lamp equipped with a Vycor sleeve. The solution was filtered giving 158 mg of a pale yellow oil. The material was subjected to silica gel chromatography with a benzene–acetonitrile mixture (7:3) to give 153 mg of a colorless oil whose NMR showed it to be a mixture of two isomeric cycloadducts. Further purification by silica gel chromatography with a 7:3 hexane–ether mixture as the eluent gave two cycloadducts. The slower moving isomer (40%) was assigned the structure of 2,5-diphenyl-*cis*-4-(carbomethoxy)-5-methyl-Δ^1-pyrroline (**24a**) on the basis of its spectral data: NMR ($CDCl_3$, 360 MHz) δ 1.52 (s, 3 H), 3.23 (dd, 1 H, J = 17.0 and 9.3 Hz), 3.44 (dd, 1 H, J = 9.3 and 7.6 Hz), 3.64 (dd, 1 H, J = 17.0 and 7.6 Hz), 3.80 (s, 3 H), and 7.0–8.0 (m, 10 H); m/e 293, 278, 207 (base), 166, 115, 103, and 77; IR (neat) 3030, 2910, 1720, 1620, 1480, 1440, 1340, 1160, 760, and 700 cm^{-1}; UV (methanol) 245 nm ($\epsilon \simeq 13\,200$).

Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.58; H, 6.48; N, 4.65.

The major cycloadduct was assigned the structure of 2,5-diphenyl-trans-4-carbomethoxy-5-methyl-Δ^1-pyrroline (**24b**) on the basis of its spectral data: NMR ($CDCl_3$, 360 MHz) δ 1.58 (s, 3 H), 3.23 (s, 3 H), 3.31 (dd, 1 H, J = 7.8 and 5.2 Hz), 3.33 (dd, 1 H, J = 15.0 and 7.8), 3.55 (dd, 1 H, J = 15.0 and 5.2 Hz), and 7.2–8.0 (m, 10 H); m/e 293, 278, 207 (base), 166, 115, 103, and 77; UV (hexane) 242 nm ($\epsilon \simeq 15\,400$); IR (neat) 2910, 1722, 1615, 1562, 1480, 1440, 1340, 1260, 1200, 1160, 1120, 1060, 1020, 920, 860, 760, and 695 cm^{-1}.

Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.64; H, 6.37; N, 4.59.

Irradiation of 2-Methyl-2,3-diphenyl-2*H*-azirine (14) in Methanol. A solution containing 80 mg of azirine **14** in 175 mL of methanol was irradiated through a Vycor filter sleeve for 10 min. Removal of the solvent under reduced pressure left 110 mg of a pale yellow oil whose structure was assigned as a 2:3 mixture of acetophenone *N*-(methoxyphenylmethyl)imine (**25**) and benzaldehyde *N*-(1-methoxy-1-phenylethyl)imine (**26**) on the basis of its NMR spectrum and by its hydrolysis to acetophenone and benzaldehyde: NMR ($CDCl_3$, 90 MHz) δ **25** 2.02 (s, 3 H), 3.31 (s, 3 H), 5.67 (s, 1 H), and 7.0–8.0 (m, 10 H); **26** 1.58 (s, 3 H), 3.02 (s, 3 H), 7.0–8.0 (m, 10 H), and 8.42 (s, 1 H).

Acknowledgment. The authors wish to acknowledge the National Science Foundation (AP and NJT) and the Air Force Office for Scientific Research (NJT) for their generous support of this research. Support from the National Council of Scientific and Technological Development Department (CNPQ) of Brazil for P.F. is gratefully acknowledged.

Registry No. **13**, 16483-98-0; **14**, 22752-16-5; **15**, 65817-54-1; **18**, 90968-49-3; **19**, 90968-50-6; **20**, 70509-13-6; **23**, 90968-51-7; **24a**, 90968-52-8; **24b**, 90968-53-9; **25**, 90968-54-0; **26**, 90968-55-1; 1,1-diphenylacetone, 781-35-1; dimethylhydrazide, 57-14-7; 1,1-diphenylpropan-2-one *N*,*N*-dimethylhydrazone, 90968-56-2; methyl iodide, 74-88-4; 1,1-diphenylpropan-2-one trimethylhydrazonium iodide, 69543-13-1; desoxybenzoin, 451-40-1; 1,2-diphenylethan-1-one *N*,*N*-dimethylhydrazone, 33785-81-8; 1,2-diphenylpropan-1-one *N*,*N*-dimethylhydrazone, 90968-57-3; methyl acrylate, 96-33-3; methanol, 67-56-1; acrylonitrile, 107-13-1; fumaronitrile, 764-42-1; diethyl fumarate, 623-91-6.

A Novel Friedel–Crafts Reaction of Hindered Ketones

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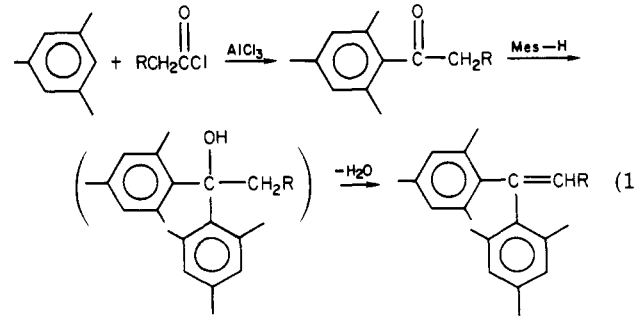
Received February 6, 1984

Mesitylene has been shown to react with acetyl chloride in the presence of aluminum chloride to form 1,1-dimesitylethene. Acetomesitylene has been demonstrated to be an intermediate in the reaction, which proceeds in the second step by nucleophilic attack by the arene on the carbonyl group of acetomesitylene, which is activated by the formation of a polarized complex with aluminum chloride. Mesitylene reacts similarly with propionyl chloride, forming 1,1-dimesitylpropene; propiomesitylene is an intermediate. Steric and electronic factors responsible for this unique Friedel–Crafts reaction are discussed.

Although in the past we have commented on the fact that Friedel–Crafts alkylations have often been conducted at higher temperatures than are necessary, thereby leading to complications,[1] nevertheless one of us carried out an acylation under more strenuous conditions than apparently are required,[2] with interesting results. With the aim of preparing acetomesitylene, mesitylene, acetyl chloride, and aluminum chloride were heated at 100 °C for 6 h in a molar ratio of 2:1:0.25, respectively. The desired product was obtained in low yield (17%), but the major product (41% yield) was 1,1-dimesitylethene (**2a**). Under similar conditions, the reaction of propionyl chloride with mesitylene gave propiomesitylene (54%) and 1,1-dimesitylpropene (**2b**, 31%). We suspected that the dimesitylalkenes were produced by reaction of initially formed acylmesitylenes with a second mole of mesitylene, followed by dehydration of the intermediate alcohols **1a** and **1b** (eq 1). This was confirmed by preparing acetomesitylene and propiomesitylene at low temperature and then heating the pure acylmesitylenes with mesitylene and aluminum chloride at 150–160 °C. The dimesitylalkenes (**2a** and **2b**) were



(1)

1a, R = H
b, R = CH_3

2a, R = H
b, R = CH_3

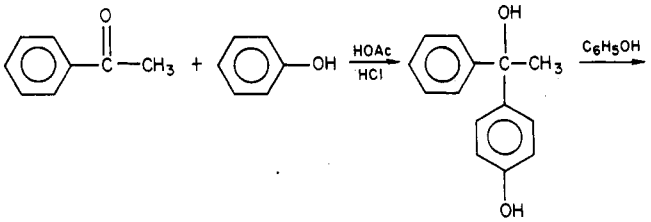
†Robert A. Welch Postdoctoral Fellow, on leave from Assiut University, Assiut, Egypt.

(1) Roberts, R. M. *Intra-Sci. Chem. Rep.* **1972**, *6* (2), 89.
(2) Gore, P. H.; Hoskins, J. A. *J. Chem. Soc. C* **1970**, 517 and references cited there.

0022-3263/84/1949-3180$01.50/0

obtained in yields of 70% and 74%, respectively.

These two 1,1-dimesitylalkenes were described earlier as products in low yield from reaction of mesitylene with acetic acid and propionic acid in the presence of polyphosphoric acid.[3] The acylmesitylene was assumed to be the intermediate in these reactions also. In the long history of Friedel–Crafts acylations of arenes, this isolated example is the only previous report of a secondary reaction of an acylarene with a second mole of the arene to give a diarylalkene.[4] A related reaction, however, is that of acetophenone with phenol in acetic acid/HCl to give (in low yield) 1-phenyl-1,1-bis(4-hydroxyphenyl)ethane (**4**, eq 2).[5]



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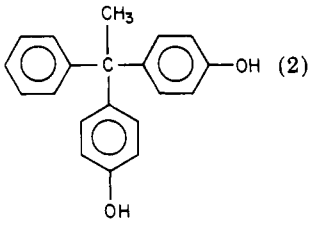

(2)

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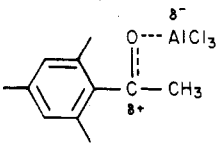
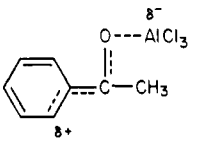
In this case, the intermediate diarylethanol **3** undergoes a second nucleophilic attack by phenol rather than eliminating a molecule of water to produce a diarylethene. The failure of 1,1-dimesitylethanol (**1a**) to react with a second mole of mesitylene can be ascribed to steric crowding in the transition state leading to 1,1,1-trimesitylethane, which would be analogous to **4**, so that the 1,1-dimesitylethanol instead undergoes dehydration to the observed product **2a**. The fact that no 1,1-diphenylethene has ever been observed as a product from acylations of benzene by acetyl chloride may be attributed to the much lesser nucleophilicity of benzene compared to mesitylene. Thus the novel formation of 1,1-dimesitylethene from mesitylene and acetyl chloride may be explained as the result of a unique combination of properties of mesitylene; it is a highly nucleophilic aromatic hydrocarbon, and its derivatives, such as acetomesitylene, are subject to powerful steric interferences. This latter property is exemplified by the well-known difficulty with which acetomesitylene undergoes common nucleophilic reactions. For example, the preparation of the oxime requires very special conditions,[6] and methylmagnesium iodide does not add to acetomesitylene.[7] Phenylmagnesium bromide has been made to add only by operating in an acetal solvent at 165 °C[8] for more than 14 h. It is noteworthy that the formation of **2a** and **2b** from the reaction of acetic acid and propionic acid with mesitylene in polyphosphoric acid[3] took place only at temperatures above 125 °C.

Although the *o*-methyl groups in acylmesitylenes produce steric hindrance toward nucleophilic addition to the carbonyl group, they may actually make the carbonyl carbon more electrophilic, because the carbonyl group cannot be coplanar with the aromatic ring.[2] In the case of the reaction of acetomesitylene with mesitylene catalyzed by aluminum chloride, we assume that the reactive intermediate which undergoes nucleophilic attack by mesitylene is a polarized complex that may be represented as in **5**. As a result of the noncoplanarity of the carbonyl

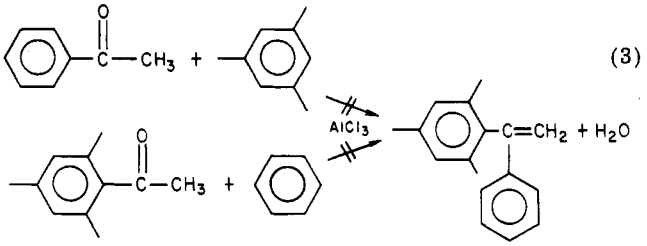


5



6

group and the aromatic ring, the positive charge on the carbonyl carbon cannot be dissipated by conjugation with the ring, as shown in **6**. Two experiments which support this theory were our attempted reactions between acetophenone and mesitylene (eq 3) and between aceto-



(3)

7

(4)

mesitylene and benzene (eq 4), both of which failed to produce 1 phenyl-1-mesitylethene (**7**). Presumably, the first reaction (eq 3) failed because of the low electrophilicity of the carbonyl carbon in acetophenone compared to acetomesitylene, and the second reaction (eq 4) failed because of the low nucleophilicity of benzene compared to mesitylene.

When the reactions of acetyl chloride and propionyl chloride with mesitylene and aluminum chloride were carried out at room temperature, acetomesitylene and propiomesitylene were obtained in good yields (81% and 80%, respectively). In the experiment with acetyl chloride, there was no evidence of the formation of 1,1-dimesitylethene, but from the reaction of propionyl chloride, a 10% yield of 1,1-dimesitylpropene was also observed. Reaction of acetyl chloride with mesitylene and aluminum chloride with carbon disulfide or dichloromethane as solvents gave only acetomesitylene after 20 h at reflux temperatures. At this time we are not sure of the reason for the more facile production of the dimesitylpropene than the dimesitylethene,[9] but we note that Snyder and Roeske[3] observed that their yields of the 1,1-dimesitylalkenes from acetic, propionic, and butyric acids in reaction with mesitylene in polyphosphoric acid increased with increasing size of the carboxylic acids.

The similarity in the melting points of 1,1-dimesitylpropene (95–96 °C,[3] 98–99 °C, this work) and dipropionylmesitylene (101–102 °C,[9] 100–100.5 °C[2]) led us to wonder if the latter compound might have been mistaken for the former one in previous work. Weil[10] first described dipropionylmesitylene in 1897 and reported a

(3) Snyder, H. R.; Roeske, R. W. *J. Am. Chem. Soc.* **1952**, *74*, 5820.
(4) Gore, P. H. "Friedel–Crafts and Related Reactions"; Interscience Publishers: New York, 1964; Chapter 31.
(5) McGreal, M. E.; Niederl, V.; Niederl, J. B. *J. Am. Chem. Soc.* **1939**, *61*, 345.
(6) Pearson, D. E.; Keaton, O. D. *J. Org. Chem.* **1963**, *28*, 1557.
(7) Kadesh, R. G. *J. Am. Chem. Soc.* **1944**, *66*, 1207.
(8) Kulibekov, M. R. *Azerb. Khim. Zh.* **1963**, *5*, 55; *Chem. Abstr.* **1963**, *62*, 9038b.
(9) Possibly the greater stability of the more substituted ethene formed by the dehydration step is responsible.
(10) Weil, H. *Chem. Ber.* **1897**, *30*, 1285.

satisfactory C,H analysis. In more recent work,[2] only the melting point was given, with a reference to Weil's report. In both instances the reactions were carried out in carbon disulfide at reflux temperature with a molar ratio of mesitylene, propionyl chloride, and aluminum chloride of 1:4:6. To remove any doubt about the identity of the products, we repeated the preparation of dipropionylmesitylene following Weil's procedure, and we subjected the crystalline product, mp 101–102 °C, to ^1H NMR and mass spectrometric analysis. These analyses proved the product unmistakably to be dipropionylmesitylene. A mixture of this material with 1,1-dimesitylpropene melted more than 20 °C lower than the two pure compounds.

We have not yet attempted to optimize yields of the diarylalkenes produced in these novel Friedel–Crafts reactions. We intend to do this, and to explore further the scope of the reaction, employing ketones and arenes of different steric and electronic properties and various catalysts at different temperatures and time periods.

Experimental Section

All melting points are uncorrected. ^1H NMR spectra were obtained on an NT-200 spectrometer. GC/MS analyses were performed on a Finnigan MAT 4023 spectrometer with an Incos data system, using a J&W Scientific Inc. 50-m DB1 bonded-phase capillary column (0.25 micron film thickness). Mesitylene was commercially available from Aldrich Chemical Co. and was distilled before use. Acetomesitylene and propiomesitylene were prepared by using CS_2 as solvent according to literature procedures.[2,11]

Reaction of Mesitylene with Acetyl Chloride at 100 °C. To a 100-mL three-necked flask fitted with a magnetic stirrer and reflux condenser protected by a drying tube was added 22 g (0.184 mol) of mesitylene and 7.2 g (0.092 mol) of acetyl chloride. The reaction mixture was cooled to 0 °C in an ice bath and 3.1 g (0.023 mol) of $AlCl_3$ was added to start the reaction. The reaction mixture was stirred at 100 °C in an oil bath for 6 h, allowed to cool to room temperature, poured into 50 mL of ice water, and extracted with ether. The ether extract was washed with 10% $NaHCO_3$ solution and water and dried over anhydrous $MgSO_4$. Ether and unreacted mesitylene were removed by rotary evaporation and the residue was distilled under reduced pressure. A 3.5-g fraction, bp 105–180 °C (12 torr), and a 10.5-g fraction, bp 180–240 °C (12 torr), were collected. The lower boiling fraction was subjected to preparative gas chromatography (20-ft silicone SE-30 column at 180 °C); 2.6 g (17% yield) of acetomesitylene was obtained and identified by GC/MS. Mass spectrum, m/e 162 (M^+), 147, 119, 91, 77, 43, 39.

The higher boiling fraction solidified in the receiver and was recrystallized from methanol to produce 10 g (41% yield, based on acetyl chloride) of 1,1-dimesitylethene as needle-like crystals: mp 99–101 °C; ^1H NMR ($CDCl_3$) 2.05 (s, 12 H), 2.23 (s, 6 H), 5.40 (s, 2 H), 6.70 (s, 4H); mass spectrum, m/e 264 (M^+), 249, 243, 91.

The previous experiment was repeated under the same conditions except that a full molar ratio of catalyst to acetyl chloride was used; i.e., the proportions of reactants were as follows: mesitylene (0.184 mol), acetyl chloride (0.092 mol), $AlCl_3$ (0.092 mol). This led to the formation of a very complex mixture of products.

The Reaction of Mesitylene with Acetyl Chloride in Inert Solvents at 25 °C. To a 100-mL three-necked flask fitted with a magnetic stirrer and a condenser protected with a drying tube was added 33 g (0.275 mol) of mesitylene, 7.2 g (0.092 mol) of acetyl chloride, 16.65 g (0.092 mol) of 1,2,4-trichlorobenzene (as internal standard), and 50 g (0.60 mol) of dichloromethane. The reaction mixture was stirred at 25 °C in a water bath, and aluminum chloride (3.19 g 0.023 mol) was added to start the reaction. At desired intervals, 15-mL aliquots of the reaction mixture were withdrawn, decomposed with 1% NaOH solution, washed, and dried over anhydrous $MgSO_4$. The filtrates from each sample were analyzed with a Varian series 2400 gas chromatograph equipped with a hydrogen flame detector and a 2% silicone oil 50-ft column at 180 °C and 60 psi. The analysis showed that acetomesitylene was the only product after a 20-h period of time.

A similar reaction with identical molar ratios of solvent, reagent, and catalyst, but with carbon disulfide instead of dichloromethane as solvent, was carried out at reflux temperature. Analysis of the products showed that after 20 h acetomesitylene was the only reaction product.

Reaction of Mesitylene with Acetyl Chloride at Room Temperature without Solvents. To a 100-mL three-necked flask fitted with a magnetic stirrer and condenser protected by a drying tube was added 33 g (0.275 mol) of mesitylene. The flask was cooled to 0 °C in an ice–water bath and $AlCl_3$ (3.19 g, 0.023 mol) was added. The mixture was stirred while 7.2 g (0.092 mol) of acetyl chloride was added dropwise during 1 h. The ice–water bath was removed and the reaction mixture was stirred at room temperature for 6 h. The contents of the flask was poured into ice water and extracted with ether. The ether extract was washed with $NaHCO_3$ solution and water and then dried over anhydrous $MgSO_4$. The ether was removed and the residue was distilled under reduced pressure; 12 g (81%) of acetomesitylene was obtained.

Reaction of Acetomesitylene with Mesitylene at 150–160 °C. A mixture of 5.0 g (0.031 mol) of acetomesitylene, 12.0 g (0.092 mol) of mesitylene, and 0.84 (0.0062 mol) of $AlCl_3$ was heated under reflux at 150–160 °C with vigorous stirring for 3 h. The reaction mixture was allowed to cool to room temperature, decomposed with water, and extracted with ether. The ether extract was washed with 10% $NaHCO_3$ solution and water and dried over anhydrous $MgSO_4$. After removal of ether, the residue was distilled under reduced pressure; 5.75 g (70%) of material, bp 158–160 °C (2 torr), was collected. It solidified in the receiver and was recrystallized from methanol yielding colorless needles of 1,1-dimesitylethene, mp 101–102 °C.

Reaction of Mesitylene with Propionyl Chloride at 100 °C. The procedure was the same as that for reaction of acetyl chloride with mesitylene at 100 °C except that 8.5 g (0.092 mol) of propionyl chloride and 6.18 g (0.046 mol) of $AlCl_3$ was used. Vacuum distillation gave 8.7 g (54% yield) of propiomesitylene, bp 120–121 °C (5 torr), and an 8.3-gfraction, bp 140–200 °C (5 torr), which crystallized in the receiver. The higher boiling fraction was recrystallized from methanol and gave 8 g of 1,1-dimesitylpropene (31% yield) as white rhombic crystals, mp 90–92 °C. A second recrystallization raised the melting point to 98–99 °C. ^1H NMR ($CDCl_3$) 1.65 (d, 3 H), 2.11 (s, 12 H), 2.22 (s, 6 H), 5.7 (q, 1 H), 6.85 (s, 4 H); mass spectrum, m/e 278 (M^+), 262, 249, 234.

Repetition of this experiment under the same conditions with the exception that half the amount of catalyst was used (3.1 g, 0.023 mol) gave the same results.

Reaction of Mesitylene with Propionyl Chloride at Room Temperature without Solvent. In a 100-mL three-necked flask fitted with a magnetic stirrer, a condenser protected with a drying tube, and a dropping funnel was placed 33 g (0.275 mol) of mesitylene and 3.1 g (0.23 mol) of $AlCl_3$. Propionyl chloride (8.5 g, 0.092 mol) was added dropwise to the stirred mixture during 1 h. The reaction mixture was stirred for an additional 5 h, decomposed with ice water, and extracted with ether. The ether extract was washed with 10% $NaHCO_3$ solution and water and dried over anhydrous magnesium sulfate. The ether was evaporated and the residue was vacuum distilled, giving 13.0 g (80%) of propiomesitylene, bp 90–91 °C (1.0 torr). The residue in the distillation flask was treated with methanol to give 6.8 g of white solid material. Recrystallization from methanol gave 6.5 g (10%) of 1,1-dimesitylpropene as white rhombic crystals: mp 98–99 °C; ^1H NMR ($CDCl_3$) 1.65 (d, 3 H), 2.11 (s, 12 H), 2.22 (s, 6 H), 5.7 (q, 1 H), 6.85 (s, 4 H); mass spectrum, m/e 278 (M^+), 262, 249, 234.

This experiment was repeated under the same conditions except that the amount of catalyst was doubled. The same products in the same yields were obtained.

Reaction of Propiomesitylene with Mesitylene at 150–160 °C. A mixture of 12 g (0.07 mol) of propiomesitylene, 20 g (0.17 mol) of mesitylene, and 2.26 g (0.014 mol) of $AlCl_3$ was heated and stirred under reflux at 150–160 °C for 4 h. The reaction mixture was decomposed with water and worked up as before, yielding 14 g (74%) of crude 1,1-dimesitylpropene, bp 192–194

(11) Smith, L. I.; Guss, C. J. Am. Chem. Soc. 1937, 59, 804.

°C (7 torr), which crystallized in the receiver. Recrystallization from 95% ethanol gave crystals, mp 98–99 °C.

Preparation of Dipropionylmesitylene. In a 250-mL three-necked flask fitted with a condenser protected by a drying tube and a magnetic stirrer was placed 5.0 g (0.04 mol) of mesitylene, 14.8 g (0.16 mol) of propionyl chloride, and 75 mL of carbon disulfide. Aluminum chloride (30 g, 0.22 mol) was added to the stirred mixture and the reaction mixture was heated to reflux for 1 h. Carbon disulfide was removed by distillation and the residue was decomposed with ice water, producing a white solid precipitate. The solid was collected on a filter, dried, and recrystallized from petroleum ether (bp 60–80 °C), giving 8.0 g (83%) of white fluffy crystals: mp 101–102 °C (a mixture with 1,1-dimesitylpropene melted at 77–80 °C); ^{1}H NMR ($CDCl_3$) 1.2 (t, 6 H), 2.05 (s, 3 H), 2.18 (s, 6 H), 2.68 (q, 4 H), 7.25 (s, 1 H); mass spectrum, m/e 232 (M^+), 203, 160, 145, 115, 91, 77, 57, 43.

Acknowledgment. Support for this work by the Robert A. Welch Foundation is gratefully acknowledged.

Registry No. $CH_3C(O)Cl$, 75-36-5; $CH_3CH_2C(O)Cl$, 79-03-8; $AlCl_3$, 7446-70-0; mesitylene, 108-67-8; acetomesitylene, 1667-01-2; propionylmesitylene, 2040-15-5; 1,1-dimesitylpropene, 91190-65-7; 1,1-dimesitylethene, 38575-31-4; dipropionylmesitylene, 6335-36-0.

1,3-Carbonyl Transposition Methodology Employing α-Oxo Ketene Dithioacetals: Application in the Synthesis of Phenols and (±)-Myodesmone

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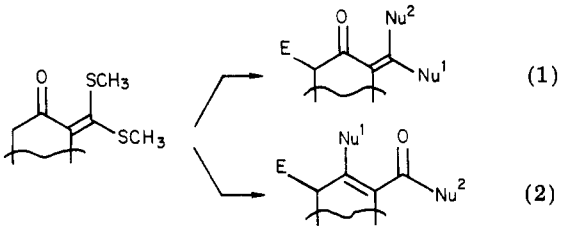
Received January 23, 1984

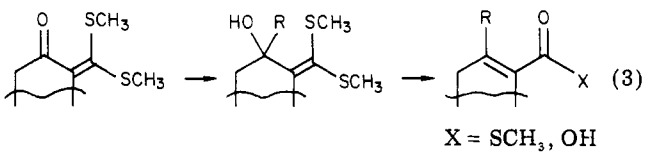
The 1,2-nucleophilic addition of organomagnesium, organolithium, and metal hydride nucleophiles to eight α-oxo ketene dithioacetals and the subsequent aniontropic rearrangement of the resultant allylic alcohols is described. This sequence of reactions represents a 1,3-carbonyl transposition methodology that is utilized in a synthesis of phenols and the furanosesquiterpene (±)-myodesmone (**51**). The aniontropic rearrangement is sensitive to reaction conditions and substrate structure. Tertiary allylic alcohols **15a,d**, **16a**, **17a,c**, **19a,c**, **20a,b**, and **21a,b** are efficiently converted to α,β-unsaturated thiol esters upon treatment with 10% HBF_4 in THF while the secondary allylic alcohols **15b**, **16b**, and **17b** require the addition of HgO or utilization of $HgCl_2$ in acetonitrile for efficient conversion. ^{13}C NMR data for the thiol esters are reported. Utilization of 2 equiv of HgO cleanly transforms allylic alcohols **15a,b**, **17a,b**, and **19a,b** into α,β-unsaturated carboxylic acids **35a,b**, **35c,d**, **36**, and **37**, respectively. Allylic alcohols **15e** and **17d** underwent cyclization to benzenoid aromatic compounds upon attempted aniontropic rearrangement. The methodology establishes the utility of α-oxo ketene dithioacetals as versatile substrates for the sequential regioselective construction of new carbon–carbon bonds.

Introduction

We have been engaged in a systematic investigation of the chemistry of α-oxo ketene dithioacetals[1] aimed at exploiting this rich functionality for the sequential regio- and stereoselective construction of new carbon–carbon bonds (eq 1 and 2). This effort has resulted in the development



of a stereoselective synthesis of α-alkylidene ketones[2] and a 1,3-carbonyl transposition methodology[3] in which the original ketone carbonyl emerges as the carbonyl of a thiol ester or carboxylic acid (eq 3). We now report our extensive examination of this carbonyl transposition sequence, the stereochemical outcome of the process in acyclic substrates, and synthetic applications of the method. The synthesis of the furanosesquiterpene (±)-myodesmone[4] is described and illustrates the powerful synthetic potential of this methodology for sequential regioselective carbon–carbon bond constructions.



Simple and alkylative 1,3-carbonyl transpositions are of considerable synthetic importance as a strategy for introducing new carbon–carbon bonds in a regiospecific manner. Carbon–carbon bond formation occurs during the transposition sequence in an alkylative carbonyl transposition procedure while alkylation of the original and/or transposed carbonyl compound provides additional bond-forming opportunities. Methods for effecting 1,3-carbonyl transpositions[5a] include the Wharton epoxy ke-

(1) β,β-Bis(alkylthio)-α,β-unsaturated ketones have been described in the literature by several convenient and simple descriptive names. These include α-oxo ketene dithioacetals, α-keto ketene mercaptals, α-bis(alkylmercapto)methylene] ketones, and α-(dithiomethylene) ketones.

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