**, **6**,[11] and **7–10** were prepared as previously described.[1d] Previously unreported **5** was likewise prepared: mp 142–144 °C; IR ($CHCl_3$) 3000, 1645, 1655, 1548, 1435, 1375, 1295, 1105, 1009 cm^{-1}; ^{1}H NMR ($CDCl_3$, 100 Mhz) δ 0.62 (t, 3 H, OCH_2CH_3, J = 7 Hz), 2.90 (t, 2 H, CH_2CO, J = 8 Hz), 3.16 (t, 2 H, CH_2Ph, J = 8 Hz), 3.62 (q, 2 H, OCH_2), 7.06 (s, 5 H, Ph), 7.1–7.7 (m, 15 H, PhP). Anal. Calcd for $C_{31}H_{29}O_3P$: C, 77.48; H, 6.08. Found: C, 77.52; H, 6.08.

Hydrocinnamic Acid (Table I, Entry 2). Typical Procedure for the Oxidation of Acylcarbethoxytriphenylphosphoranes. A solution containing 1.44 g (3.0 mmol) of ylide **5** in 18 mL of THF was stirred at 20 °C and treated with 8.4 mL (6.9 mmol) of 0.82 N NaOCl solution over 1 min followed by the addition of 1.2 mL of 4 N NaOH. The mixture was stirred at 20–25 °C for 17 h whereupon excess NaOCl was destroyed by the addition of small portions of $NaHSO_3$ until a negative acidic starch–iodide paper test resulted. (The addition of excess $NaHSO_3$ may require readjustment of the solution to pH 10 by the addition of 4 N NaOH). THF was removed under reduced pressure (25 °C, 15 mmHg) whereupon triphenylphosphine oxide separated and crystallized. The mixture was extracted twice with 15-mL portions of Et_2O to remove the triphenylphosphine oxide and neutral materials. The aqueous phase was acidified to pH 1 by the addition of hydrochloric acid and extracted twice with 15-mL portions of pentane. The combined extracts were concentrated, and bulb-to-bulb distillation of the residue (180 °C, 1.0 mmHg) gave 422 mg (94%) of hydrocinnamic acid spectrally identical with authentic material.

The remaining ylides in Table I were oxidized in a similar manner by using the conditions cited in Table I. Products corresponding to known carboxylic acids were identified by comparison with authentic samples. The oxidation of **10** gave heretofore unreported 2-ethyl-3-phenylbutanoic acid (**10**, Z = OH): IR ($CHCl_3$) 3080 (br), 2980, 1700, 1455, 1275 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 Mhz) δ 0.83 (t, 3 H, CH_3CH_2, J = 7.3 Hz), 1.1–1.5 (br, 2 H, CH_2), 1.30 (d, 3 H, CH_3CH, J = 6.6 Hz), 2.48 (dt, 1 H, CHCOO, J = 4.8, J = 9.0 Hz), 2.7–3.1 (m, 1 H, $CHCH_3$), 7.06–7.47 (m, 5 H, Ph), 10.74 (br, 1 H, COOH); ^{13}C NMR ($CDCl_3$, major diastereoisomer) δ 11.7 (CH_3), 20.9 (C-4), 24.3 (CH_2), 42.5 (C-3), 54.8 (C-2), 126.6 (C-4′), 127.5 (C-3′), 128.6 (C-2′), 144.5 (C-1′), 182.5 (C-1). (Additional peaks arising from the minor diastereoisomer were seen at δ 16.1, 20.7, 43.3, 46.9, and 144.1.) An analytical sample, mp 61–69 °C, was prepared by PTLC (3:1 CH_2Cl_2–EtOAc) followed by bulb-to-bulb distillation (170 °C, 1 mmHg). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.75; H, 8.46.

Ethyl 7-Methyl-3-oxo-2-(triphenylphosphoranylidene)-(*E*)-4,6-octadienoate (11). Sodium hydride (250 mg, 5.8 mmol, 57% in oil) was stirred in 25 mL of THF for 10 min followed by the addition of 3.03 g (5.75 mmol) of diethyl 2,4-dioxo-4-ethoxy-3-(triphenylphosphoranylidene)butanephosphonate,[12] 570 μL (6.0 mmol) of 3-methyl-2-butenal, and 2 drops of MeOH. The reaction proceeded with evolution of H_2 and was stirred at 25 °C for 2 h. Solvent was removed under reduced pressure, the residue was treated with 25 mL of water, and the mixture was extracted with 25 mL of dichloromethane. The extract was washed successively with water and brine, dried over Na_2SO_4, and concentrated. Crystallization of the residue from ethyl acetate–hexane gave, after two crops, 2.08 g (80%) of **11** as yellow crystals: mp 153–156 °C; IR ($CHCl_3$) 3082, 3000, 1637, 1601, 1512, 1435, 1366, 1291, 1100, 1088 cm^{-1}; ^{1}H NMR ($CDCl_3$, 90 Mhz) δ 0.66 (t, 3 H, CH_2CH_3, J = 7.1 Hz), 1.77, 1.79 (brd, brs, 6 H, $CH_3C{=}C$), 3.72 (q, 2 H, OCH_2), 6.08 (dq, 1 H, C=CH, J = 10.5, 1.2 Hz), 7.1–7.9 (m, 17 H, Ph and CCH); ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3), 18.7 (CH_3), 26.4 (CH_3), 58.4 (CH_2), 72.1 (d, C-2, $^1J_{CP}$ = 111.5 Hz), 125.4 (C-6), 127.0 (d, Ph, $^1J_{CP}$ = 93.9 Hz), 127.5 (d, C-4 $^3J_{CP}$ = 9.4 Hz), 128.4 (d, Ph, $^2J_{CP}$ = 12.5 Hz), 131.3 (d, $^4J_{CP}$ = 2.5 Hz), 132.9 (d, $^3J_{CP}$ = 10.0 Hz), 134.4 (C-5), 141.8 (C-7).

Anal. Calcd for $C_{29}H_{29}O_3P$: C, 76.30; H, 6.40. Found: C, 76.51; H, 6.49.

Ethyl 5-Ethenyl-4,7-dimethyl-3-oxo-2-(triphenylphosphoranylidene)-6-octenoate (12). A solution containing

(9) We thank Professor Epstein for an authentic synthetic sample of both diastereoisomers.

(10) Skoog, D. A.; West, D. M. "Fundamentals of Analytical Chemistry", 2nd ed.; Holt, Rinehart and Winston: New York, 1969; pp 453–459.

(11) Shevchuk, M. I.; Tolochko, A. F.; Dombrovskii, A. V. *Zh. Obsch. Khim.* **1970**, *40*, 57.

(12) Cooke, M. P., Jr.; Biciunas, K. P. *Synthesis* **1981**, 283.

95 mg (0.21 mmol) of **11** in 3 mL of THF was cooled to -78 °C and treated with 0.15 mL (0.33 mmol) of 2.2 M vinyllithium in THF. The yellow mixture was stirred for 5 min at -78 °C and then for 10 min at 0 °C whereupon 31 μL (0.5 mmol) of methyl iodide was added. The yellow color of the vinyllithium adduct was discharged in approximately 1 min whereupon the mixture was warmed to 20 °C and stirred for an additional 2 min. Solvent was removed under reduced pressure, and the residue was treated with water and extracted with dichloromethane. The extract was washed with water and dried over Na_2SO_4. The residue obtained upon solvent removal was purified by PTLC (silica gel, 20:1 CH_2Cl_2–EtOAc, two developments) giving 73 mg (73%) of a mixture of diastereomers (approximately 9:1). The more mobile major 4*R**,5*R** isomer, **12**, could be obtained as an oil free of the minor isomer **13** by careful PTLC: IR ($CHCl_3$) 3070, 3000, 1656, 1648, 1550, 1437, 1376, 1290, 1100, 1090 cm^{-1}; ^1H NMR (90 Mhz, $CDCl_3$) δ 0.64 (t, 3 H, OCH_2CH_3, J = 7.1 Hz), 1.01 (d, 3 H, 4-Me, J = 6.8 Hz), 1.56 (d, 3 H, $C{=}C(CH_3)_2$, J = 1.2 Hz), 1.69 (d, 3 H, $C{=}C(CH_3)_2$, J = 1.2 Hz), 3.22 (m, 1 H, 4-H), 3.71 (q, 2 H, OCH_2, J = 7.1 Hz), 3.6–4.1 (m, 1 H, 4-H), 4.7–5.1 (m, 3 H, vinyl protons), 5.55–5.93 (m, 1 H, $HC{=}CH_2$), 7.2–7.8 (m, 15 H, PhH). The spectrum of the 4*S**,5*R** isomer, **13**, is very similar with vinyl methyl resonances at δ 1.69 and 1.36. ^{13}C NMR ($CDCl_3$, 22.5 Mhz) of **12**: δ 13.8 (CH_3), 16.0 (4-Me), 18.2 (7-Me), 26.0 (C-8), 44.4 (d, C-4, $^3J_{CP}$ = 6.7 Hz), 45.9 (C-5), 58.3 (OCH_2), 72.0 (d, C-2, $^1J_{CP}$ = 108.8 Hz), 113.0 ($C{=}CH_2$), 126.1 (C-6); PPh_3 127.5 (d, $^1J_{CP}$ = 94.0 Hz), 128.3 (d, $^2J_{CP}$ = 12.1 Hz), 131.3 (d, $^4J_{CP}$ = 2.7 Hz), 133.2 (d, $^3J_{CP}$ = 9.4 Hz); 131.9 (C-7), 141.2 ($CH{=}CH_2$), 167.5 (d, C-1, $^2J_{CP}$ = 14.8 Hz), 200.0 (d, C-3 $^2J_{CP}$ = 2.7 Hz).

Methyl (2*R,3*R**)-2,5-Dimethyl-3-ethenyl-4-hexenoate (Methyl *epi*-Santolinate, 14).** A solution containing 300 mg (0.6 mmol) of **12** and **13** from above in 4.0 mL of acetonitrile was treated with 270 μL of 4 N NaOH and then cooled with an ice bath. A solution of 0.82 N NaOCl (1.8 mL, 1.48 mmol) was added over 30 min (approximately 0.5-mL portions every 7 min) followed by stirring at 0 °C for 2.5 h. The mixture was warmed to 20 °C, stirred for 0.5 h, and then treated with an additional 400 μL of 4 N NaOH followed by continued stirring for an additional 2.5 h. Small portions of $NaHSO_3$ were added until excess NaOCl was consumed (negative acidic starch–iodide paper test), and the acetonitrile was removed in vacuo. The remaining aqueous phase was brought to 4-mL volume and pH ≥10 by the addition of water and 4 N NaOH, respectively, and the mixture was extracted thrice with 10-mL portions of Et_2O to remove triphenylphosphine oxide and a small amount of unreacted **12** and **13**. The aqueous phase was acidified with aqueous HCl to pH 1 and extracted with 15 mL of pentane. Concentration of this extract (25 °C, 15 mmHg) gave 72 mg (71%; 77% based on 25 mg of **12** and **13** recovered by chromatography of the neutral extracts) of *epi*-santolinoic acid containing a small amount of santolinoic acid which was used without further purification; ^1H NMR ($CDCl_3$, 90 Mhz) δ 1.12 (d, 3 H, CH_3, J = 7.0 Hz), 1.63 (d, 3 H, $C{=}CCH_3$, J = 1.2 Hz), 1.73 (d, 3 H, $C{=}CCH_3$, J = 1.2 Hz), 2.43 (m, 1 H, CH_3CH), 3.21 (m, 1 H, allylic CH), 4.83–5.95 (m, 4 H, vinyl protons), 11.73 (s, 1 H, COOH).

The crude acid (65 mg, 0.39 mmol) in 3 mL of diethyl ether was treated portionwise with CH_2N_2 in diethyl ether until the yellow color of CH_2N_2 persisted for 1 min. Solvent and excess CH_2N_2 were removed by distillation, and the residue was dissolved in 5 mL of pentane. This solution was washed with saturated $NaHCO_3$ and then with water and dried over Na_2SO_4. Solvent removal gave 65 mg (92%) of the isomeric esters **14** and **15** shown by GLC (10% UCW-98, 135 °C) to consist of 91% **14** and 8% diasteromer **15**. The major less mobile component in our sample corresponded to authentic methyl *epi*-santolinate in a 1:1 mixture of the two diastereomers kindly provided by Professor Epstein.[9] An analytical sample was obtained by PTLC (silica gel, dichloromethane) followed by bulb-to-bulb distillation (160 °C, 13 mmHg); IR (neat) 2983, 1735, 1640, 1452, 1432, 1350, 1258, 1203, 1160, 912 cm^{-1}; ^1H NMR ($CDCl_3$), 90 Mhz) δ 1.09 (d, 3 H, 2-Me, J = 6.8 Hz), 1.63 (d, 3 H, $C{=}CCH_3$, J = 1.0 Hz), 1.73 (d, 3 H, $C{=}CCH_3$, J = 1.5 Hz), 2.43 (m, 1 H, CH_3CH), 3.18 (m, 1 H, allylic CH), 3.63 (s, 3 H, OCH_3), 4.84–5.90 (m, 4 H, vinyl protons) (the presence of the minor isomer is evidenced by a doublet at δ 1.12 (3 H, CH_3CH) and a singlet at δ 3.62 (3 H, OCH_3)); ^{13}C NMR ($CDCl_3$) δ 14.6 (2-Me), 18.1 (5-Me), 25.9 (C-6), 44.8 (C-2), 46.0 (C-3), 114.4 (CH_2), 123.6 (C-4), 134.0 (C-5), 139.3 ($CH{=}CH_2$, 176.0 (C-1). Additionally, resonances from the minor isomer (methyl santolinate) were found at δ 17.9, 44.5, 46.3, 115.2, 124.1, 133.3, and 138.6. Peak positions for both isomers correspond to those in the spectrum of the authentic mixture.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.58; H, 9.97.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Registry No. **4** (Z = $C(PPh_3)COOEt$), 83269-72-1; **4** (Z = OH), 142-62-1; **5** (Z = $C(PPh_3)COOEt$), 84454-74-0; **5** (Z = OH), 501-52-0; **6** (Z = $C(PPh_3)COOEt$), 1474-31-3; **6** (Z = OH), 65-85-0; **7** (Z = $C(PPh_3)COOEt$), 83269-74-3; **7** (Z = OH), 5636-65-7; **8** (Z = $C(PPh_3)COOEt$), 72449-05-9; **8** (Z = OH), 4541-43-9; **9** (Z = $C(PPh_3)COOEt$), 62251-85-8; **9** (Z = OH), 149-57-5; **10** (Z = $C(PPh_3)COOEt$), 84454-75-1; **10** (Z = OH) (isomer 1), 84454-72-8; **10** (Z = OH) (isomer 2), 84454-73-9; (*E*)-**11** (Z = $C(PPh_3)COOEt$), 84454-76-2; (±)-**12** (Z = $C(PPh_3)COOEt$), 84454-77-3; (±)-**13** (Z = $C(PPh_3)COOEt$), 84454-78-4; (±)-**14**, 61009-02-7; (±)-**15**, 61009-01-6; 3-Methyl-2-butenal, 107-86-8; diethyl 2,4-dioxo-4-ethoxy-3-(triphenylphosphoranylidene)butanephosphonate, 78980-76-4; (±)-episantolinic acid, 61009-00-5; (±)-santolinic acid, 61008-99-9; Methyl 5-methoxy-4-hexenoate, 84454-79-5.

A Convenient Route to *N*-(*p*-Tolylsulfonyl)phenanthren-9,10-imine and Related Compounds

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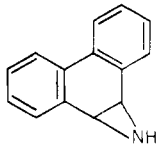
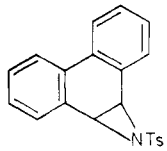
Because of their relationship to the carcinogenic epoxides of certain polynuclear aromatic hydrocarbons the corresponding imines have been the object of several synthetic studies.[1-9] The first such unsubstituted imine **1** was reported in 1978 by Blum and co-workers.[1] Subsequently a number of reports on this and related compounds appeared.[4-9] A number of *N*-alkyl and *N*-acyl derivatives had been reported earlier.[2,3] The *N*-tosyl derivative **2** was reported by Shudo and Okamoto[4] who obtained it by a tedious procedure starting from phenanthrene 9,10-oxide. Blum and co-workers[5] recently described the preparation of **2** via reaction of the *N*-trimethylsilyl derivative of **1** with *p*-toluenesulfonyl chloride. Direct tosylation of **1** led to ring opening.



1



2

The Japanese and Israeli workers appear to have been unaware of the previous report in the Russian patent literature[10] of a prior claim for the preparation of **2**. Un-

(1) Ittah, Y.; Sasson, Y.; Shahak, I.; Tsaroom, S.; Blum, J. *J. Org. Chem.* **1978**, *43*, 4271.
(2) Ittah, Y.; Shahak, I.; Blum, J. *J. Org. Chem.* **1978**, *43*, 397.
(3) Blum, J.; Ittah, Y.; Shahak, I. *Tetrahedron Lett.* **1975**, 4607.
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(8) Blum, J.; Yona, I.; Tsaroom, S.; Sasson, Y. *J. Org. Chem.* **1979**, *44*, 4178.
(9) Denis, J. N.; Krief, A. *Tetrahedron* **1979**, *35*, 2901.

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