sequence[10b] and was converted to **3** by zinc debromination[2a,b] of *t*-BuC(Br)PhCOCl.

For the product studies on **1**, three 25-mL solutions of water/acetonitrile (20%/80%) were prepared: acid (2×10^{-2} M HCl), base (1×10^{-3} N NaOH), and neutral (buffered at pH 7.00 with sodium hydroxide/potassium monobasic phosphate). To each solution was added approximately 75 mg of ketene **1** directly from the VPC (OV-17 column at 120 °C and helium flow of 85 mL/min) without collection of the ketene. The solutions were allowed to react for 88 h at room temperature in acid and 39 h at 65 °C for the basic and buffered solutions. Ether (20 mL) was added to each solution, and the solutions were extracted against dilute acid and then saturated sodium chloride. The solutions were treated with diazomethane, extracted again with saturated sodium chloride, and dried over calcium sulfate. Excess ether was removed under reduced pressure. Relative quantities of the esters **9** and **10** were measured by VPC using the OV-17 column at 120 °C and a helium flow of 85 mL/min.

Kinetic measurements were carried out as reported previously[1a] by observing the decrease in the UV absorbance at 232 nm for **1** and 254 nm for **2** and **3**.

Kinetic studies of **1** in NaOH solution below 0.1 M NaOH were carried out in solutions maintained at ionic strength $\mu = 0.1$ by the addition of NaCl, but above 0.1 M NaOH no NaCl was added and the ionic strengths were greater and increased with [NaOH]. The reactions maintained at $\mu = 0.1$ gave $k_{OH} = 0.122$ M^{-1} s^{-1}, whereas if all the reactions are considered together, $k_{OH} = 0.104$ M^{-1} s^{-1} is calculated.

Acknowledgment. Financial support was provided by the Natural Sciences and Engineering Research Council of Canada. We thank Régis Leung-Toung and Lynn M. Baigrie for assistance in the preparation of **1-3**.

Registry No. 1, 61899-98-7; **2**, 38082-08-5; **3**, 57768-77-1; **9**, 28043-10-9; **10**, 49815-58-9; O_2, 7782-39-0.

Synthesis and Reactions of α-Carbomethoxy-*N*-phenylmaleimide and Related Electrophilic Ethylenes

Stacy B. Evans, Mohamed Abdelkader, Anne Buyle Padias, and H. K. Hall, Jr.*

C. S. Marvel Laboratories, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Received November 1, 1988

The synthesis of α-carbomethoxy-*N*-phenylmaleimide (CNPM) was accomplished by way of a Diels-Alder precursor from α-carbomethoxymaleic anhydride and cyclopentadiene, conversion of the anhydride functionality to *N*-phenylmaleimide, and finally thermolysis. Reactions of this highly electrophilic new olefin with donor olefins were studied. The Diels-Alder product with cyclopentadiene and unstable [2 + 2] cycloadducts with *N*-vinylcarbazole were obtained. With styrene and *p*-methoxystyrene, double Diels-Alder adducts were formed. Anionic oligomerization of CNPM occurred with triethylamine. Various trialkyl ethylenetricarboxylates have been synthesized in a one-step reaction using poly(methyl glyoxylate) and dialkyl malonates. The synthesis of α-carbomethoxymaleic anhydride has been optimized. Attempts to synthesize new carboalkoxymaleic anhydrides (and in turn other carboalkoxy-*N*-phenylmaleimides) from their corresponding trialkyl ethylenetricarboxylates have failed.

Introduction

We have been interested in spontaneous cycloaddition and polymerization reactions of tri-substituted electrophilic olefins with electron-donor olefins.[1-6]

Of the electrophilic olefins studied, α-carbomethoxymaleic anhydride, CMA, is much more reactive than other trisubstituted olefins in cycloaddition reactions with electron-rich olefins and dienes.[6] Confining two substituents in the maleic anhydride ring minimizes steric hindrance and hence increases reactivity. CMA is even more reactive than tetracyanoethylene in [4 + 2] cycloadditions.

CMA had been synthesized by reaction of trimethyl ethylenetricarboxylate with phosphorus pentoxide at 150-160 °C.[5] We have improved the synthesis of CMA. It was used as the starting material for the synthesis of a novel cyclic trisubstituted electrophilic olefin, α-carbomethoxy-*N*-phenylmaleimide, CNPM. Its reactivity with various electron-rich olefins and its polymerization tendencies will be examined.

Attempts to synthesize other α-carboalkoxymaleic anhydrides will also be described.

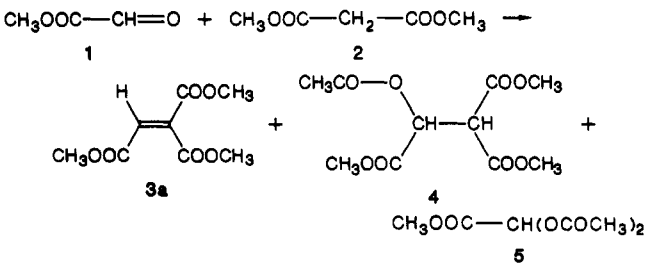
Results

Synthesis of Trialkyl Ethylenetricarboxylates. Trimethyl ethylenetricarboxylate was previously synthesized by a multistep procedure starting from dimethyl malonate and methyl chloroacetate.[2] We now introduce a one-step synthesis, which consists of a Knoevenagel reaction of methyl glyoxylate **1** with dimethyl malonate in acetic anhydride. Three possible products are formed in this reaction: trimethyl ethylenetricarboxylate **3a**, its acetate adduct **4**, and the acylal of methyl glyoxylate **5**. The yield of each compound depends on the reaction time and temperature.

Many different experimental conditions were attempted to maximize the yield of trimethyl ethylenetricarboxylate **3a** from monomeric methyl glyoxylate. When the reaction

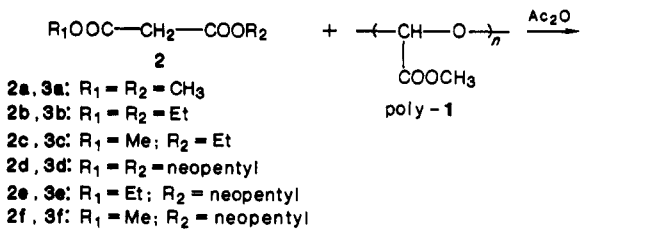
(1) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440.
(2) Hall, H. K., Jr.; Daly, R. C. *Macromolecules* **1975**, *8*, 22.
(3) Hall, H. K., Jr.; Abdelkader, M. *J. Org. Chem.* **1981**, *46*, 2948.
(4) Hall, H. K., Jr.; Padias, A. B.; Pandya, A.; Tanaka, H. *Macromolecules* **1987**, *20*, 247.
(5) Hall, H. K., Jr.; Rhoades, J. W.; Nogues, P.; Wai, G. *Polym. Bull.* **1981**, *4*, 629.
(6) Hall, H. K., Jr.; Nogues, P.; Rhoades, J. W.; Sentman, R. C.; Detar, M. *J. Org. Chem.* **1982**, *47*, 1451.
(7) Abdelkader, M.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1987**, *20*, 949.

0022-3263/89/1954-2848$01.50/0



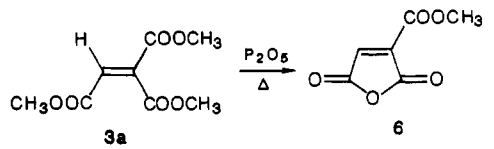
was run for 8 h, the acetate adduct 4 and triester **3a** were isolated as a mixture by distillation. A 24% yield of **3a** was obtained after reflux of this mixture for 20.5 h in toluene. Methyl glyoxylate 1 is not a very stable compound as it polymerizes spontaneously at room temperature to give poly(methyl glyoxylate). Depolymerization is achieved at 100 °C in the presence of acid. The highest yields for trimethyl ethylenetricarboxylate were obtained when poly(methyl glyoxylate) was used. A 53% yield was obtained in acetic anhydride at 125–130 °C for 31 h. Shorter time of reaction, or using xylene as a solvent, resulted in lower or no yield, respectively.

By analogy to trimethyl ethylenetricarboxylate, a series of trisubstituted ethylenetricarboxylates were synthesized with poly(methyl glyoxylate) in acetic anhydride at 125–130 °C. The yields were reasonable (60%) when the dialkyl groups on the malonate were not too bulky. The lowest yield (25%) was obtained with dineopentyl malonate (even with longer reaction time). All physical and spectral data are summarized in Table I.



When R_1 differed from R_2, a mixture of isomers was usually obtained. In each case, the major olefin was the *E* isomer.

Improved Synthesis of CMA and Attempted Syntheses of α-Carboalkoxymaleic Anhydrides. In a previous study, α-carbomethoxymaleic anhydride was synthesized by reaction of triester **3a** with P_2O_5 at 155–160 °C. This reaction has been optimized to give 73% yield.

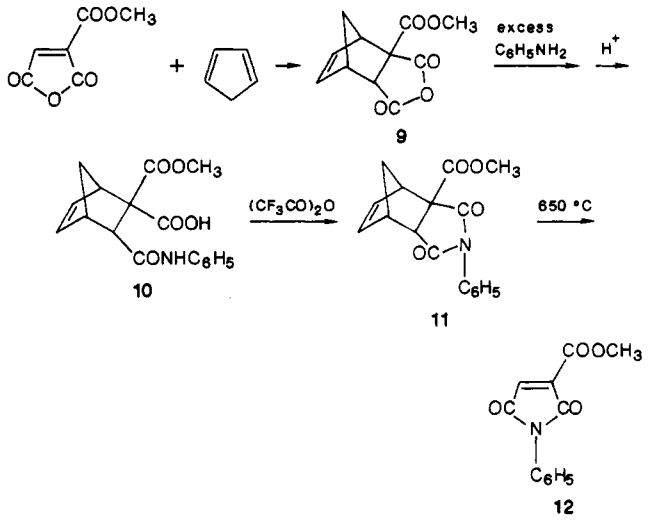


Higher temperatures (175–180 °C) were tried, but the yield was not improved.

Various attempts to synthesize (ethoxycarbonyl)- or (neopentoxycarbonyl)maleic anhydride were tried, but all failed. Using P_2O_5 and the olefins **3b–f** at 160 °C, none of the expected product formed. Curiously, low yields of carbomethoxymaleic anhydride were obtained when **3b** and **3c** were used. Olefins **3d**, **3e**, and **3f** did not form the desired products.

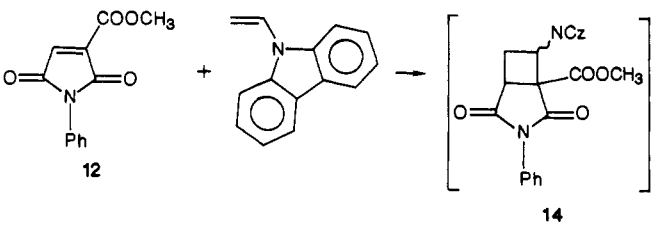
Synthesis of α-Carbomethoxy-N-phenylmaleimide (CNPM). We initially attempted to synthesize CNPM by reaction of CMA with aniline, which would then be followed by ring closure. However, oligomerization occurred in every case, illustrating the extremely electrophilic nature of the double bond. Another possible route was used in the synthesis of α-acyl-*N*-methylmaleimide, which involved benzeneselenylation to generate the double bond.[8] However, this method was also unsuccessful in the synthesis of CNPM. Therefore, the double bond of CMA was protected with cyclopentadiene, and the anhydride was reacted with aniline, followed by dehydration to *N*-phenylimide by treatment with trifluoroacetic anhydride. The cyclopentadiene protecting group was then removed by thermolysis (Scheme I). Carbomethoxy-*N*-phenylmaleimide **12** was obtained in 19% yield as a yellow crystalline solid, mp 118 °C.

Scheme I



Reactions of α-Carbomethoxy-N-phenylmaleimide (CNPM). CNPM reacted exothermally with cyclopentadiene to reform norbornene derivative **11** with the maleimide ring in the endo position. Only one isomer is formed.

With electron-rich olefins, the behavior of CNPM almost parallels the reactions of CMA. With *N*-vinylcarbazole, unstable cyclobutane adducts are formed in quantitative yield. Two isomers, **14a** (*N*-carbazolyl group cis to $COOCH_3$) and **14b** (trans), were detected by NMR. The final product is composed of 2:1 CNPM to *N*-vinylcarbazole; its structure is unknown but is probably polymeric.



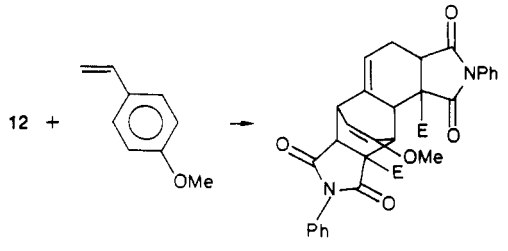
With styrene and *p*-methoxystyrene, double Diels–Alder adducts are formed. Two equivalents of CNPM react with 1 equiv of the styrene to form a 2:1 cycloadduct. This type of adduct has been reviewed by Wagner-Jauregg.[9] In the case of *p*-methoxystyrene, the reaction proceeds fast at room temperature and yields only one isomer of the adduct

(8) Durant, M. L.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1984**, 901.
(9) Wagner-Jauregg, T. *Synthesis* **1980**, 769.

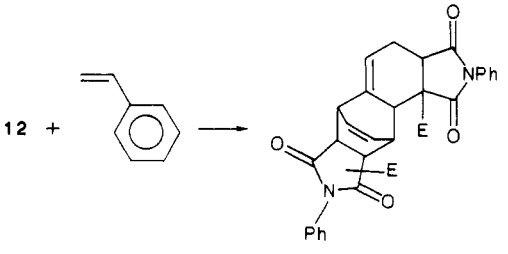
Table I

compd	bp, °C (0.2 mmHg)	yield, %	IR (KBr), cm^{-1}	^1H NMR ($CDCl_3$) δ	analysis
3a	100–110	53	3010 (w), 2957 (m), 1731 (s), 1655 (m), 1269 (s)	3.81, 3.86, 3.90 (s, 3 H), 6.90 (s, 1 H)	
3b	98	58	2983 (m), 1729 (s), 1650 (s), 1261 (s)	1.34, 1.37 (t, 3 H), 3.81 (s, 3 H), 4.32–4.38 (q, 2 H)	Calcd for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 51.79; H, 6.28.
3c	85	68	2956 (m), 1729 (s), 1648 (w), 1277 (s)	1.33–1.36 (t, 3 H), 3.87 (s, 6 H), 4.32–4.36 (2 H), 6.88 (s, 1 H)	Calcd for $C_9H_{12}O_6$: C, 50.00; H, 5.60. Found: C, 49.70; H, 5.79.
3d	116	25	2958 (s), 1730 (s), 1650 (m), 1248 (s)	0.96, 0.98 (a, 18 H), 3.79 (s, 3 H), 3.94, 3.99 (s, 2 H), 6.89 (s, 1 H)	Calcd for $C_{16}H_{26}O_6$: C, 61.69; H, 8.34. Found: C, 61.39; H, 7.93.
3e	118	33	2958 (m), 1730 (s), 1650 (w), 1256 (s)	0.96 and 0.99 (s, 9 H), 1.32 and 1.36 (t, 3 H), 3.79–3.80 (s, 3 H), 4.01 (s, 2 H), 4.32 and 4.38 (t, 2 H), 6.88 (s, 1 H)	Calcd for $C_{13}H_{20}O_6$: C, 57.57; H, 7.28. Found: C, 57.34; H, 7.40.
3f	104	56	2958 (s), 1783 (m), 1729 (s), 1650 (m), 1264 (s)	0.96 and 0.98 (s, 9 H), 3.80, 3.86, and 3.91 (s, 6 H), 3.94 and 4.01 (s, 2 H), 6.9 (s, 1 H)	Calcd for $C_{12}H_{18}O_6$: C, 55.80; H, 7.03. Found: C, 55.62; H, 6.90.

15. With styrene, the reaction is slower (4 h at 28 °C) and leads to two isomers **16a** and **16b**.



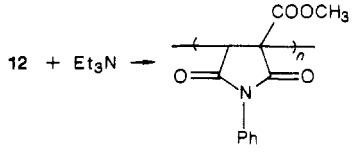
15



16a, b

E = $COOCH_3$

In the presence of triethylamine, CNPM oligomerizes at 28 °C in a few minutes. The average molecular weight of the oligomer is 1100.



Discussion

The title compound, α-carbomethoxy-*N*-phenylmaleimide, CNPM, was very electrophilic, as expected, but not as reactive as CMA. CNPM was reactive toward electron-rich vinyl monomers. With *N*-vinylcarbazole, the most reactive donor olefin used, an unstable cyclobutane adduct was formed, presumably via a zwitterionic intermediate. With the styrenes, only concerted reactions were observed, leading to double Diels–Alder adducts. In the presence of a nucleophile, triethylamine, anionic oligomerization did take place to low molecular weight polymer. This parallels the behavior of CMA. These oligomerizations are possible by reducing steric hindrance by confining two of three substituents to a ring.

A novel one-step synthesis of trimethyl ethylenetricarboxylate was devised, making this olefin much more accessible. This Knoevenagel reaction is the equivalent of the novel one-step synthesis recently described for dimethyl cyanofumarate[4] and methyl β,β-dicyanoacrylate.[10] However, in the case of triester, much stronger conditions have to be used because there are no cyano substituent(s) to provide the necessary activation of the methylene protons.

In an attempt to obtain other carboalkoxy derivatives of CMA, a series of trialkyl ethylenetricarboxylates were synthesized using this new approach. None of these could be converted to their corresponding α-carboalkoxymaleic anhydrides. Substituents larger than methyl undergo elimination reactions under the strongly acidic synthesis conditions. Ethylene can be eliminated from an ethyl ester by β-hydrogen migration. Even using a mixture of isomers which contains mostly *cis*-dicarbomethoxy groups, did not lead to the desired products.

Experimental Section

General Methods. NMR spectra were recorded on a Brucker WM-250 MHz nuclear magnetic resonance spectrometer. Infrared data were obtained from a Perkin-Elmer Model 983 infrared spectrometer. Melting points were measured with a capillary melting apparatus without correction. Size-exclusion chromatography was carried out with three columns: Du Pont Zorbax PSM 300S, PSM 60S, and IBM GPC/SEC pore type A column.

(10) Hall, H. K., Jr.; Sentman, R. C. *J. Org. Chem.* **1982**, *47*, 4572.

A Spectra-Physics detector at 254 nm was used. The columns were calibrated with polystyrene standard, and chloroform was used as eluent. HPLC was performed on an IBM analytical silica gel column with detector at 254 nm. Dichloromethane was used as eluent.

Reagents. *p*-Methoxystyrene and styrene were obtained from Aldrich, distilled from CaH_2 under vacuum, and stored under nitrogen at −15 °C. *N*-Vinylcarbazole (Polysciences) was dissolved in hexane, passed through a layer of charcoal, and then recrystallized from the same solvent at −50 °C. This process was repeated twice. Poly(methyl glyoxylate) was received as a gift from Du Pont Co., Wilmington, DE.

General Synthesis of Trialkyl Ethylenetricarboxylate 3. Equivalent amounts of poly(methyl glyoxylate), dialkyl malonate, and acetic anhydride were mixed and placed at 125–130 °C. After 15 min, stirring was started. The mixture was cooled to room temperature after 21.5 h. Excess acetic anhydride, acetic acid, and dialkyl malonate were distilled at 50–95 °C (15 mmHg). Product olefins were distilled using a Kugelrohr apparatus at 0.2 mmHg. (See Table I for boiling points, spectra, and analysis.)

Carbomethoxymaleic Anhydride. Phosphorus pentoxide was placed in a 100-mL round-bottom flask under dry conditions, and 0.5 equiv of finely ground trimethyl ethylenetricarboxylate **3a** was added. The mixture was homogenized by rotation at room temperature. The reaction vessel was equipped with a condenser and heated at 155–160 °C for 5 h. Successful reaction was indicated by a completely black reaction mixture. The black solid was cooled to room temperature. CMA was Kugelrohr distilled at 120 °C (0.5–0.1 mmHg) into a receiver at 0 °C, where it crystallized. It was recrystallized from ether (73% yield): mp 37–38 °C; NMR ($CDCl_3$) δ 4.0 (s, 3 H), 7.5 (s, 1 H) ppm; IR (KBr) 1840, 1770, 1725, 1640 cm^{-1}.

Synthetic Steps to α-Carbomethoxy-N-phenylmaleimide (12). In a three-necked round-bottom flask, equipped with a magnetic stirring bar, an additional funnel, a condenser, and a $CaSO_4$ drying tube was placed a solution of carbomethoxymaleic anhydride (5.63 g, 36 mmol) in 100 mL of dichloromethane. The reaction mixture was cooled to 0 °C, and cyclopentadiene (3 g, 45.4 mmol) in 25 mL of dichloromethane was added dropwise with stirring. Stirring was continued for another 3 h at room temperature. The solvent was rotaevaporated to leave an oil. The product was recrystallized from ether (100 mL) at −45 °C (6.3 g, yield 78.3%): mp 67–69 °C; NMR ($CDCl_3$) δ 1.85–1.88 (m, 2 H), 3.53 (m, 1 H), 3.71–3.72 (m, 1 H), 3.82–3.84 (d, 1 H, J = 4.6 Hz), 3.86 (s, 3 H), 6.38–6.40 (m, 2 H) ppm; IR (KBr) 3001, 2954 (m), 1850 (s), 1781, 1742 (s), 1568 (w), 1256 (s) cm^{-1}.

Norbornene Amic Acid 10. To norbornene **9** (6.36 g, 28.6 mmol) was added a solution of aniline (2.66 g, 28.6 mmol) in 50 mL of ether with stirring at room temperature (28 °C). Stirring was continued for 20 h. The insoluble material was filtered (5.6 g) and washed with ether and then with dichloromethane. From the filtrate, the solvent was evaporated to leave an oil, which after drying under full vacuum and washing with dichloromethane yielded a white powder (2.3 g). The products were combined, washed with dilute HCl and twice with water, and finally dried: yield 7.98 g, (88.5%); mp 127–128 °C with evolution of gas; NMR (DMSO-d_6) δ 1.3 (s, 2 H), 2.98–3.3 (broad, 2 H), 3.68 (s, 3 H), 4.00 (d, 1 H, J = 4.5 Hz), 5.9–6.1 (m, 1 H), 6.28–6.5 (m, 1 H), 6.8–7.68 (m, 6 H), 10.00 (s, 1 H) ppm; IR (KBr) 3371 (sharp), 2954–2599 (broad), 1732 (s), 1657 (s), 1598 (s) cm^{-1}.

Cyclopentadiene–CNPM Adduct 11. Amic acid **10** (10.42 g, 33 mmol) and 100 mL of CH_2Cl_2 were mixed to give a heterogeneous mixture. After the mixture was chilled to 0 °C, trifluoroacetic anhydride (15.7 g, 74.7 mmol) was added with stirring. The homogeneous solution was stirred for 6 h. The solvent and excess trifluoroacetic anhydride were evaporated to give the oily maleimide in quantitative yield. The oily material was dissolved in 5 mL of CH_2Cl_2 and dropped in 200 mL of hexane. The insoluble material was discarded. The solvent was evaporated, and full vacuum was applied at 40 °C to leave **11** as an oil (9.5 g, 96.9%): NMR ($CDCl_3$) δ 1.85–1.88 (m, 2 H), 3.51–3.53 (m, 1 H), 3.64–3.66 (d, 1 H, J = 4.5 Hz), 3.75–3.78 (m, 1 H), 3.85 (1 s, 3 H), 6.33–6.35 (m, 2 H), 7.14–7.18 (m, 2 H), 7.38–7.47 (m, 3 H) ppm; IR (neat) 2956 (w), 1785 (m), 1743 (s) 1711 (s), 1596 (s), 1497 (w) cm^{-1}. Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.34; H, 5.16; N, 4.33.

α-Carbomethoxy-N-phenylmaleimide (12). The reaction apparatus was composed of a temperature controller, a furnace, a quartz column (40 cm) packed with quartz chips (20 cm packing), an addition funnel, and three traps (two ice baths and one in dry ice/acetone bath). The furnace was heated to 650 °C and left overnight to stabilize. A solution of the maleimide adduct **11** (13.42 g, 45.1 mmol) in 10 mL of dry benzene was placed in the addition funnel. Full vacuum (0.5 mmHg) was applied. The solution was added to the column in five-drop portions, waiting each time for the pressure, which rises during the addition, to return to 0.5 mm. Crystals and oil formed in the traps at 0 °C (a lot of black material formed on the column), which were washed with hexane. The hexane solution contained starting material **11**. The rest (solid) was dissolved in dry CH_2Cl_2, and hexane was added. The solution was placed at −45 °C. The solution was decanted and replaced at −45 °C. Crystals that formed were recrystallized twice from CH_2Cl_2/ether to yield 2 g (19.2%) of pure compound **12**, mp 117–118 °C. The oil and the solution contained both **11** and **12**: NMR ($CDCl_3$) δ 3.9 (s, 3 H), 7.2 (s, 1 H), 7.3 (5 H) ppm; IR (KBr) 3094 (m) 3060 (weak) 2962 (weak) 1784 (m), 1715 (s) 1627 (m), 1597 (m) cm^{-1}. Anal. Calcd for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.26; H, 3.96; N, 5.85.

Reaction of CNPM with Cyclopentadiene 11. Carbomethoxy-*N*-phenylmaleimide was mixed with an equimolar amount of cyclopentadiene in $CDCl_3$ in an NMR tube. The reaction is exothermic and was complete when observed by NMR after 10 min (yield 100%). Only one isomer of **11** was observed with the maleimide ring: endo, as confirmed by NMR (J = 4.5 Hz).

Reaction with N-Vinylcarbazole. CNPM (50 mg, 0.22 mmol) in $CDCl_3$ (0.5 mL) was added to *N*-vinylcarbazole (43 mg, 0.22 mmol) at 28 °C. Immediately an orange-red color formed, which faded quickly. After 5 min cyclobutane was formed in 100% yield as confirmed by NMR. The cyclobutane is very unstable. After 19 h, it was dropped into 100 mL of petroleum ether, and a pink, insoluble powder (54 mg) was obtained. The final material is composed of 2:1 of CNPM and NVC by chemical analysis: NMR of cyclobutanes ($CDCl_3$) δ 2.7–4.5 (m, 4 H), 2.92 (*cis*-**14a**) and 3.75 (*trans*-**14b**) (s, 3 H), 5–5.4 (t, 1 H) 5.5–5.9 (q, 1 H), 7–7.8 (m, 2 H, aromatic), 7.95–8.25 (m, 2 H, aromatic). Anal. Calcd for $C_{38}H_{29}O_8N_3$: C, 69.60; H, 4.46; N, 6.41. Found: C, 69.54; H, 4.63; N, 6.40.

Reaction with p-Methoxystyrene. CNPM (40 mg, 17.3 mmol) is dissolved in $CDCl_3$ (0.5 mL) and placed in an NMR tube. *p-Methoxystyrene (24 mL, 17.9 mmol) is added. The reaction* is complete when observed after 15 min by NMR. The solvent is evaporated, and full vacuum is applied at ~40 °C overnight to remove any unreacted *p*-methoxystyrene. The product is dissolved in 2 mL of CH_2Cl_2 and dropped in 50 mL of hexane. After evaporation of CH_2Cl_2, crystals formed at 28 °C in hexane. After a second recrystallization following the same procedure, white crystals (38 mg, 73.6%), mp 218–220 °C, were obtained: NMR ($CDCl_3$) δ 1.6 (m, 1 H, CH), 2.17 (m, 1 H, CH), 2.89–3.00 (m, 1 H, CH_2), 3.02 (m, 1 H, bridgehead H), 3.12 (s, 3 H, OCH_3), 3.53–3.56 (m, 1 H, bridgehead H), 3.78–3.87 (m, 1 H, CHCO), 3.81 (s, 3 H, CO_2CH_3), 3.91 (s, 3 H, CO_2CH_3), 4.07–4.10 (d, 1 H, J = 1.7 Hz, CHC), 4.82–4.86 (dd, 1 H, HC=$COCH_3$), 5.92–5.95 (m, 1 H, HC=C), 7.11–7.47 (m, 10 H, aromatic) ppm; IR (KBr) 2955 (m), 1784 (m), 1714 (s), 1632 (m), 1596 (m), 1250 (s), 1199 (s) cm^{-1}.

Reaction with Styrene. To styrene (18 mg, 0.175 mmol) in an NMR tube was added a solution of CNPM (40 mg, 0.173 mmol) in 0.5 mL of $CDCl_3$. The reaction was complete when observed after 4 h. The solvent was evaporated, and a full vacuum was applied at 40 °C overnight to remove unreacted styrene. The residue was dissolved in 2 mL of CH_2Cl_2 and dropped in 50 mL of hexane. After evaporation of the CH_2Cl_2, crystals precipitated from hexane at 28 °C. Recrystallization following the same procedure gave white crystals (26 mg, 52.6%): mp 227–229 °C; NMR ($CDCl_3$) δ 1.8–2.4 (m, 3, and $CHCH_2$), 2.65–3.2 (m, 2, bridge), 3.69, 3.70, 3.78, 3.85 (s, 6 H, CO_2CH_3 groups), 3.3 and 4.3 (m, 2 H adjacent to maleimide), 5.8–6.1 (m, 1 H, HC=C), 6.1–6.32 (m, 1 H, HC=C), 6.9–7.7 (m, aromatic), 7.95–8.2 (m, 1 H, HC=C) ppm; IR (KBr) 3073 (w), 3005 (w), 2955 (m), 1783 (s), 1727 (br), 1595 (sh) cm^{-1}.

Oligomerization by Triethylamine. In a typical experiment, injection of 3 μL of triethylamine caused complete oligomerization of 40 mg of CNPM in 0.5 mL of $CDCl_3$ within 15 min. The oligomer could be separated into roughly equal amounts of ether-insoluble and ether-soluble oligomers. The former showed MW ~1100 (DP ~5). The latter had MW 600–920 (DP 2–4). Their infrared spectra were identical: IR (KBr) 3067 (w), 2954 (m), 1714 (br), 1596 (sh), 1238 (br cm^{-1}); NMR ($CDCl_3$) δ 3.3–4.4 (br, 4 H), 6.7–7.7 (br, 5 H) ppm.

Acknowledgment. We respectfully thank the Exxon Corp. and the National Science Foundation (Grant DMR 8700616) for their generous financial support of this research.

A New Super-Electrophile: α-(Phenylsulfonyl)maleic Anhydride

Merrikh Ramezanian, Mohamed Abdelkader, Anne Buyle Padias, H. K. Hall, Jr.,* and Stanley J. Brois†

C. S. Marvel Laboratories, Department of Chemistry, The University of Arizona, Tucson, Arizona 85721

Received November 1, 1988

α-(Phenylsulfonyl)maleic anhydride is synthesized by oxidation of α-(phenylthio)maleic anhydride. The title compound reacts extremely fast with isoprene, 2,3-dimethylbutadiene, and chloroprene to form the expected [4 + 2] cycloadducts. With cyclopentadiene, the endo adduct is formed, while with furan the exo adduct is obtained in an equilibrium reaction. With *p*-methoxystyrene and styrene, the double Diels–Alder adducts are obtained. Determination of the rate constant for the reaction of chloroprene with α-(phenylsulfonyl)maleic anhydride proves it is more reactive than tetracyanoethylene or α-(carbomethoxy)maleic anhydride.

Introduction

1,2-Disubstituted ethylenes are rather unreactive and sluggish in cycloaddition and copolymerization reactions. Maleic anhydride, however, is reactive in these reactions; its higher reactivity is ascribed to the minimization of the steric effect by confining the two substituents into a ring and also to the planar structure that permits effective resonance stabilization of radical and anionic intermediates and favors concerted cycloadditions.[1]

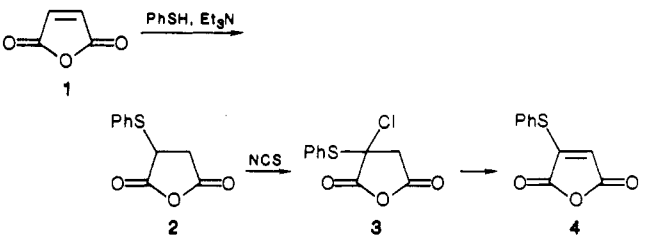
Our extensive study of the trisubstituted electrophilic ethylenes has shown that these are much more reactive than 1,2-disubstituted olefins. The unfavorable steric effects are overcome by the additional stabilization provided by the two α-substituents at the reactive center. Perfectly alternating copolymers of these trisubstituted olefins with electron-rich olefins are formed spontaneously, and cycloadducts are also frequently formed in these reactions.[2,3]

Accordingly, an electrophilically substituted maleic anhydride derivative should be especially reactive in reactions with electron-rich olefins. We have previously synthesized α-(carbomethoxy)maleic anhydride (CMA)[4] and studied its reactions with 1,3-dienes, styrenes, and vinyl ethers.[5] In these cycloaddition reactions, CMA proved to be much more reactive than tetracyanoethylene (TCNE).

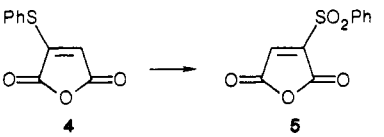
In the present work, we report the synthesis and reactions of another highly electrophilic maleic anhydride derivative, namely α-(phenylsulfonyl)maleic anhydride.

Results

Synthesis of α-(Phenylsulfonyl)maleic Anhydride. α-(Phenylthio)maleic anhydride is synthesized by using literature procedures. Nucleophilic addition of thiophenol to maleic anhydride (1) forms the sulfide **2**,[6] which is then chlorinated to **3**.[7] Elimination to the unsaturated sulfide **4** can be achieved with triethylamine, but is more conveniently accomplished by thermal elimination of HCl.[8] Oxidation of pure **4** with *m*-chloroperbenzoic acid affords



the desired sulfone **5** in 85% yield. An alternative procedure starts from acetylenedicarboxylic acid to which thiophenol is added in glacial acetic acid. The resulting α-(phenylthio)maleic anhydride is then oxidized using peracetic acid.[9]



α-(Phenylsulfonyl)maleic anhydride is a colorless crystalline solid, mp 170 °C, which is stable at room temperature in dry conditions.

Reactions with 1,3-Dienes. α-(Phenylsulfonyl)maleic anhydride (**5**) was reacted with isoprene, 2,3-dimethylbutadiene, and chloroprene in acetone at room temperature. The reactions were followed by NMR and TLC. The

† Paramins Division, Exxon Chemical Co., Linden, NJ 07036.

(1) Sauer, J.; Sustmann, R. *Angew, Chem., Int. Ed. Engl.* **1980**, *19*, 779.
(2) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *20*, 440.
(3) Hall, H. K., Jr.; Padias, A. B.; Pandya, A.; Tanaka, H. *Macromolecules* **1987**, *20*, 247.
(4) Hall, H. K., Jr.; Rhoades, J. W.; Nogues, P. *Polym. Bull.* **1981**, *4*, 629.
(5) Hall, H. K., Jr.; Nogues, P.; Rhoades, J. W.; Sentman, R. C.; Detar, M. *J. Org. Chem.* **1982**, *47*, 1451.
(6) Zienty, F. B.; Vineyard, B. D.; Schweppnik, A. A. *J. Org. Chem.* **1962**, *27*, 3140.
(7) Tuleen, D. L.; Marcum, V. C. *J. Org. Chem.* **1967**, *32*, 204.
(8) Kaydos, J. A.; Smith, D. L. *J. Org. Chem.* **1983**, *48*, 1096.
(9) Thaler, W. A.; Brois, S. J.; Hall, H. K., Jr. U.S. Pat. Appl. 174380 (1988).

0022-3263/89/1954-2852$01.50/0