Diels-Alder Reactions of 2-Pyrones. Direction of the Addition Reaction with Acetylenes[1a]

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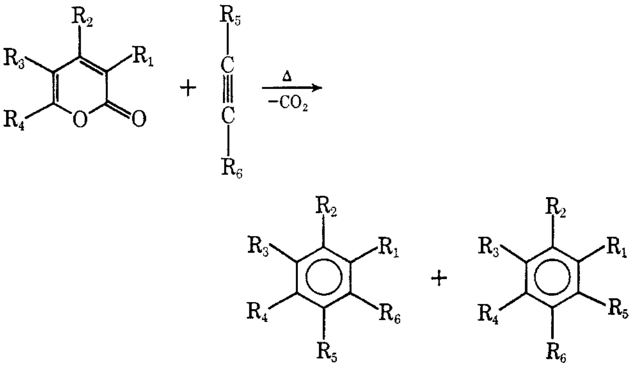
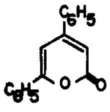
The Diels-Alder reactions of unsymmetrically substituted acetylenes with 2-pyrones containing unsymmetrically substituted diene fragments reveal varying degrees of stereoselectivity with regard to the direction of addition, depending on the positions and types of substituents. Extended Hückel MO calculations of the net charge distribution on the reactants can be used to predict the direction of addition when phenylacetylene is the dienophile, but the method is not general when methyl propiolate is the dienophile.

Diels-Alder reactions of 2-pyrones with acetylenes produce benzene derivatives by loss of carbon dioxide from the intermediate adduct.[2] Alder and Rickert initially reported the reactions of 5-carbomethoxy-2-pyrone, 4,6-dimethyl-5-carbomethoxy-2-pyrone, and 4-hydroxy-6-methyl-2-pyrone with diethyl acetylenedicarboxylate.[2] The methyl or ethyl diesters of acetylenedicarboxylic acid have also been employed as dienophiles in reactions with 4-methoxy-6-methyl-,[3] 6-carbomethoxy-,[4] 4,5-diphenyl-,[5] 3-methyl-4-ethyl-,[6] 3-methyl-4-propyl-,[6] 3-methyl-4-*n*-butyl-,[6] and 3,5,6-trimethyl-2-pyrones.[7] 5-Carbomethoxy-2-pyrone, 5-methyl-2-pyrone, and 2-pyrone itself undergo this reaction with bis(trimethylstannyl)acetylene.[8] 2-Pyrone also reacts with phenyltrimethylstannylacetylene and bis(trimethylsilyl)acetylene,[8] with an unusual rearrangement occurring in the latter case. With this last exception, the Diels-Alder reaction in each of these examples has given rise to a single benzene derivative since either the acetylene or the diene fragment of the 2-pyrone was symmetrically substituted. When the acetylene and the diene fragment are both unsymmetrically substituted, however, the possibility of forming two isomeric benzene derivatives exists. One such reaction has been reported,[9] but only one isomer was formed.



In the interest of preparing phenylated polyphenylenes from bis-2-pyrones and diethynylbenzenes, model reactions of phenylated and unphenylated 2-pyrones with acetylenic dienphiles were studied to examine relative reactivities and stereochemical preferences. Accordingly, 4,6-diphenyl-[10] (**1**), 4,5,6-triphenyl-[11] (**2**), 5-carbomethoxy-[12] (**3**), 4,5-diphenyl-[5] (**4**), and 3-carboethoxy-2-pyrone[13] (**5**) were prepared. Their reactions with one or more of the following dienophiles: maleic anhydride (**6**), N-phenylmaleimide (**7**), dimethyl acetylenedicarboxylate (**8**), methyl or ethyl propiolate (**9**), diphenylacetylene (**10**), and phenylacetylene (**11**), were carried out.



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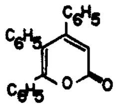

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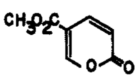

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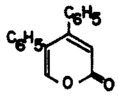

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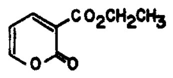

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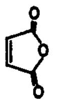

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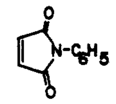

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$CH_3O_2CC{\equiv}CCO_2CH_3$

8

$HC{\equiv}CO_2R$, R = $-CH_3$, $-CH_2CH_3$

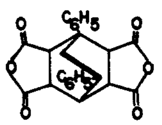
9

$C_6H_5C{\equiv}CC_6H_5$

10

$C_6H_5C{\equiv}CH$

11



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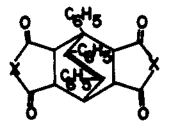

13, X = O

14, X = N-C_6H_5

Results

Pyrones **1** and **2** react with **6**, and **2** with **7** in refluxing xylene, to form the crystalline double adducts **12-14**, respectively. Dimethyl 3,4,5-triphenylphthalate (**15**)

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[1] (a) Supported in part by the U. S. Army Research Office, Durham, N. C. (b) To whom communications regarding this paper should be sent.

[2] K. Alder and H. Rickert, *Ber.*, **70**, 1354 (1937).

[3] J. Bu'Lock and H. Smith, *J. Chem. Soc.*, 502 (1960).

[4] E. Wenkert, D. Johnston, and K. Dave, *J. Org. Chem.*, **29**, 2534 (1964).

[5] A. Padwa and R. Hartman, *J. Amer. Chem. Soc.*, **88**, 1518 (1966).

[6] N. Shusherina, R. Levina, and V. Shostakovskii, *Zh. Obshch. Khim.*, **29**, 3237 (1959); *Chem. Abstr.*, **54**, 13057*g* (1960).

[7] N. Dmitrieva, A. Shil'nikova, N. Shusherina, and R. Levina, *Zh. Obshch. Khim.*, **34**, 2835 (1964); *Chem. Abstr.*, **61**, 16042*f* (1964).

[8] A. Evnin and D. Seyferth, *J. Amer. Chem. Soc.*, **89**, 952, 4793 (1967).

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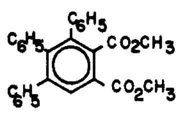
[10] F. Feist, H. Pauschardt, and H. Dibbern, *Ber.*, **58B**, 2311 (1925).

[11] S. Ruhemann, *J. Chem. Soc.*, **97**, 459 (1910).

[12] J. Boyer and W. Schoen, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 532.

[13] T. Windholz, L. Peterson, and G. Kent, *J. Org. Chem.*, **28**, 1443 (1963).

is produced from **2** and **8**, also in refluxing xylene. The reactions of **3**[2] and **4**[5] with **8** have been reported. Pyrones **1** and **2** react in refluxing xylene with **9** (R = CH_3) to form methyl 2,4-diphenylbenzoate (**16**) and methyl 2,3,4-triphenylbenzoate (**17**), respectively, while **3** and **9** (R = CH_3) yield a 3:2 mixture of dimethyl terephthalate (**18**, R = CH_3) and dimethyl isophthalate (**19**, R = CH_3) under the same conditions.



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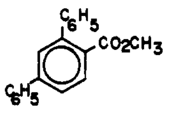

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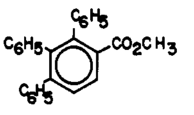

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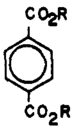

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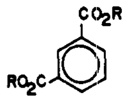

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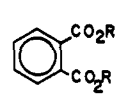

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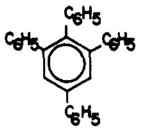

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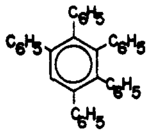

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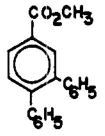

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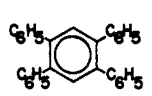

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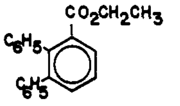

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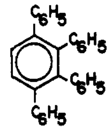

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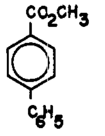

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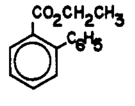

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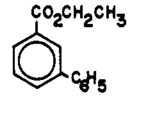

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The dienophiles **10** and **11** require stronger conditions (200–300°, sealed tube) for reaction. Under these conditions, **1–5** react with **10** to form 1,2,3,5-tetraphenylbenzene (**21**), pentaphenylbenzene (**22**), methyl 3,4-diphenylbenzoate (**23**), 1,2,4,5-tetraphenylbenzene (**24**), and ethyl 2,3-diphenylbenzoate (**25**), respectively. Pyrone **2** and **11** yield both **21** and 1,2,3,4-tetraphenylbenzene (**26**) in an approximately 1:5 ratio, while **3** and **11** yield methyl 4-phenylbenzoate (**27**). The reaction of **5** and **11** yields a 2:1 mixture of ethyl 2-phenylbenzoate (**28**) and ethyl 3-phenylbenzoate (**29**), while **5** and **9** (R = CH_3CH_2) yield a 4:1 mixture of diethyl isophthalate (**19**, R = CH_3CH_2) and diethyl phthalate (**20**, R = CH_3CH_2).

The reactions of **5** are in contrast to an earlier report that electron-withdrawing substituents such as nitro, sulfo, or carboxyl groups in the 3 position of the 2-pyrone ring completely deactivate the diene system, making it inert to the diene synthesis.[14] Compound **5** and its 6-methyl and 6-phenyl derivatives have also been shown to undergo diene syntheses with ethylene, to yield double adducts.[15]

Discussion

The olefin dienophiles maleic anhydride (**6**), N-phenylmaleimide (**7**), and the acetylenes (**8**, **9**) containing carboxylic acid functions react with pyrones under much less vigorous conditions than those required for phenyl-substituted acetylenes. The results summarized in Table I indicate that the direction of addition in these reactions, where a choice is available, is similar to that observed for unsymmetrically substituted butadienes.[16] The relative energies of activation with respect to the direction of addition may be a result of polar attraction between the diene and the dienophile, steric effects, or a combination of these. The fact that dienophiles substituted with highly polar groups react more readily suggests that polar attraction is an important factor in determining the direction of addition.

In order to assess the influence of the polar nature of the reactants, charge distributions on 2-pyrone (**30**), 5-carbomethoxy-2-pyrone (**3**), 3-carbomethoxy-2-pyrone (**5**), methyl propiolate (**9**), and phenylacetylene (**11**) were calculated with an iterative extended Hückel computer program.[17] Coulomb integrals H_{ii} were obtained from the valence-state ionization potentials[18] and were adjusted for charge with Cusachs' B term in the equation $H_{ii} = H^0_{ii} - Bq_i$, where H_{ii} is the adjusted Coulomb integral, q_i the charge, and B the parameter for each particular orbital of each element.[19] The resonance integrals were calculated according to the Wolfsberg–Helmholz geometric mean[20] with $K = 1.75$.[17] Orbital exponents were taken from tables by Clementi and Raimondi[21] and were not adjusted for charge. The hydrogen exponent was set at 1.20. In order to correct excessive charge buildup at the more electronegative oxygen atoms, the Hamiltonian matrix elements were iterated using a damping technique to a set of self-consistent matrix elements and charges. Through the equation $q_i = (\lambda q_{i-1} + C_i)/(1 + \lambda)$ ($\lambda = 9.0$), the newly calculated charges C_i are damped and q_i is used to calculate the new H_{ii}. This is repeated until the charge distribution no longer changes more than 0.05 on iteration. Where the bond distances and angles for the compounds had not been experimentally determined, they were obtained from the angles and distances listed for similar compounds and/or functional groups.[22] The following electron densities were obtained.

The net atomic charge has been successfully used as a reactivity index in aromatic substitution.[23-25] The close agreement between the experimental dipole moment and that calculated from the extended Hückel program lends support to the use of the net atomic charges as representative isolated molecule reactivity

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(14) N. Shusherina, N. Dmitrieva, E. Luk'yanets, and R. Levina, *Usp. Khim.*, **36**, 436 (1967).

(15) F. Baker and L. Stock, *J. Org. Chem.*, **32**, 3344 (1967).

(16) A. S. Onishchenko, "Diene Synthesis," Israel Program for Scientific Translations, Ltd., Jerusalem, 1964, pp 22–34.

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(19) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, **43**, s160 (1965).

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(24) H. H. Greenwood and R. McWeeney, *Advan. Phys. Org. Chem.*, **4**, 73 (1966).

(25) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 288–297.

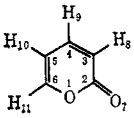
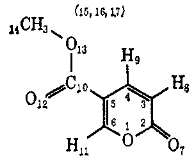
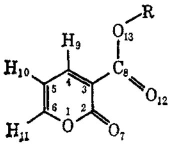
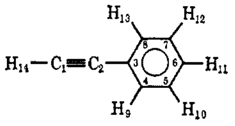
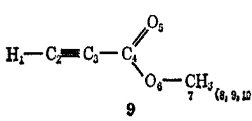
TABLE I

DIELS–ALDER REACTIONS BETWEEN ASYMMETRICALLY SUBSTITUTED 2-PYRONES AND ACETYLENES

Diene	Dienophiles	Product(s) (yield, %, and ratio)
1	**9**, R = CH_3	Methyl 2,4-diphenylbenzoate (**16**) (70)
2	**9**, R = CH_3	Methyl 2,3,4-triphenylbenzoate (**17**) (55)
2	**11**	1,2,3,4- and 1,2,3,5-tetraphenylbenzenes (**26** and **21**) (38.9, 5:1)
3	**9**, R = CH_3	Dimethyl isophthalate and dimethyl terephthalate, (**19** and **18**) (40, 2:3)
3	**11**	Methyl 4-phenylbenzoate (**27**) (60)
5	**9**, R = CH_3CH_2	Diethyl phthalate and diethyl isophthalate (**20** and **19**) (50, 1:4)
5	**11**	Ethyl 2- and 3-phenylbenzoates (**28** and **29**) (60, 2:1)

TABLE II

NET ATOMIC CHARGES

Compd	Atom, charge		
 30	1, −0.275	5, 0.041	9, 0.050
	2, 0.183	6, 0.104	10, 0.056
	3, 0.048	7, −0.398	11, 0.087
	4, 0.043	8, 0.060	
		Total charge −0.001	
 3	1, −0.233	7, −0.359	13, −0.256
	2, 0.231	8, 0.045	14, 0.108
	3, 0.048	9, 0.040	15, 0.059
	4, 0.048	10, 0.230	16, 0.060
	5, 0.082	11, 0.068	17, 0.060
	6, 0.125	12, −0.360	
		Total charge −0.004	
 5 (R = CH_3) 14 (15,16,17)	1, −0.256	7, −0.380	13, −0.295
	2, 0.212	8, 0.200	14, 0.101
	3, 0.110	9, 0.064	15, 0.072
	4, 0.074	10, 0.062	16, 0.075
	5, 0.055	11, 0.094	17, 0.075
	6, 0.120	12, −0.387	
		Total charge −0.004	
 11	1, −0.079	6, −0.020	11, 0.027
	2, −0.052	7, −0.017	12, 0.027
	3, 0.008	8, −0.011	13, 0.030
	4, −0.011	9, 0.030	14, 0.056
	5, −0.017	10, 0.027	
		Total charge −0.002	
		μ(calcd) 0.90 D	
		μ(obsd) 0.72–0.84 D[a]	
 9	1, 0.080	6, −0.298	
	2, 0.008	7, 0.104	
	3, 0.033	8, 0.070	
	4, 0.207	9, 0.072	
	5, −0.350	10, 0.073	
		Total charge −0.001	

[a] A. L. McClellan, "Tables of Experimental Dipole Moments," Freeman and Co., San Francisco , Calif., 1963.

indices. The net atomic charges calculated (Table II) can be used to correctly predict the direction of addition of phenylacetylene to **2**, **3**, and **5**. Alignment of the reactants, so that the most electronegative (terminal) carbon in phenylacetylene and the most electropositive carbon in the corresponding pyrone form the new bond, predicts the product and allows the greatest dissipation of charge in the formation of the new bond. In the calculation, pyrone itself was taken as a model for both the phenyl-substituted pyrones **1** and **2** on the assumption that the phenyl groups would not alter the net atomic charges on the pyrone ring.

In the case of the reaction of **2** with **11**, however, product **26** is predicted while in fact a mixture of **26** and **21** is obtained (5:1). In the reaction of **5** with **11**, there is a slight difference in the charges on atoms 3 and 6 of **5**, but product **28**, which is formed in the greatest amount, is that which is predicted. The reaction of **3** with **9** yields mostly **18**, and the reaction of **5** with **9** affords two isomers. However, isomers obtained from the reactions of **1** and **2** with **9** are not those which would be expected from a consideration of charges.

The extended Hückel method neglects steric factors, so that this contribution cannot be evaluated easily. For the reactions of methyl propiolate with dienes, calculation of the energies of activation of the transition state leading to the two isomers would probably provide a more suitable answer.

Experimental Section

Reactants.—Pyrones 1,[10] 2,[11] 3,[12] 4,[5] and 5[13] were synthesized according to published procedures, as was diphenylacetylene (10).[26] The dienophiles 6–9 and 11 were obtained commercially. Reagent grade xylene and toluene were used as solvents. Nmr spectra were run on a Varian A60A spectrometer; microanalyses were peroformed by Micro-Tech Laboratories, Inc., of Skokie, Ill. Melting points are uncorrected.

1,3-Diphenyl-2-bicyclo[2.2.2]octene-5,6,7,8-tetracarboxylic Dianhydride (12).—A solution of 1.5 g (6.0 mmoles) of 4,6-diphenyl-2-pyrone[10] and 1.2 g (12 mmoles) of maleic anhydride in 20 ml of xylene was heated at reflux for 8 hr. After cooling, the solid product was collected and recrystallized from toluene. The yield of the product, mp 322–325°, was 0.83 g (35%). *Anal.* Calcd for $C_{24}H_{16}O_6$: C, 72.00; H, 4.00. Found: C, 71.75; H, 4.05.

1,2,3-Triphenyl-2-bicyclo[2.2.2]octene-5,6,7,8-tetracarboxylic Dianhydride (13).—4,5,6-Triphenyl-2-pyrone[11] (3.0 g, 9.0 mmoles), maleic anhydride (1.9 g, 20 mmoles), and 55 ml of xylene were heated at reflux for 24 hr. The solid product was recrystallized from toluene to yield 1.9 g (44%) of product, mp 333–334°. *Anal.* Calcd for $C_{30}H_{20}O_6$: C, 75.63; H, 4.20. Found: C, 75.63; H, 4.37.

1,2,3-Triphenyl-2-bicyclo[2.2.2]octene-5,6,7,8-tetracarboxylic Di(N-phenyl)imide (14).—A solution of 2.0 g (6.0 mmoles) of 4,5,6-triphenyl-2-pyrone[11] and 2.1 g (12 mmoles) of N-phenylmaleimide in 50 ml of xylene was heated at reflux for 14 hr. The solid product, 2.2 g (60%) after recrystallization from toluene, had mp 330–332°. *Anal.* Calcd for $C_{42}H_{30}O_4N_2$: C, 80.51; H, 4.79. Found: C, 80.80; H, 5.03.

Dimethyl 3,4,5-Triphenylphthalate (15).—Dimethyl acetylenedicarboxylate (2.0 g, 14 mmoles) and 4,5,6-triphenyl-2-pyrone (2.0 g, 6.0 mmoles) were heated at reflux in 50 ml of xylene for 46 hr. Removal of solvent under vacuum left dimethyl 3,4,5-triphenylphthalate, which, after recrystallization from methanol, yielded 1.8 g (75%), mp 174–176° (lit.[27] mp 174–175°).

Methyl 2,4-Diphenylbenzoate (16).—A solution of 0.52 g (2.1 mmoles) of 4,6-diphenyl-2-pyrone[10] and 0.4 g (4.2 mmoles) of methyl propiolate in 10 ml of xylene was heated at reflux for 60 hr. Removal of solvent left a gummy solid. On several extractions with small portions of Skellysolve BX and after recrystallization from Skellysolve BX 0.43 g (70%) of methyl 2,4-diphenylbenzoate, mp 76–78° (lit.[28] mp 75.5–76°), was obtained.

Methyl 2,3,4-Triphenylbenzoate (17).—4,5,6-Triphenyl-2-pyrone[11] (1.5 g, 4.6 mmoles) and methyl propiolate (0.50 g, 6.0 mmoles) were heated at reflux for 22 hr. Cooling precipitated 0.6 g of starting pyrone. Concentration of the mother liquor yielded 0.56 g (55%) of methyl 2,3,4-triphenylbenzoate, mp 147–149°, after recrystallization from methanol (lit.[27] mp 141.5–142.5° for methyl 3,4,5-triphenylbenzoate). The nmr spectrum showed an AB quartet centered at δ 7.7 in accordance with the assigned structure of methyl 2,3,4-triphenylbenzoate. *Anal.* Calcd for $C_{26}H_{20}O_2$: C, 85.71; H, 5.49. Found: C, 85.47; H, 5.62.

Dimethyl Terephthalate (18) and Dimethyl Isophthalate (19).—A solution of 0.79 g (5.0 mmoles) of 5-carbomethoxy-2-pyrone[12] and 0.84 g (10 mmoles) of methyl propiolate in 10 ml of xylene was heated at reflux for 90 hr. Removal of solvent and recrystallization from Skellysolve B yielded 0.37 g (40%) of product, mp 65–90°. Two recrystallizations of this material from a minimum amount of 95% ethanol yielded 0.15 g of dimethyl terephthalate, mp 139–140°.[29] Evaporation of the combined Skellysolve B and ethanol mother liquors, and recrystallization of the residue once from 95% ethanol and twice from Skellysolve B yielded 0.10 g of dimethy isophthalate, mp 67–68° (lit.[29] mp 68°). Both isomers were further identified by their nmr spectra. The terephthalate: isophthalate ratio was 3:2.

Diethyl Isophthalate (19) and Diethyl Phthalate (20).—3-Carboethoxy-2-pyrone[13] (0.84 g, 5.0 mmoles), ethyl propiolate (0.70 g, 7.0 mmoles), and 5 ml of xylene were heated at reflux for 30 hr. Removal of solvent and vacuum distillation of the residual oil yielded one cut, bp 95–100° (0.3 mm), 0.56 g (50%), identified as a 4:1 mixture of diethyl isophthalate and diethyl phthalate by nmr and glpc comparisons with authentic samples.

Reactions of 4,6-diphenyl-, 4,5,6-triphenyl-, 5-carbomethoxy-, 4,5-diphenyl-, and 3-carboethoxy-2-pyrones with diphenylacetylene or phenylacetylene were run in 20-ml lyophilization tubes using 10 ml of toluene as solvent. After filling, each tube was subjected to three freeze–thaw cycles in liquid nitrogen under reduced pressure and was sealed under reduced pressure. The tubes were heated at 250° for 24 hr for the 5-carbomethoxy- and 3-carboethoxy-2-pyrones and at 300° (unless otherwise noted) for 24 hr for the others, in a 476-ml Parr bomb containing 75–100 ml of toluene. Heat was applied by electric mantle, the temperature being controlled by a Jelrus automatic controller connected to a thermocouple in the bomb head. Tubes were cooled in a Dry Ice–acetone bath before opening and products were isolated by removal of solvent and recrystallization or vacuum distillation.

1,2,3,5-Tetraphenylbenzene (21).—4,6-Diphenyl-2-pyrone[10] (1.3 g, 5.0 mmoles) and diphenylacetylene (0.97 g, 5.5 mmoles) yielded, after recrystallization from 6:1 benzene–methanol, 1.4 g (74%) 1,2,3,5-tetraphenylbenzene, mp 222–224° (lit.[30] mp 224–226°).

Pentaphenylbenzene (22).—4,5,6-Triphenyl-2-pyrone (1.62 g, 5.00 mmoles) and diphenylacetylene (0.97 g, 5.50 mmoles) yielded, after recrystallization from 1:1 benzene–methanol, 1.24 g (54%) of pentaphenylbenzene, mp 247–250° (lit.[31] mp 251°).

Methyl 3,4-Diphenylbenzoate (23).—5-Carbomethoxy-2-pyrone[12] (1.1 g, 8.0 mmoles) and diphenylacetylene (1.4 g, 8.0 mmoles) yielded, after recrystallization from methanol, 0.99 g (43%) of methyl 3,4-diphenylbenzoate, mp 130–131° (lit.[32] mp 127°).

1,2,4,5-Tetraphenylbenzene (24).—4,5-Diphenyl-2-pyrone[5] (0.76 g, 3.0 mmoles) and diphenylacetylene (0.55 g, 3.0 mmoles) yielded, after recrystallization from toluene, 0.78 g (68%) of 1,2,4,5-tetraphenylbenzene, mp 263–265° (lit.[31] mp 262–263°).

Ethyl 2,3-Diphenylbenzoate (25).—3-Carboethoxy-2-pyrone[13] (1.0 g, 6.0 mmoles) and diphenylacetylene (1.2 g, 6.0 mmoles) yielded an oily product. Vacuum distillation yielded recovered diphenylacetylene and an oil, bp 14–180° (0.3 mm), which crystallized from 95% ethanol giving 0.38 g (21%) of product. After three recrystallizations from 95% ethanol, the analytical sample melted at 90–91.5°. *Anal.* Calcd for $C_{21}H_{18}O_2$: C, 83.44; H, 5.96. Found: C, 83.25; H, 5.96.

1,2,3,5- and 1,2,3,4-Tetraphenylbenzenes (21 and 26).—4,5,6-Triphenyl-2-pyrone[11] (3.51 g, 10.9 mmoles) and 1.11 g (10.9 mmoles) of phenylacetylene were combined as above in a 50-ml lyophilization tube with 30 ml of toluene. The tube was heated at 200° for 90 hr, followed by 225° for 24 hr. Cooling, opening the tube, and allowing it to stand for 2 days caused the crystallization of 0.753 g (21.4%) of starting 2-pyrone. Addition of a few milliliters of methanol to the mother liquor crystllized two successive crops of 1,2,3,4-tetraphenylbenzene (0.727 g, 17.4%), mp 190–192° (lit.[31] mp 190–191°). Evaporation of the mother liquor and extraction of the residue with 50 ml of methanol left a mixture of products, 1.797 g (43.2%), from which 1,2,3,4-tetraphenylbenzene (0.625 g, 15.1%) and 1,2,3,5-tetraphenylbenzene (0.268 g, 6.98%) were isolated by numerous fractional recrystallizations.

The same reaction, run at 300° for 24 hr, yielded no recovered 2-pyrone, and gave compounds 21 and 26 in yields of 12 and 14%, respectively, from an 80% yield of crude products.

Methyl 4-Phenylbenzoate (27).—5-Carbomethoxy-2-pyrone[12] (1.1 g, 8.0 mmoles) and phenylacetylene (0.82 g, 8.0 mmoles) yielded, after recrystallization from methanol, 1.0 g (60%) of methyl 4-phenylbenzoate, mp 118–120° (lit.[32] mp 118°).

Ethyl 2-Phenylbenzoate (28) and Ethyl 3-Phenylbenzoate (29).—3-Carboethoxy-2-pyrone (2.2 g, 13 mmoles) and phenylacetylene (1.8 g, 19 mmoles) yielded 1.7 g (60%) of oil, bp 115–140° (0.3 mm), consisting of ethyl 2-phenylbenzoate and ethyl 3-phenylbenzoate in a ratio of 2:1, as shown by nmr.

Registry No.—**12,** 19926-51-3; **13,** 19926-52-4; **14,** 19926-53-5; **17,** 19926-47-7; **25,** 19926-48-8; **28,** 19926-49-9; **29,** 19926-50-2.

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Molecular Rearrangements. An Interannular Acylation of Enol Esters

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Several enol esters of 2-benzylcyclohexane-1,3-diones (**5**) were treated with polyphosphoric acid (PPA). The reaction products were the aryl alkyl ketones (**6**). This constitutes a new acylation at aromatic carbon using enol esters as acylating agents, and also a novel molecular rearrangement comprising an interannular migration of the acyl group. The chemical and spectroscopic properties of these compounds, as well as that of other new compounds prepared in the synthetic sequence, are described. When **2b** was treated with cyclohexane-1,3-dione enol acetate in the presence of PPA, **6b** was obtained. Stereochemical considerations suggest the reaction mechanism as intermolecular.

Two of the most well-known organic reactions are the Friedel–Crafts acylation[1] and alkylation and its familiar Fries modification.[2] Acid catalysts are used in both reactions, polyphosphoric acid (PPA) being one that is gaining more adepts.[3] In the Fries rearrangement,[4] treatment of phenol esters with acid catalysts gives rise to 1,3 or 1,5 shifts of the acyl group, producing the *o*- or *p*-acylphenols.

In the present paper we wish to report the results obtained when some enol esters of 2-benzylcyclohexane-1,3-diones are treated with PPA. A rapid, general method for the preparation of enol esters was developed; it consists in the heating of the 1,3-diketone with excess anhydride and a catalytic amount of *p*-toluenesulfonic acid on the steam bath, followed by the high-vacuum distillation of the mixture. This allowed the recovery of the excess anhydride and avoided the hydrolysis of the labile enol esters.

In the cases under study the products obtained from the treatment of the esters with PPA resulted from the migration of the acyl group to the C-4 position of the aromatic ring (Scheme I: **5a** → **6a**, **5b** → **6b**, etc.).

The mentioned sequences appear to be the first reported on acylations of aromatic hydrocarbons by the action of aliphatic enol esters. At the same time they constitute the interesting case of an interannular 1,8 migration of the acyl group. Chemical and spectroscopic evidence of the mentioned structures is given below.

The simplest example of the sequence is the one starting with 2-benzylcyclohexane-1,3-dione (**2a**) which was obtained by the general method of Stetter and Klauke.[5]

A small amount of the 2,2-dibenzyl derivative (**3**) was also obtained in this experiment. It possesses a peculiar nmr spectrum, in which, for example, the C-5 methylene protons are found at a higher field δ 0.83) than the usual for such protons (δ 2); this must be due to the shielding by the phenyl rings, as a result of the geometry in the molecule.[6]

The enol acetate of **2a** was prepared by its treatment with acetic anhydride and *p*-toluenesulfonic acid. The product **5a** shows in its ir spectrum the characteristic absorption bands for the vinyl ester (1750 cm^{-1}), the α,β-unsaturated carbonyl (1665 and 1645 cm^{-1}), and the monosubstituted benzene (690 cm^{-1}). In its nmr spectrum three singlets are observed at δ 2.06 (3 H), 3.48 (2 H), and 7.15 (5 H), corresponding successively to the acetate, the benzylic methylene, and the aromatic protons; the annular methylene groups exhibit a multiplet centered at δ 2.31 (6 H).

A crystalline product ($C_{15}H_{18}O_3$) could be isolated when this acetate (**5a**) was heated in the presence of PPA, and the reaction mixture was purified by chromatography. The acidic character of this substance, its positive ferric chloride test, and its ir spectrum (which shows bands at 3150 (broad), 1620 and 1630 cm^{-1}) indicated that this product is an isomer of **5a** containing the free enol grouping.

The fact that the acetyl group had migrated to the aromatic ring in this compound was deduced from its ir spectrum which exhibits a strong peak at 1670 cm^{-1} (Ar–CO) and lacks the band in the 700-cm^{-1} region. This group was assigned to C-4 position in the aromatic ring, based on the nmr spectrum which has a singlet at δ 2.54 (3 H) (due to the CH_3COAr) and two doublets at 7.33 (2 H, J = 8 cps) and 7.72 (2 H, J = 8 cps) (due to the aromatic protons); the shape and position of the doublets are in full agreement with the ABA′B′ aromatic system of a *p*-alkylacetophenone.[7] The other bands in the nmr spectrum, those due to the methylene protons of this compound (**6a**), appear as a quintet at δ 1.96 (2 H, J = 5.5 cps) (C-5), a triplet at 2.45 (4 H, J = 5.5 cps) (C-4 and C-6), and a singlet at 3.70 (benzylic methylene).

The propionic enol ester (**5c**) of the 2-benzylcyclohexane-1,3-dione was also prepared; all of these spectra are also in accord with its structure.

Transposition of the propionyl group by heating the ester with PPA gave the 2-(4-propionylbenzyl)cyclohexane-1,3-dione. Its spectroscopic behavior is very similar to that of the acetylbenzyl derivative (**6a**) and fully supports the proposed structure (**6c**).

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