

Inhalt

Contents

A

Teil A: Anorganische und elementorganische Chemie / Part A: Inorganic and Organometallic Chemistry

- Wood, G. L., Dou, D., Narula, C. K., Duesler, E. N., Paine, R. T., Nöth, H. 1455 Beiträge zur Chemie des Bors, 205. – Bildung von Phosphinoboran-Ringen. Eine erneute Untersuchung der Reaktion von $[(CH_3)_3Si]_3P$ mit Boran(3) ▶ Contributions to the Chemistry of Boron, 205. – Formation of Phosphinoborane Rings. A Reinvestigation of the Reaction of $[(CH_3)_3Si]_3P$ with Borane(3)
- Gleiter, R., Karcher, M., Kratz, D., Ziegler, M. L., Nuber, B. 1461 ▶ Silber(I)- und Kupfer(I)-Komplexe von 1,6-Cyclododecadiin und 1,7-Cyclododecadiin Silver(I) and Copper(I) Complexes of 1,6-Cyclododecadiene and 1,7-Cyclododecadiene
- Lindner, E., Karle, B. 1469 ▶ Neuartige basische Liganden für die homogenkatalytische Methanolcarbonylierung, XXVI. – Dynamisches und reaktives Verhalten von (Ether-Phosphan)ruthenium(II)-Komplexen in Abhängigkeit von der O-Basizität Novel Basic Ligands for the Homogeneous Catalytic Carbonylation of Methanol, XXVI. – Dynamic and Reactive Behaviour of (Ether-Phosphane)Ruthenium(II) Complexes in Dependence on the O-Basicity
- May, A., Roesky, H. W., Stalke, D., Pauer, F., Sheldrick, G. M. 1475 ▶ Darstellung der ersten Sulfin-imide (Thion-S-imide) mit Perfluormethylgruppen unter Verwendung von Natrium-hexamethyldisilazanid als schonendes Dehydrohalogenierungsreagenz Preparation of the First Thione S-Imides with Perfluoromethyl Groups by the Use of Sodium Hexamethyldisilazide as a Mild Dehydrohalogenation Reagent

Notizen / Notes

- Gök, Y., Kantekin, H. 1479 Ein neuartiges *vic*-Dioxim mit Kronenether-Einheiten ▶ A Novel *vic*-Dioxime with Crown Ether Moieties
- Lentz, D., Michael, H. 1481 ▶ Nonacarbonylbis(μ_3 -methylidin)triseisen Nonacarbonylbis(μ_3 -methylidyne)triiron

Berichtigung / Correction

- Brunner, H., Hankofer, P., Treittinger, B. 1485 Synthese und Antitumor-Aktivität von Pt(II)-Komplexen mit Benzyl-1,2-diaminoethan-Liganden Synthesis and Antitumor Activity of Pt(II) Complexes of Benzyl-1,2-diaminoethane Ligands

Querverweise / Cross References

- Bogdanovic, B. et al. 1507 Anwendung von Magnesium-Anthracen · 3 THF in der Synthese ▶ Use of Magnesium Anthracene · 3 THF in the Synthesis
- Bogdanovic, B. et al. 1517 Aktives Magnesium und seine Anwendungen in der Synthese Active Magnesium and its Uses in the Synthesis
- Bogdanovic, B. et al. 1529 Magnesium-Addukte von substituierten Anthracenen Magnesium Adducts of Substituted Anthracenes
- Opitz, G. et al. 1563 ▶ Über die konkurrierende Bildung von Sulfen – Trialkylamin-S,N- und -C,N-Addukten On the Competing Formation of Sulfene – Trialkylamine S,N- and C,N-Adducts

B

Teil B: Organische Chemie / Part B: Organic Chemistry

Nachruf / Obituary

- Schellenberger, A. I ▶ Wolfgang Langenbeck (1899 – 1967) Wolfgang Langenbeck (1899 – 1967)

- Schellenberger, A. 1489 ▶ Die Funktion der 4'-Aminopyrimidin-Komponente im Katalysemechanismus von Thiaminpyrophosphat-Enzymen aus heutiger Sicht The Function of the 4'-Aminopyrimidine Component in the Mechanism of the Catalysis of Thiamine Pyrophosphate Enzymes from Today's View

▶ Publikationssprache

▶ Language of Publication

Inhalt (Fortsetzung)

Contents (Continued)

- Kottirsch, G., Szeimies, G. 1495 ▶ Nickel(0)-katalysierte Kupplung von (Tricyclo[4.1.0.0^{2,7}]hept-1-yl)magnesiumbromid und verwandte Grignard-Verbindungen mit Aryl-, Vinyl- und Alkynylhalogeniden
- Bogdanovic, B., Janke, N., Kinzelmann, H.-G. 1507 Anwendung von Magnesium-Anthracen · 3 THF in der Synthese: Herstellung von Grignard-Verbindungen und andere Reaktionen mit organischen Halogeniden
- Bartmann, E., Bogdanovic, B., Janke, N., Liao, S., Schlichte, K., Spliethoff, B., Treber, J., Westeppe, U., Wilczok, U. 1517 Aktives Magnesium aus katalytisch dargestelltem Magnesiumhydrid oder aus Magnesium-Anthracen und seine Anwendungen in der Synthese
- Bogdanovic, B., Janke, N., Kinzelmann, H.-G., Seevogel, K., Treber, J. 1529 Magnesium-Addukte von substituierten Anthracenen – Darstellung und Eigenschaften
- Jochims, J. C., Glocker, M. O. 1537 Die Reaktionen von Nitrilium-Salzen mit primären, sekundären und tertiären Carboxamiden
- Katritzky, A. R., Rachwal, S., Offermann, R. J., Najzarek, Z., Yagoub, A. K., Zhang, Y. 1545 Nukleophiler Angriff an heterocyclischem Stickstoff: Ungewöhnliches Reaktionsverhalten des Benzotriazol-Ringsystems
- Werry, J., Stamm, H., Sommer, A. 1553 ▶ Arenhydride, 8. – Konkurrenz zwischen SET und nucleophilem Angriff bei Reaktionen von α -Bromisobutyrophenon mit Carbanionen. Fragmentierung des Anions von Tetrahydrobianthracen
- Opitz, G., Rieth, K., Ehlis, T. 1563 ▶ Folgereaktionen von Sulfenen aus Sulfonylchloriden und tertiären Aminen, 1. – Über die konkurrierende Bildung von Sulfen-Trialkylamin-S,N- und -C,N-Addukten

Notizen / Notes

- Mayr, H., Cambanis, A., Bäuml, E. 1571 Synthese von β -Oxoestern aus Silylenol-ethern und Dichlorbis(phenoxy)methan
- Moderhack, D., Goos, K.-H., Preu, L. 1575 ▶ Dimroth-Umlagerung von Iminen des 1,5-Diaminotetrazols
- Manero, J., Feigel, M., Knoch, F. 1579 ▶ Struktur von *N,N'*-(Phenoxathiin-4,6-dicarbonyl)bis(prolin-methylester). – Konformation im Kristall und in Lösung sowie nach semiempirischen Methoden
- Dange, O., Steinrück, N., Stöckigt, D., Schwarz, H. 1583 Metall-Ionen-gesteuerte Konkurrenz von β - und γ -Wasserstoff-Transfer bei der Bildung von Propen aus 1,7-Octadien in der Gasphase
- Massa, W., Schween, M., Steuber, F. W., Wocadlo, S. 1587 ▶ Darstellung und Konformationsanalyse von 9,11-Diphenyl[5](2,6)-pyranophan-10-on

Kurzmitteilung / Short Communication

- Ipaktschi, J., Brück, M. 1591 ▶ Mikrowellen-induzierte Reaktionen organischer Substrate im Hohlraum von Zeolithen

Berichtigung / Correction

- Figueredo, M., Font, J., de March, P. 1595 Stereochemische Analyse der Cycloaddition eines cyclischen Nitrons an 5-Methyl-2(5H)-furanon

Querverweise / Cross References

- Gleiter, R. et al. 1461 ▶ Silber(I)- und Kupfer(I)-Komplexe von 1,6-Cyclododecadiin und 1,7-Cyclododecadiin
- Roesky, H. W. et al. 1475 ▶ Sulfin-imide (Thion-S-imide) mit Perfluoromethylgruppen
- Gök, Y. et al. 1479 Ein neuartiges *vic*-Dioxim mit Kronenether-Einheiten
- ▶ Publikationssprache
- Nickel(0)-Catalyzed Cross Coupling Reactions of (Tricyclo[4.1.0.0^{2,7}]hept-1-yl)magnesium Bromide and Related Grignard Reagents with Aryl, Vinyl, and Alkynyl Halides
- Use of Magnesium Anthracene · 3 THF in Synthesis: Generation of Grignard Compounds and Other Reactions with Organic Halides
- Active Magnesium from Catalytically Prepared Magnesium Hydride or from Magnesium Anthracene and its Uses in the Synthesis
- Magnesium Adducts of Substituted Anthracenes – Preparation and Properties
- The Reactions of Nitrilium Salts with Primary, Secondary, and Tertiary Carboxamides
- Nucleophilic Attack at Heterocyclic Nitrogen: Unusual Reactivity of the Benzotriazole Heterocyclic Ring
- Arene Hydrides, 8. – SET vs. Nucleophilic Attack in Reactions of α -Bromoisobutyrophenone with Carbanions. Fragmentation of the Anion of Tetrahydrobianthracene
- Secondary Reactions of Sulfenes from Sulfonyl Chlorides and Tertiary Amines, 1. – On the Competing Formation of Sulfene-Trialkylamine S,N- and C,N-Adducts
- Synthesis of β -Oxo Esters from Silyl Enol Ethers and Dichlorobis(phenoxy)methane
- Dimroth Rearrangement of Imines Derived from 1,5-Diaminotetrazole
- Structure of *N,N'*-(Phenoxathiine-4,6-dicarbonyl)bis(proline methyl ester). – Conformation in the Crystal, in Solution, and According to Semiempirical Methods
- Metal Ions Control the Competition between β - and γ -Hydrogen Transfer in the Generation of Propene from 1,7-Octadiene in the Gas Phase
- Preparation and Conformational Analysis of 9,11-Diphenyl[5](2,6)-pyranophan-10-one
- Microwave-Induced Reactions of Organic Substrates in the Cage of Zeolites
- Stereochemical Study on the Cycloaddition of a Cyclic Nitron to 5-Methyl-2(5H)-furanone
- Silver(I) and Copper(I) Complexes of 1,6-Cyclododecadiene and 1,7-Cyclododecadiene
- Thione S-Imides with Perfluoromethyl Groups
- A Novel *vic*-Dioxime with Crown Ether Moieties
- Language of Publication

Notizen / Notes

Synthesis of β -Oxo Esters from Silyl Enol Ethers and Dichlorobis(phenoxy)methane

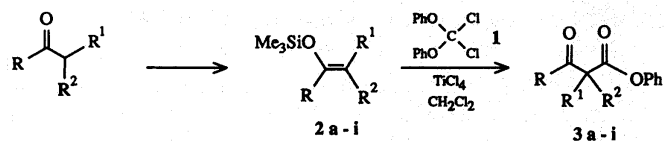
Herbert Mayr*, Anton Cambanis, and Englbert Bäuml

Institut für Chemie, Medizinische Universität zu Lübeck,
Ratzeburger Allee 160, D-2400 Lübeck 1, Federal Republic of Germany

Received February 2, 1990

Key Words: Carboxylation / Aryloxyacylation / Siloxyalkenes / Silyl Enol Ethers / Acetals, dichloro / β -Oxo estersDichlorobis(phenoxy)methane (**1**) reacts with trimethylsiloxyalkenes in the presence of 1.2 equiv. of TiCl_4 to give β -oxo esters in 44–82% yield. The title compound **1** is thus employed as a $\text{PhO}_2\text{C}^\oplus$ equivalent.

Bis(aryloxy)dichloromethanes (e. g. **1**) are readily available by radical-induced chlorination of formaldehyde diaryl acetals¹⁾. Like 2,2-dichloro-1,3-benzodioxol, which is used for the electrophilic carboxylation of aromatic compounds²⁾ and of alkenes³⁾, they represent $\text{RO}_2\text{C}^\oplus$ equivalents and have been employed for the synthesis of β,γ -unsaturated esters from allylsilanes⁴⁾. In this paper we report on the reaction of bis(aryloxy)dichloromethanes with silyl enol ethers under Lewis-acidic conditions yielding β -oxo esters in moderate to good yields. Since silyl enol ethers may regioselectively be synthesized from the corresponding ketones⁵⁾, the two-step sequence according to eq. (1) represents a useful alternative for the generation of β -oxo esters from ketones, which has previously been carried out under strongly basic conditions using dialkyl carbonates⁶⁾, dialkyl oxalates⁷⁾, methyl methoxymagnesium carbonate⁸⁾, or methyl cyanofornate⁹⁾.



The experimental conditions of the reaction of **1** with the silyl enol ether **2g** have been optimized. Poor yields of **3g** are obtained, when **1** is treated with **2g** in CH_2Cl_2 in the presence of $\text{ZnCl}_2/\text{Et}_2\text{O}$ ¹⁰⁾ (1.5 equiv.) or in the presence of 0.1 equiv. of TiCl_4 (<20%). With SnCl_4 (1.3 equiv.) in CH_2Cl_2 , 27% of **3g** is isolated, and an almost quantitative yield of crude **3g** is obtained, when 1.2 equiv. of TiCl_4 is added to a mixture of **1** and **2g** in CH_2Cl_2 at -78°C ¹¹⁾.

Table 1 (entries a–f) shows that silyl enol ethers, generated from saturated ketones, may efficiently be converted into β -oxo esters according to this method. Only one of the possible diastereoisomers is obtained from compounds **2e** and **2f**. Though some of these compounds are enolizable (**3b–e**), the NMR spectra, taken immediately after dissolving these compounds in CDCl_3 , indicate the presence of pure keto compounds, and only in the case of **3b**, 10–15% of an enol has been detected. After several days, a ketone-to-enol ratio of 60:40 is observed for **3e**, while the spectra of the other compounds have remained unchanged¹²⁾.

Table 1. Titanium(IV) chloride promoted reactions of dichlorobis(phenoxy)methane (**1**) with trimethylsiloxyalkenes **2**

Reactants	Products	Yield (%)	IR $\nu(\text{CO})$ [cm^{-1}]
2a	3a	71	1758, 1714
2b	3b	81	1764, 1701
2c	3c	68	1763, 1696
2d	3d	75	1748, 1708
2e	3e	54	1772, 1731
2f	3f	46	1757, 1708
2g	3g	74	1761, 1727
2h	3h	44	1755, 1670
2i	3i	82	1760, 1738

Examples g–i suggest that **1** may also be used for the carboxylation of silyl enol ethers derived from aldehydes (**2g**), of siloxy dienes (**2h**), and ketene silyl acetals (**2i**), but experiments with 1-(trimethylsilyloxy)indene and 1-(trimethylsilyloxy)-1,3-butadiene have not been successful.

Experimental

IR: IR-435 (Shimadzu). — NMR: XL 200 (Varian), internal standard TMS; for spectra of higher order, virtual couplings are listed. — MS: 70-250E (VG-Instruments).

Dichlorobis(phenoxy)methane (**1**) was prepared by chlorination of bis(phenoxy)methane¹¹. The silyl enol ethers **2a–h** were synthesized from the corresponding carbonyl compounds by treatment with Me₃SiCl, NaI, and (C₂H₅)₃N in CH₃CN according to the procedures A and D described by Cazeau et al.¹³. The silylated ketene acetal **2i** is commercially available (Fluka).

Caution: Because of the known toxicity of chloro ethers, all operations should be carried out in an efficient hood, and skin contact should be avoided.

Phenyl 2,2-Dimethyl-3-oxobutyrates (3a). — *General Procedure:* Compounds **1** (0.80 g, 3.0 mmol) and **2a** (0.52 g, 3.3 mmol) were dissolved in 25 ml of CH₂Cl₂ at –78°C. A solution of TiCl₄ (0.76 g, 4.0 mmol) in 10 ml of CH₂Cl₂ was added dropwise with stirring (ca. 5 min), and the mixture was kept at –78°C. After 10 h, the dark brown solution was washed with cold 3% aqueous HCl to give a colorless mixture. The organic layer was concentrated to yield an oily residue which was dissolved in pentane and repeatedly washed with 5% aqueous Na₂CO₃ solution to remove phenol. After drying with Na₂CO₃ and evaporation of pentane, the residue was purified by layer chromatography [silica gel, hexane/ether (95:5)] yielding 0.51 g of product. Distillation [73–76°C (bath)/0.1 mbar] afforded 0.44 g (71%) of **3a**. — ¹H NMR (CDCl₃): δ = 1.52 (s, 6H), 2.30 (s, 3H), 7.05–7.40 (m, 5H). — ¹³C NMR (CDCl₃): δ = 21.86 (q, 2-CH₃), 25.77 (q, C-4), 56.02 (s, C-2), 121.11 (d, C_o), 126.10 (d, C_p), 129.49 (d, C_m), 150.50 (s, C_i), 172.18 (s, C-1), 205.32 (s, C-3). — MS (70 eV): *m/z* (%) = 206 (28) [M⁺], 164 (34), 113 (51), 94 (100), 85 (56), 70 (53), 57 (31), 43 (98).

C₁₂H₁₄O₃ (206.2) Calcd. C 69.89 H 6.84
Found C 69.87 H 6.73

Phenyl 2-Oxocycloheptanecarboxylates (3b): A mixture of compounds **1** (0.80 g, 3.0 mmol) and **2b** (0.61 g, 3.3 mmol) was treated with 0.76 g (4.0 mmol) of TiCl₄ as described before and worked up after 20 h. Layer chromatography [silica gel, hexane/ether (3:1)] afforded 0.62 g of **3b**, which was distilled to yield 0.56 g (81%) of an analytically pure material with bp 110–115°C (bath)/0.1 mbar. — ¹H NMR (CDCl₃): δ = 1.35–2.13, 2.17–2.34, 2.47–2.46 (3 m, 10H), 3.84 (dd, *J* = 10.1 Hz, *J* = 3.7 Hz, 0.9H, keto tautomer), 7.08–7.48 (m, 5H), 12.53 (br. s, 0.1 H, enol tautomer). — ¹³C NMR (CDCl₃): δ = 24.04, 27.47, 28.22, 29.45, 43.29 (5 t, C-3, C-4, C-5, C-6, C-7), 58.67 (d, C-1), 121.45 (d, C_o), 125.94 (d, C_p), 129.38 (d, C_m), 150.57 (s, C_i), 169.35 (s, CO₂Ph), 208.66 (s, C-2); signals for the enol species (<15%): δ = 24.56, 24.63, 31.95, 35.61 (t), 101.21 (s), 121.79 (d), 125.74 (d), 129.51 (d), 150.49 (s), 172.12 (s). — MS (70 eV): *m/z* (%) = 232 (1) [M⁺], 139 (58), 94 (100).

C₁₄H₁₆O₃ (232.3) Calcd. C 72.39 H 6.94
Found C 72.20 H 7.02

Phenyl 2-Oxocyclooctanecarboxylates (3c): Compound **1** (1.2 g, 4.5 mmol) was treated with **2c** (1.0 g, 5.1 mmol) in the presence of TiCl₄ (1.1 g, 5.8 mmol) for 18 h to give **3c**. Distillation [125–130°C (bath)/0.2 mbar] afforded 0.75 g (68%) of oily **3c** which solidified;

mp 70–72°C (pentane/ether). — ¹H NMR (CDCl₃, 40°C): δ = 1.25–2.27, 2.48–2.76 (2 m, 12H), 3.86 (dd, *J* = 8 Hz, *J* = 7 Hz, 1H), 7.01–7.40 (m, 5H). — ¹³C NMR (CDCl₃): δ = 24.49, 24.66, 24.74, 27.30, 29.48, 42.36 (6 t, C-3, C-4, C-5, C-6, C-7, C-8), 56.34 (d, C-1), 121.34 (d, C_o), 125.97 (d, C_p), 129.38 (d, C_m), 150.45 (s, C_i), 168.81 (s, CO₂Ph), 211.71 (s, C-2); signals for the enol species: δ = 24.06, 26.05, 26.54, 28.77, 30.04, 32.59 (6 t, C-3, C-4, C-5, C-6, C-7, C-8), 98.79 (s, C-1), 121.78 (d, C_o), 125.77 (d, C_p), 171.70 (s, CO₂Ph), 178.60 (s, C-2). — MS (70 eV): *m/z* (%) = 246 (1) [M⁺], 153 (100), 94 (32), 55 (54).

C₁₅H₁₈O₃ (246.3) Calcd. C 73.15 H 7.37
Found C 73.13 H 7.27

Phenyl 2-Oxocyclododecanecarboxylates (3d): Compound **1** (0.80 g, 3.0 mmol) was treated with **2d** (0.84 g, 3.3 mmol) and TiCl₄ (0.76 g, 4.0 mmol) for 24 h according to the described procedure. The residue, obtained after evaporation of pentane (0.90 g), was recrystallized from hexane to give 0.67 g (75%) of **3d** with mp 81–83°C. — ¹H NMR (CDCl₃): δ = 1.05–2.08, 2.10–2.56, 2.62–2.91 (3 m, 20H), 3.87 (dd, *J* = 11.0 Hz, *J* = 3.7 Hz, 1H), 6.97–7.46 (m, 5H). — ¹³C NMR (CDCl₃): δ = 22.01, 22.31, 22.83, 23.85, 24.07 (high intensity), 25.26, 25.58, 26.77, 38.38, (9 t, C-3–C-12), 57.57 (d, C-1), 121.24 (d, C_o), 126.07 (d, C_p), 129.46 (d, C_m), 150.39 (s, C_i), 168.51 (s, CO₂Ph), 206.06 (s, C-2). — MS (70 eV): *m/z* (%) = 302 (1) [M⁺], 209 (100), 94 (23), 77 (23), 55 (27), 41 (21).

C₁₉H₂₆O₃ (302.4) Calcd. C 75.46 H 8.67
Found C 75.37 H 8.57

Phenyl Camphor-3-carboxylates (3e) was synthesized by reaction of **1** (1.2 g, 4.5 mmol) with **2e** (1.1 g, 4.9 mmol) in the presence of TiCl₄ (1.1 g, 5.8 mmol) at –78°C for 20 h. Chromatographic purification of the product [silica gel, hexane/ether (4:1)] gave 0.65 g (54%) of **3e** which was recrystallized from hexane; mp 69–70°C. — ¹H NMR (CDCl₃): δ = 0.94, 0.98, 1.06 (3 s, 9H), 1.48–2.07 (m, 4H), 2.60 (br. t, *J* = 4.4 Hz, 1H), 3.58 (dd, *J* = 1.9 Hz, *J* = 4.7 Hz, 1H), 7.00–7.43 (m, 5H). — ¹³C NMR (CDCl₃): δ = 9.55 (q, 1-CH₃), 18.79, 19.54 (2 q, 7-CH₃), 22.52 (t, C-5), 29.40 (t, C-6), 45.88 (d, C-4), 47.23 (s, C-7), 55.50 (d, C-3), 58.59 (s, C-1), 121.46 (d, C_o), 126.01 (d, C_p), 129.41 (d, C_m), 150.33 (s, C_i), 168.17 (s, CO₂Ph), 210.81 (s, C-2). — MS (70 eV): *m/z* (%) = 272 (5) [M⁺], 179 (100), 151 (45), 123 (18), 94 (20), 83 (37), 55 (17), 41 (24).

C₁₇H₂₀O₃ (272.3) Calcd. C 74.97 H 7.40
Found C 74.95 H 7.46

Phenyl 1-Methyl-4-(1-methylvinyl)-2-oxocyclohexanecarboxylates (3f) was prepared by treatment of **1** (0.80 g, 3.0 mmol) with **2f** (0.74 g, 3.3 mmol), and TiCl₄ (0.76 g, 4.0 mmol) at –78°C for 17 h. Purification of the product by column chromatography [silica gel, hexane/ether (95:5)] gave 0.45 g of **3f** which was further purified by distillation yielding 0.37 g (46%) of product with bp 130 to 135°C/0.15 mbar. — ¹H NMR (CDCl₃): δ = 1.53 (s, CH₃), 1.74 to 2.05 (m, superimposed by br. s at 1.77, 7H), 2.42–2.58 (m, 1H), 2.63 (m, 2H), 4.76, 4.86 (2 br. s, 2H), 7.05–7.45 (m, 5H). — ¹³C NMR (CDCl₃): δ = 20.48, 21.20 (2 q, 1-CH₃, CH₃C=), 25.40 (t, C-5), 33.68 (t, C-6), 43.35 (t, C-3), 44.22 (d, C-4), 57.19 (s, C-1), 111.27 (t, CH₂=), 121.40 (d, C_o), 125.94 (d, C_p), 129.42 (d, C_m), 145.48 (s, C=CH₂), 150.73 (s, C_i), 171.92 (s, CO₂Ph), 208.34 (s, C-2). — MS (70 eV): *m/z* (%) = 272 (12) [M⁺], 179 (83), 151 (15), 123 (30), 109 (51), 107 (55), 97 (100), 94 (41), 81 (51), 69 (38), 67 (30), 55 (72), 41 (60).

C₁₇H₂₀O₃ (272.3) Calcd. C 74.97 H 7.40
Found C 74.92 H 7.37

Phenyl 2,2-Dimethyl-3-oxopropanoates (3g): The crude material obtained from **1** (1.2 g, 4.5 mmol), **2g** (0.79 g, 5.5 mmol), and TiCl₄ (1.1 g, 5.8 mmol) according to the general procedure was purified

by column chromatography [silica gel, hexane/ether (4:1)] to yield 0.75 g of **3g**. Distillation [84–88°C (bath)/0.4 mbar] afforded 0.63 g (74%) of analytically pure **3g**. — $^1\text{H NMR}$ (CDCl_3): δ = 1.50 (s, 6H), 7.05–7.41 (m, 5H), 9.80 (s, 1H). — $^{13}\text{C NMR}$ (CDCl_3): δ = 19.71 (q, 2- CH_3), 54.03 (s, C-2), 121.24 (d, C_o), 126.21 (d, C_p), 129.51 (d, C_m), 150.32 (s, C_i), 171.30 (s, C-1), 198.50 (d, C-3). — MS (70 eV): m/z (%) = 192 (12) [M^+], 164 (25), 99 (49), 94 (100), 71 (47), 70 (43), 43 (82).

$\text{C}_{11}\text{H}_{12}\text{O}_3$ (192.2) Calcd. C 68.74 H 6.29
Found C 68.70 H 6.33

Phenyl (5,5-Dimethyl-3-oxo-1-cyclohexen-1-ylacetate) (**3h**): Compound **1** (0.80 g, 3.0 mmol) was treated with **2h** (0.70 g, 3.3 mmol) and TiCl_4 (0.76 g, 4.0 mmol) for 18 h to give crude **3h** which was purified by column chromatography [silica gel, ether/hexane (2:1)] and distillation [145–150°C (bath)/0.08 mbar] yielding 0.40 g of product. Recrystallization from hexane afforded 0.34 g (44%) of **3h** with mp 68–69°C. — $^1\text{H NMR}$ (CDCl_3): δ = 1.09 (s, 6H), 2.28 (s, 2H), 2.38 (br. s, 2H), 3.47 (br. s, 2H), 6.09 (br. s, 1H), 7.05–7.50 (m, 5H). — $^{13}\text{C NMR}$ (CDCl_3): δ = 28.13 (q, 5- CH_3), 33.73 (s, C-5), 43.12, 43.56 (2 t, C-6, O_2CCH_2), 50.85 (t, C-4), 126.26 (d, C_o), 126.13 (d, C_p), 128.17 (d, C-2), 129.49 (d, C_m), 150.29 (s, C_i), 154.01 (s, C-1), 167.86 (s, CO_2Ph), 199.39 (s, C-3). — MS (70 eV): m/z (%) = 258 (4) [M^+], 165 (100), 109 (12), 108 (25), 94 (22), 77 (7), 67 (10), 53 (10).

$\text{C}_{16}\text{H}_{18}\text{O}_3$ (258.3) Calcd. C 74.40 H 7.02
Found C 74.31 H 7.10

Methyl Phenyl (2,2-Dimethylmalonate) (**3i**): The product generated from **1** (0.80 g, 3.0 mmol) and **2i** (0.58 g, 3.3 mmol) in the presence of TiCl_4 (0.76 g, 4.0 mmol) within 14 h was purified by layer chromatography [silica gel, hexane/ether (95:5)] to yield 0.60 g of **3i**. Distillation [74–78°C (bath)/0.1 mbar] afforded 0.54 g (82%) of analytically pure **3i**. — $^1\text{H NMR}$ (CDCl_3): δ = 1.59 (s, 6H), 3.81 (s, 3H), 7.04–7.45 (m, 5H). — $^{13}\text{C NMR}$ (CDCl_3): δ = 22.75 (q, 2- CH_3), 50.08 (s, C-2), 52.69 (q, OCH_3), 121.21 (d, C_o), 125.99 (d, C_p), 129.43 (d, C_i), 150.67 (s, C_i), 171.36, 172.99 (2 s, CO_2CH_3 , CO_2Ph). — MS (70 eV): m/z (%) = 222 (30) [M^+], 129 (97), 101 (100), 94 (80), 73 (45), 41 (27).

$\text{C}_{12}\text{H}_{14}\text{O}_4$ (222.2) Calcd. C 64.85 H 6.35
Found C 64.48 H 6.57

CAS Registry Numbers

1: 4885-03-4 / **2a**: 17510-44-0 / **2b**: 22081-48-7 / **2c**: 50338-42-6 / **2d**: 51584-36-2 / **2e**: 56613-17-3 / **2f**: 72311-10-5 / **2g**: 6651-34-9 / **2h**: 80239-27-6 / **2i**: 31469-15-5 / **3a**: 103439-34-5 / **3b**: 126256-23-3 / **3c**: 126256-24-4 / **3d**: 126256-25-5 / **3e**: 126256-26-6 / **3f**: 126256-27-7 / **3g**: 89635-72-3 / **3h**: 126256-28-8 / **3i**: 126256-29-9

- ¹ A. Cambanis, E. Bäuml, H. Mayr, *Synthesis* **1988**, 961; Bayer AG (H. Mayr, A. Cambanis, E. Bäuml, Inv.), D.A.S. 3821 130.0.
- ² H. Gross, J. Rusche, M. Mirsch, *Chem. Ber.* **96** (1963) 1382.
- ³ H. Mayr, U. von der Brüggel, *Chem. Ber.* **121** (1988) 339.
- ⁴ H. Mayr, A. Cambanis, E. Bäuml, *Synthesis*, **1988**, 962.
- ^{5a)} E. W. Colvin, *Silicon Reagents in Organic Synthesis*, p. 99, Academic Press, London 1988. — ^{5b)} E. W. Colvin, *Silicon in Organic Synthesis*, p. 198, Butterworths, London 1981. — ^{5c)} W. P. Weber, *Silicon Reagents for Organic Synthesis*, p. 255, Springer Verlag, Berlin 1983.
- ^{6a)} A. P. Krapcho, J. Diamanti, C. Cayen, R. Bingham, *Org. Synth., Coll. Vol. V* (1973) 198. — ^{6b)} S. B. Soloway, F. B. LaForge, *J. Am. Chem. Soc.* **69** (1947) 2677.
- ⁷ C. R. Hauser, F. W. Swamer, J. T. Adams, *Org. React.* **8** (1954) 59.
- ^{8a)} M. Stiles, *J. Am. Chem. Soc.* **81** (1959) 2598. — ^{8b)} S. W. Pelletier, R. L. Chappell, P. C. Parthasarthy, N. Lewin, *J. Org. Chem.* **31** (1966) 1747. — ^{8c)} A. Pavia, F. Winternitz, R. Wylde, *C. R. Acad. Sci.* **261** (1965) 1026. — ^{8d)} S. Julia, C. Huynh, *C. R. Acad. Sci., Ser. C*, **270** (1970) 1517.
- ⁹ L. N. Mander, S. P. Sethi, *Tetrahedron Lett.* **24** (1983) 5425.
- ¹⁰ H. Mayr, W. Striepe, *J. Org. Chem.* **50** (1985) 2995.
- ¹¹ Similar conditions have previously been applied for the tertiary alkylation of silyl enol ethers: M. T. Reetz, W. F. Maier, H. Heimbach, A. Giannis, G. Anastassios, *Chem. Ber.* **113** (1980) 3734.
- ¹² Detailed studies on keto-enol equilibria of the corresponding ethyl and methyl esters have been described: ^{12a)} S. J. Rhoads, C. Pryde *J. Org. Chem.* **30** (1965) 3212. — ^{12b)} S. J. Rhoads *J. Org. Chem.* **31** (1966) 171. — ^{12c)} K. R. Kallury, U. J. Krull, M. Thompson *J. Org. Chem.* **53** (1988) 1320.
- ¹³ P. Cazeau, F. Duboudin, F. Moulines, O. Babot, J. Dunogues, *Tetrahedron* **43** (1987) 2075.

[45/90]