methylpropyl)benzene. By a combination of peak intensities, sford, previously related assignments,[14] and the data for the 1,1-diphenyl-2,2-dimethylpropane above it was possible to assign each line in this spectrum as follows: (1) For the 1,1-diphenyl-2,2-dimethylpropyl group, 64.8 (C-1), 39.6 (C-2), 32.5 (CH_3), phenyl 147.2 (C-1), 126.9 (C-2,6), 131.4 (C-3,5), and 125.7 (C-4); (2) For the 1-phenyl-2,2-dimethylpropyl group, 63.8 (C-1), 35.1 (C-2), 29.2 (CH_3), phenyl 143.2 (C-1), 129.9 (C-2,6), 127.8 (C-3,5), and 126.0 (C-4); and finally for the benzene moiety, 140.4 (C-1), 128.4 (C-2,6), 130.9 (C-3,5), and 144.5 ppm (C-4).

Acknowledgment. Grateful acknowledgment is hereby extended to The Robert A. Welch Foundation for their support of this work.

Registry No. 1,1-Diphenyl-2,2-dimethylpropyl radical, 51974-45-9; 1,1-diphenyl-2,2-dimethylpropane, 38842-11-4; 1,1-diphenyl-2,2-dimethylpropyl dimer, 86943-05-7; 4-(1,1-diphenyl-2,2-dimethylpropyl)-1-(1-phenyl-2,2-dimethylpropyl)benzene, 86943-06-8.

High Pressure [4 + 2] Cycloaddition of Dichloromaleic Anhydride and Furan

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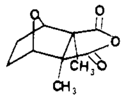
The total synthesis of cantharidine (1) has long been an intriguing pursuit, owing to its simple structure as well as its physiological properties. The obvious [4 + 2] Diels–Alder cycloaddition reaction between dimethylmaleic anhydride and furan was investigated as early as the 1920's;[1,2] however, such a direct synthetic approach failed, even at pressures as high as 42 000 atm.[3,4]



1

It was suggested that the failure of the [4 + 2] cycloaddition of dimethylmaleic anhydride to furan was a result of both electronic and steric factors. The electron-donating methyl groups of the dimethylmaleic anhydride decrease its dienophilicity and create a sterically hindered environment in the transition state. Efforts to utilize very high pressure in order to react furan and 2,5-dihydrothiophene-3,4-dicarboxylic anhydride led to the quantitative production of the cycloaddition adduct.[4] This work demonstrated for the first time that a single Diels–Alder reaction can generate the vicinally tetrasubstituted 7-oxabicyclo[2.2.1]heptenyl system.

It was suggested that another reason for the failure of the cycloaddition reaction between dimethylmaleic anhydride and furan was due to the aromaticity of furan (poor Diels–Alder diene). The cycloaddition products derived from furan are generally susceptible to thermal cycloreversion so as to prevent the use of high reaction temperatures.

Recently two groups have successfully shown that more reactive furan derivatives, isobenzofuran[5] and 3,4-dimethoxyfuran,[6] reacted quantitatively with dimethylmaleic anhydride to form mostly the exo-cycloaddition products. These furan derivatives possess excellent Diels–Alder reactivity owing to their favorable resonance stability. They are therefore able to overcome the steric effect during the course of the cycloaddition. These investigators[5,6] showed that suitable modifications, both in maleic anhydride and furan, overcome the electronic and/or steric problems, and the [4 + 2] cycloaddition will proceed to yield tetrasubstituted 7-oxabicyclo[2.2.1]heptenyl compounds.

In order to examine further this possibility, we investigated the reaction between dichloromaleic anhydride and furan.

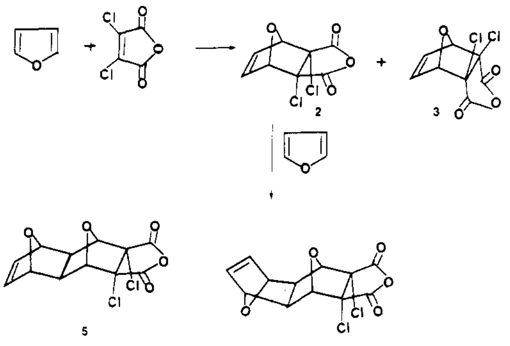
Results and Discussion

Dichloromaleic anhydride dissolved in excess furan was placed in a sealed tube and allowed to stand at room temperature. The solution gradually turned red and after 2 weeks became black. However, mostly unreacted dichloromaleic anhydride was recovered. When the same solution was heated at 80–90 °C, a black solid and hydrogen chloride were produced. After 3 days the dichloromaleic anhydride was converted quantitatively to the black material that did not dissolve in common organic solvents and did not melt, even at 350 °C.

The dichloromaleic anhydride–furan solution was pressurized to 5000 atm and heated at 50 °C for 15 h. A white solid product was isolated and purified (mp 224 °C). The analytical data for the compound showed that it corresponded to the endo, exo 1:2 adduct 4.

The tetrahydrofuran solution of dichloromaleic anhydride and furan in a 1:1 mole ratio was pressurized to 5000 atm and heated at 50 °C. The same 1:2 adduct was obtained in 22.4% yield and no detectable quantity of monoadduct was isolated.

These results suggest that the electron-withdrawing chloro groups of dichloromaleic anhydride increased its dienophilicity, and the application of high pressure overcame the steric hindrance. Thus, the reaction gave first the [4 + 2] cycloaddition product. Jurczak and co-workers[6] reported that the Diels–Alder reaction of 3,4-dimethoxyfuran and dimethylmaleic anhydride under high pressure yielded the exo-cycloaddition product and that no endo product was detected. Similarly, the reaction of dichloromaleic anhydride and furan may first form the exo 1:1 adduct 2, which may then be more reactive toward furan to produce the endo,exo 1:2 adduct 4. Another reason for the inaccessibility of the exo 1:1 adduct 2 may be due to the instability of this adduct at atmospheric pressure. Reaction of furan and dichloromaleic anhydride first proceeded to yield 2 under high pressure. However,



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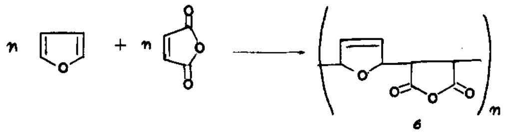
0022-3263/83/1948-3830$01.50/0

upon the release of high pressure the 1:1 adduct may undergo a retro-Diels-Alder reaction to yield the starting materials.

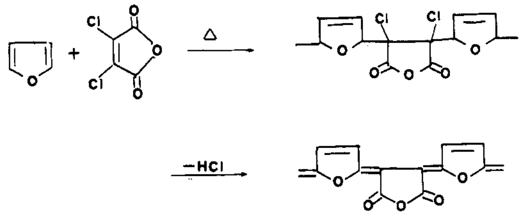
The configurational isomer exo,exo diadduct **5** was not detected, probably as a result of the great steric hindrance associated with the syn oxo configuration. The nonbonding lone pairs of electrons on both oxygens may constitute an undesirable steric interaction due to their close proximity in the exo,exo configuration. Therefore, the second furan molecule orients itself so that the oxygen atoms are anti to each other.

It is well-known that furan and maleic anhydride readily undergo the Diels-Alder reaction to form the cyclic adduct. However, the reaction also gives an alternating copolymer of structure **6** in the presence of a free-radical catalyst.[7,8]



6

When dichloromaleic anhydride in excess furan was heated under 1 atm of pressure in a sealed tube, polymerization was initiated and enhanced by the elimination of hydrogen chloride. The hydrogen chloride was readily eliminated due to the stabilization resulting from the π-electron conjugation associated with the growing polymer chain. The insolubility and infusibility of the black polymer obtained suggested that the polymer may either be high molecular weight or somewhat cross-linked.



Experimental Section

General Aspects. Infrared spectra were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer. Nuclear magnetic resonance spectra were recorded on a JEOL JNM-FX-90Q. Melting points were measured on an electrothermal apparatus and are uncorrected. High-pressure experiments were performed in Teflon capsules (3-mL capacity) in a stainless steel die and were compressed via a piston with a 200-ton hydraulic press.

Materials. Dichloromaleic anhydride and furan were purchased from Aldrich and purified by sublimation or distillation.

Reactions between Dichloromaleic Anhydride and Furan. Several reactions of dichloromaleic anhydride with furan were carried out under various conditions. A representative experiment follows. Dichloromaleic anhydride (5.0 g) dissolved in 30 mL of furan was placed in a sealed tube. After 2 weeks at room temperature, the solution turned a deep red color and a small amount of a black solid was isolated. The same solution (freshly prepared) was heated at 80-90 °C for 3 days. A black solid (3.5 g) was isolated and hydrogen chloride gas evolved from the solution as the tube was opened. The black material did not melt, even at 350 °C, and did not dissolve in organic solvents such as acetone, methylene chloride, benzene, and ethyl acetate. The chlorine content of the compound was found to be in the range of 0.1-2%. IR (KBr) 2950, 1740, 1600, 1250, 1000, 780 cm^{-1}.

Preparation of Endo,Exo Diadduct 4 of Dichloromaleic Anhydride with Furan. Dichloromaleic anhydride (0.85 g) dissolved in 3 mL of furan was pressurized to 5000 atm for 18 h at 50 °C. A red viscous solution was obtained and the liquid was removed under vacuum. The solid obtained was treated with ethyl acetate and a pale yellow solid (1.2 g) was obtained, mp 214-218 °C. The solid was recrystallized from acetone, mp 224 °C. Dichloromaleic anhydride (0.43 g) and furan (0.20 g) were dissolved in 3 mL of tetrahydrofuran and pressurized to 5000 atm at 50 °C for 20 h. The crude product (0.15 g) was isolated and purified by recrystallization (from acetone), mp 224 °C. The unreacted dichloromaleic anhydride (0.18 g) was recovered from the ethyl acetate solution and the monoadduct **2** or **3** could not be detected. White product **4**: mp 224 °C; IR (KBr) 3010, 2925, 1880, 1852, 1804, 1568 cm^{-1}; MS, m/e (relative intensity) 303 (73), 167 (100), 137 (30), 69 (80). Anal. Calcd for $C_{12}H_8O_5Cl_2$: C, 47.52; H, 2.64; Cl, 23.43. Found: C, 47.37; H, 2.70; Cl, 23.37; ^1H NMR ($Me_2(SO-d_6)$) δ 2.98 (2, m), 4.61 (2, s), 4.91 (2, m) 6.20 (2, t).[9]

Acknowledgment. This research was supported in part by a grant from Koppers Co., Inc.

Registry No. 4, 86969-99-5; dichloromaleic anhydride, 1122-17-4; furan, 110-00-9.

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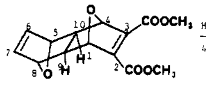
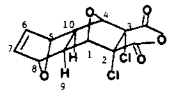
[8] Gaylord, N. G.; Maiti, S.; Patmiak, B. K.; Takahashi, A. *J. Macromol. Sci., Chem.* **1972**, *A6*, 1459.

[9] ^1H NMR spectra data for the endo,exo diadduct of dimethyl acetylenedicarboxylate with furan was reported[10] and these data were compared with those of **4**.

	Chemical Shifts (δ)				Coupling Constants J_{pq} (Hz)	
	H_1H_4	H_9H_{10}	H_5H_8	H_6H_7	5,6 7,8	5,10 8,9
	4.76	2.85	4.87	6.34	1.8	4.9
	4.61	2.98	4.91	6.20	1.7	4.8

[10] McCulloch, M. W.; Smith, D. G.; McInnes, A. G. *Can. J. Chem.* **1973**, *51*, 4125.

A New, Effective Catalytic System for Epoxidation of Olefins by Hydrogen Peroxide under Phase-Transfer Conditions

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Direct epoxidation of olefins by hydrogen peroxide is a long-standing goal in oxidation chemistry. This can be achieved only by means of suitable catalysts which are based mainly on group 5A,B and 6A,B metal oxides.[1,2] To date, however, valuable results in the case of simple, monosubstituted olefins have been obtained only by working under virtually anhydrous conditions.[3,4]

We now have found that the two-component association consisting of tungstate and phosphate (or arsenate) ions, under acidic conditions, represents a valuable catalytic

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[1] (a) Payne, G. B.; Williams, P. H. *J. Org. Chem.* **1959**, *24*, 54. (b) Reich, H. J.; Chow, F.; Peake, S. L. *Synthesis* **1978**, 299. (c) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689.

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[4] Dilute (30%) hydrogen peroxide has also been used for a highly selective epoxidation of terminal olefins (1-octene) in a triphase system, but a very low conversion has been attained.[2]