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Thermal reaction of 2,5-dimethylfuran (1) and ethyl propiolate (2) affords the Diels-Alder adduct (3) and seven additional products, all of which are derived from 3. The major products, depending on the conditions, are the *endo-exo* 2:1 diadducts (4 and 5) and two nortricyclenes (8 and 10). The last two products arise by homo Diels-Alder type dimerization of 3 (to give 10) and subsequent Diels-Alder retrogression (to give 8). The minor reaction products include a third nortricyclene (9), isomeric with 8.

ARCHIBALD WILSON MCCULLOCH et ALISTER GAVIN MCINNES. Can. J. Chem. 53, 1496 (1975). La réaction thermique du diméthyl-2,5 furanne (1) et du propiolate d'éthyle (2) conduit à l'adduit de Diels-Alder (3) et à sept produits additionnels qui sont tous dérivés de 3. Les produits majeurs, dépendant des conditions expérimentales, sont les diadduits *endo-exo* 2:1 (4 et 5) et les deux nortricyclènes (8 et 10). Les deux derniers produits proviennent d'une dimérisation du type homo Diels-Alder de 3 (pour donner 10) et d'une rétrogration Diels-Alder subséquente (pour donner 8). Les produits mineurs de la réaction incluent un troisième nortricyclène (9) isomère de 8. [Traduit par le journal]

Introduction

Although Diels-Alder reactions of substituted furans with esters of acetylenedicarboxylic acid have been thoroughly investigated (1-3), the corresponding reactions utilizing propiolic acid esters have received little attention. In recent communications we have described AlCl₃ acceleration of the reactions of 2-methyl-, 2-phenyl-, 2,5-dimethyl-, and 2,5-diphenylfuran with the latter type of dienophile. The adducts produced in this way were shown to rearrange readily in situ to substituted phenolic compounds (4, 5). In the present communication we wish to describe the results of an investigation of the thermal reaction of 2,5-dimethylfuran 1 and ethyl propiolate 2: this has revealed the high reactivity of the 2-carbethoxyoxanorbornadiene system.

Results and Discussion

The reaction of 1 and 2 at 95° proceeds slowly. In addition to the expected oxanorbornadiene adduct 3 we have isolated *seven* other products. These are the 2:1 diadducts 4 and 5, the cyclobutene 6, the β -carbethoxyfuran 7, and the nortricyclene derivatives 8, 9, and 10. The product composition is dependent on the initial reactant ratio, as well as reaction time and temperature (Table 1).

Adducts of type 3 are difficult to obtain. In fact 3 is the only 1:1 adduct of any furan with 2 as yet isolated. We have previously reported its formation (15%) via the AlCl₃-promoted reaction of 1 and 2 at -60° (5). The problem in obtaining such compounds is due to the lesser dienophilic reactivity of propiolate esters compared to esters of acetylenedicarboxylic acid and the susceptibility of the adducts to further reaction, as evidenced by their facile AlCl₃-catalyzed aromatization (5).

The results from Table 1, together with those derived from monitoring (p.m.r.) reactions between 1 and 2, and from several additional independent experiments (see Experimental), showed that the formation of all seven products in the present study can be traced to the initially formed Diels-Alder adduct 3. The reaction pathways involve (i) further Diels-Alder reaction of 3 with 1 (to give 4 and 5); (ii) homo Diels-Alder reaction of 3 with itself (to give 10) or with 2 (to give 8 and/or 9?); (iii) Diels-Alder retrogressions of 3 (to give 7) or of product 10 (to give 8); and (iv) 2 + 2 cycloaddition of 2 to 3 (to give 6). These transformations are summarized in Scheme 1. It is noteworthy that product 8 arises predominantly via dimerization

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Reaction	paramete	ers								
Reactant ratio	Time	Tempera- ture				Yields	• (%)		_	
1:2	(days)	(°C)	3	4	5	6	7	8	9	10
2:1	2	120†	_	_	20		1	62	_	
1:2	7	95‡	1.7	2.6	3.4	1.6	0.4	37	0.8	15
2:1	2	95†	3.6	23	4			7		3
2:1	7	95†	2.3	8	4		0.4	23	_	12
1:1	2	95†	11	18	1.4			14		8

TABLE 1 Effect of reaction parameters on product composition

*Yields were estimated by integration of the appropriate p.m.r. signals in the various column fractions. Isolated yields (see Experimental) are somewhat lower due to normal losses during separation and purification. †Yields based on 2. ‡Yields based on 1.



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Formation of diadducts 4 and 5 is not surprising since Diels-Alder additions of furans to oxanorbornadienes are well known (6-8). Thus, initial reaction of 3 with 1 affords 4, derived by addition at the activated double bond of 3. (Diadduct 4 is thermally unstable and when heated alone at 95° undergoes partial retrogression to 3 and 1.) Addition of 1 to 3 under more forcing conditions (120°) occurs at the less substituted double bond of 3 to give 5. Such behavior would be anticipated (see below) on the basis of previous work on related systems (6). An unexpected aspect of these additions, however, is their regioselectivity; we could not





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detect any stereoisomers of 4 or 5. Slee and LeGoff (8) have recently reported that analogous addition of 1 to oxanorborandiene 11 at 100° gives a low yield (10%) of diadduct 12 only.

The nortricyclenes 8, 9, and 10 (and the structurally related derivative 13, isolated from the thermal reaction of furan with 2(7), are the first such compounds to be derived from the oxanorbornadiene system, although similar compounds have been produced from norbornadienes (9-11). Although the most important route to 8 obviously involves dimerization of 3 to 10, we cannot completely rule out the possibility of direct homo Diels-Alder addition of 2 to 3. It may be that the minor isomer 9 is the product of such addition.² Direct 2,6-addition (107°/7 days) of 2 to methyl bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate 14 has been reported to give a 30% yield of 15 (9). This latter product may actually arise via an intermediate analogous to 10.

The 2 + 2 cycloadduct structure **6** has been tentatively assigned to one of our minor products on the basis of spectral evidence (see below). Its formation may be accounted for by an ionic cycloaddition mechanism similar to that proposed by Sasaki *et al.* (11) to explain their isolation of the cyclobutene **16** as a by-product (6%) from the reaction of norbornadiene with chlorocyanoacetylene.

Structures

The elucidation of the structures of the various reaction products was based primarily on their p.m.r. (Tables 2 and 3), i.r., and mass spectral properties (see Experimental). The monoadduct 3 has been isolated and characterized previously (5).

Diadducts 4 and 5

The p.m.r. spectrum (Table 2) of each of these compounds shows signals for one carbethoxyl and four methyl groups and for five other hydrogens, indicating an overall diadduct structure. In the case of 4 there are four olefinic (two AB quartets) and one methine hydrogen, indicating a diadduct formed by addition of 1 to the activated double bond of 3. In the spectrum of 5, on the other hand, there are signals for three olefinic (one at low field, deshielded by the carbethoxyl) and two methine (AB quartet) protons, an arrangement compatible only with a diadduct formed by addition of 1 to the less substituted double bond of 3.

No molecular ion is observed in either mass spectrum. The base peak in each case is at m/e

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 $^{^{2}}$ We were unable to detect any product analogous to 10 which could be postulated as a precursor of 9.

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TABLE 2. 60 MHz p.m.r. data for 4, 5, 6, and 7

			Chemic	cal shifts* (δ)	
Compound	$-CO_2CH_2CH_3$ (q)	$-CO_2CH_2CH_3$ (t)	—CH ₃ (s)		Ring junction —CH
4†	4.02	1.05	1.17, 1.44, 1.47, 1.55	Superimposed AB quartets: (i) centered at 6.16, $\Delta v_{ab} = 6.5$, $J_{ab} = 5.4$ Hz (ii) centered at 6.17 $\Delta v_{ab} = 3.9$, $J_{ab} =$ 5.6 Hz	3.00 (s)
5‡	4.23	1.30	1.43, 1.53, 1.57 (6H)	6.32 (2H, s), 7.02 (1H, s)	AB quartet centered at 2.55, $\Delta v_{ab} = 6.6$, $J_{ab} = 7.5$ Hz
6‡	4.15, 4.23	1.23, 1.30	1.47, 1.68	AB quartet centered at 6.33 , $\Delta v_{ab} = 12.8$, $J_{ab} = 5.4$ Hz; 7.20 (1H, d, $J \sim 0.8$ Hz)	2.95(1H, d, J ~ 0.8 Hz)
7‡	4.27	1.33	2.25 (b), 2.52	6.24 (bs, coupled to CH ₃)	

*b = broad, s = singlet, d = doublet, t = triplet, q = quartet. †In C₆D₆. ‡In CDCl₃.

96, reflecting the overwhelming tendency of these compounds to eliminate 1 by Diels-Alder retrogression.

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The assignment of endo-exo stereochemistry to both 4 and 5 was based on their p.m.r. spectra and the fact that such additions are kinetically favored (6). The expected mode of addition of 1to either double bond of 3 is to the oxygenbridged face of the latter (12). Thus two product configurations are likely in each case, namely endo-endo 17a (or b) and endo-exo 4 (or 5). The presence of signals for four nonequivalent olefinic hydrogens in the spectrum of 4 eliminates the symmetrical endo-endo isomer 17a in this case. It is impossible to assign endo-endo or endo-exo stereochemistry unequivocally to isomer 5 on the basis of its p.m.r. spectrum, which is compatible with either. However, all previous work in this (6, 7) and other (8) laboratories indicates that the kinetically favored diadducts possess endo-exo stereochemistry. Supporting evidence for this assignment in the case of 5 is derived from the chemical shift of the ringjunction hydrogens (quartet, $\Delta v_{ab} = 6.6$ Hz, centered at 2.55 δ), which is close to that (2.72 δ) of the corresponding hydrogens in 12 (8).

Nortricyclenes 8, 9, and 10

The mass and p.m.r. spectra of 8 indicate a product derived from one molecule of 1 and two of 2. The p.m.r. spectrum (Table 3) shows

signals for four single hydrogens, only one of which appears in the olefinic region. The chemical shifts of the three methine protons are in accord with those of similar hydrogens in related compounds (7, 9, 11). Two of these protons have approximately the same chemical shift, suggesting that they occupy similar environments (H-1, H-5), while the third is located at high field, consistent with it being on a cyclopropane ring. Moreover, the chemical shift of the vinylic hydrogen is consistent with deshielding by a carbethoxyl group and is very similar to that of the corresponding proton in 15 (9). In addition it is vicinally coupled to only one hydrogen. As expected, the chemical shifts of the two bridgehead methyl groups are significantly different. Verification of the structure was provided by the ¹³C n.m.r. spectrum. We have reported full ¹³C data for 8 (and 13) elsewhere (7).

The spectral properties of compound 9 are, as expected, very similar to those of its isomer 8. The main points of difference, leading to the assignment of structure 9 are in the chemical shifts and multiplicities of H-1 and H-5 (Table 3). These changes reflect the new position of the olefinic proton in 9. The hydrogen at C-1, now subject to the deshielding effect of a second carbethoxyl group and no longer vicinal to any other hydrogen, appears as a narrow triplet at 3.49 δ (a downfield shift relative to the same

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					Chemical shifts* (δ)			
Compound	$\begin{array}{c} -\text{CO}_2\text{CH}_2\\ \text{CH}_3 \left(q \right) \end{array}$	$-CO_2CH_2$ $CH_3(t)$		Ring junction CH	=CH	H-1	H-4	H-5
œ	3.90, 4.02	0.90, 1.00	1.03, 1.81	1	7.16(q, H-7) $J_{1,7} = 3.6, J_{5,7} = 1.1 \text{ Hz}$	2.90(q) $J_{1,7} = 3.6,$ $J_{1,5} = 0.9 \text{ Hz}$	2.27(d) $J_{4,5} = 2.0 \text{ Hz}$	3.07(quintet) $J_{4,5} = 2.0,$ $J_{5,7} = 1.1,$ $J_{1,5} = 0.9 \text{ Hz}$
6	3.98, 4.10	0.99, 1.05	1.01, 1.84	I	6.90(q, H-6) $J_{5,6} = 3.6$, $J_{1,6} = 1.0 \text{ Hz}$	3.49(t) $J_{1,5} = 1.1$, $J_{1,6} = 1.0$ Hz	2.04(d) <i>J</i> _{4,5} = 1.9 Hz	2.24(m) $J_{5,6} = 3.6,$ $J_{4,5} = 1.9,$ $J_{1,5} = 1.1$ Hz
10	3.89, 4.07	0.97, 1.03	1.38, 1.66, 1.77, 1.90	3.02(s)	AB quartet centered at 5.96, $\Delta V_{ab} = 4.0$, $J_{ab} = 5.6$ Hz	2.50(s)	1.75(d) $J_{4,5} = 1.8$ Hz (partially obscured by CH ₃)	2.35(d) J _{4,5} = 1.8 Hz
*s = singlet, (f = doublet, t = 1	triplet, q = quarter	t, m = multiplet.					

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TABLE 3. 60 MHz p.m.r. data for nortricyclenes 8, 9, and 10 (in C_6D_6)

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proton in 8 of 0.59 p.p.m.). The hydrogen at C-5, on the other hand, which is now coupled vicinally to two other hydrogens but is no longer deshielded by an adjacent carbethoxyl, is observed as a broad multiplet centered at 2.24 δ (an upfield shift of 0.83 p.p.m.).

The weak molecular ion at m/e 388 and base peak at m/e 96 indicate that compound 10 is a 2:2 product from which 1 may be readily lost. Infrared absorptions at 1737 and 1718 cm⁻¹ suggest two quite different types of ester group. The p.m.r. spectrum of 10 (Table 3) shows signals for two carbethoxyl and four *C*-methyl groups, an AB quartet for two olefinic hydrogens, and signals for four single methine hydrogens (at 1.75, 2.36, 2.50, and 3.02 δ). The signal at highest field was assigned to the cyclopropyl



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hydrogen H-4: this is coupled (J = 1.8 Hz) to the hydrogen resonating at 2.36 δ which can therefore be assigned to H-5. Since H-1 and H-5 are located in similar environments, the remaining signals may be assigned to H-1 (2.50 δ) and the ring-junction hydrogen (3.02 δ). The lack of coupling between the latter two protons necessitates that the dihedral angle between them approximates 90° and allows assignment of stereochemistry **18** or **19**. The latter configuration, however, would require approach of the diene component to the face of the dienophile opposite to the oxygen bridge. Such an approach is unlikely on steric grounds (6, 12).

Compound 6

The molecular ion of this compound is at m/e 292 indicating a 1:2 product. The p.m.r. spectrum (Table 2) shows two nonequivalent carbethoxyl groups and two nonequivalent C-methyl groups, together with an AB quartet for two olefinic hydrogens and two one-proton doublets ($J \approx 0.8$ Hz), one due to a methine (2.95 δ) and the other to an olefinic (7.20 δ) hydrogen. The i.r. spectrum shows absorptions in the carbonyl region at 1727 and 1737 cm^{-1} , in accord with the presence of both conjugated and saturated ester groups. The cyclobutene ring is assigned an exo relationship to the bridged ring since approach in this direction is known to be least sterically hindered (12). The available evidence is equally consistent with cyclobutene structure 20. However, the requirements of the proposed ionic cycloaddition mechanism (cf. 11) would favor 6.

Compound 7

The mass spectrum indicates a molecular weight of 168 and the p.m.r. spectrum (Table 2) shows characteristic signals for one carbethoxyl and two *C*-methyl groups, and for one single hydrogen in the olefinic region. Confirmatory evidence for the furan structure is provided by the chemical shifts of the hydrogens of the two ring methyl groups and the magnitude of the coupling (~ 1 Hz) between the hydrogens of one of these groups (2.25 δ) and the adjacent ring hydrogen (6.24 δ).

Experimental

The p.m.r. spectra were recorded on a Varian A-60A spectrometer equipped with a V-6058A spin decoupler, using tetramethylsilane as internal standard. The i.r. spectra were obtained in CCl_4 solution on a Perkin-Elmer 521 spectrometer and the mass spectra with a

Dupont-C.E.C. 21-491 spectrometer. Unless stated otherwise the source of heat used in all reactions was a steam bath. Column chromatography was performed on Mallinckrodt silicic acid, 100 mesh, using CHCl₃ to elute. For preparative thin-layer chromatography (p.l.c.) Merck silica gel HF-254 (1.5 mm layers) was used, with CHCl₃ to elute.

Reaction of 2,5-Dimethylfuran 1 with Ethyl Propiolate 2 General Procedure

The reaction of 1 and 2 was carried out under varying conditions (Table 1) using the following procedure. A mixture of 1 and 2 was heated and at the end of the desired reaction period unreacted starting materials were removed by azeotroping with EtOH. The oily residue obtained was then submitted to column chromatography. The products eluted in the following order: 7, 8, 3, 9, 6, 10, 5, and 4.

(A) A reaction mixture of 1 (6.98 g, 0.073 mol) and 2 (3.67 g, 0.037 mol) was maintained at reflux for 48 h (heating mantle). Obtained as products. (i) compound 7 as a pale yellow oil (0.060 g, 1%), n_p^{23} 1.4690; parent ion at m/e 168 (51%) ($C_9H_{12}O_3$ requires 168), base peak at m/e 43, strong ions at m/e 139 (77%) and 123 (70%); v_{max} 1717 cm⁻¹; (ii) compound 8 as a pale yellow oil (3.34 g, 62%), n_p^{25} 1.4844; parent ion at m/e 292 (5%) ($C_{16}H_{20}O_5$ requires 292), base peak at m/e 43, strong ions at m/e 249 (17%), 247 (11%), 246 (12%), 221 (12%), 219 (22%), 218 (11%), 204 (10%), 176 (7%), 175 (9%), 173 (10%), 152 (13%), 147 (12%), 139 (13%), 96 (32%); and 77 (16%); v_{max} 1715, 1721 cm⁻¹; (iii) an oil (2.40 g), containing ca. 90% compound 5 (ca. 19%). The pure compound was obtained by repeated p.l.c. as a pale yellow oil, n_p^{26} 1.4813. No parent ion was observed, base peak at m/e 96, strong ions at m/e 168 (7%), 139 (7%), and 43 (29%); v_{max} 1713 cm⁻¹.

(B) From a reaction of 1 (9.6 g, 0.10 mol) and 2 (19.6 g, 0.20 mol) at 95° for 7 days were obtained: (i) an oil (1.14 g), mainly 8, contaminated by a small amount of 7; (ii) pure 8 (1.90 g); (iii) an oil (6.01 g), mainly 8 but contaminated by 3; (iv) an oil (0.340 g), which on p.l.c. gave compound 9 as a pale yellow oil (0.076 g, 0.3%), $n_{\rm D}^{26}$ 1.4888; parent ion (very weak) at m/e 292 (C₁₆H₂₀O₅ requires 292), base peak at m/e 43, strong ions at m/e 249 (23%), 246 (27%), 221 (18%), 200 (53%), 175 (16%), 173 (23%), and 77 (23%); v_{max} 1717 (sh), 1721 cm⁻¹; (v) an oil (1.128 g), which on repeated p.l.c. gave compound 6 (0.368 g, 1.3%) as a pale yellow oil, n_D^{26} 1.4911; parent ion at m/e 292 (48%) (C16H20O5 requires 292), base peak at m/e 218, strong ions at m/e 248 (16%), 247 (25%), 219 (26%), 203 (68%), 190 (30%), 175 (48%), 173 (68%), 96 (74%), and 43 (74%); v_{max} 1727, 1737 (sh) cm⁻¹ This fraction also afforded compounds 9 (0.061 g, 0.2%) and 10 (0.418 g, 2.2%); (vi) compound 10 (1.174 g, 9.1%) as a pale yellow oil, $n_{\rm D}^{25}$ 1.6553; parent ion (very weak) at m/e 388 (C₂₂H₂₈O₆ requires 388), base peak at m/e 96, strong ions at m/e 249 (30%), 227 (13%), 178 (33%), and 43 (88%); v_{max} 1718, 1737 cm⁻¹; (vii) an oil (0.765 g), which on p.l.c. gave a mixture (0.599 g, 4.2%) of 4 and 5 in an approximate ratio of 3:5.

(C) From a reaction of 1 (6.98 g, 0.073 mol) and 2 (3.67 g, 0.037 mol) at 95° for 48 h were obtained: (i) a yellow oil (3.68 g), repeated p.l.c. of which gave (a) compound 8 (0.342 g, 6%), (b) compound 3 (0.260 g, 3.6%), identical to material obtained previously (5), and (c)

compound 4 (1.634 g, 15%) as an oil which gradually crystallized, m.p. $40-43^{\circ}$; no parent ion was observed, ion of highest mass at m/e 217 (3%) ($M - CO_2Et$), base peak at m/e 96, strong ions at m/e 201 (3%), 159 (3%), 152 (4%), 149 (3%), 81 (6%), 77 (4%), and 43 (39%); v_{max} 1711, 1738 cm⁻¹; (*ii*) an oil (2.06 g), p.l.c. of which gave (a) compound 10 (0.162 g, 2%) and (b) a mixture of 4 and 5 (1.14 g, 11%) in a ratio of 7:4.

(D) Two other reactions were performed, both at 95°. One used a 1:1 (2 days) and the other a 2:1 (7 days) reactant ratio. The product compositions of these and of reactions A-C above were estimated by integration of the appropriate p.m.r. signals in the various column fractions and are summarized in Table 1.

(E) A reaction of 1 (9.6 g, 0.1 mol) and 2 (19.6 g, 0.2 mol) at 95° was monitored daily by p.m.r. for 1 week. This showed that 3 and 4 were the major products initially, and that the amounts of 8 and 10 increased with time, at the expense of 3 and 4.

Retrogression of Compound 4

A sample of pure $\overline{4}$ was heated at 95°. Thermal breakdown to a mixture of 3 and 1 of 12% (1 h) and 25% (4 h) was observed (p.m.r.).

Attempted Reaction of 8 with 1

Equimolar amounts of 8 and 1 were heated at 95° for 48 h. Compound 8 remained unreacted, the only change being some oxidative breakdown of 1.

Dimerization of 3 to Compound 10

(a) Attempted Reaction of 3 with 2

Equimolar amounts of 3 and 2 were heated at 95° ; p.m.r. showed that 2 remained unreacted while 3 was converted to 10 (10:3 = 1:1 after 3 h, = 3:1 after 9 h). Small amounts of 8 were also formed. There was also evidence of considerable polymerization.

(b) Reaction of 3 with 1

Equimolar amounts of 3 and 1 were heated at 95° . After 2.5 h the molar ratio of products (p.m.r.) was 3:4:10 = 7:2:4. No 5 was observed. After 7 h only a trace of 3 remained, the major products being 10 and 4 (approximate ratio 2:1).

(c) Direct Thermolysis of 3

A 100 mg sample of 3 was heated at 95° for 21 h. Repeated p.l.c. (1% MeOH-CHCl₃) gave compounds 8 (10 mg) and 10 (27 mg, 27%).

Retrogression of 10: Formation of Compound 8

A pure sample of 10 was heated on an oil bath maintained at 120°. Smooth conversion to 8 (20% in 2 h, 50% in 6 h, 80% in 12 h) was observed (p.m.r.). The reaction was significantly slower at 95°.

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