TABLE IV

4-*N*-ARYLCARBAMOYLOXY-2-BUTENYLTRIALKYLAMMONIUM CHLORIDES[a]

$$ArNHCOOCH_2CH{=}CHCH_2\overset{\oplus}{N}R_3\overset{\ominus}{Cl}$$

Ar	R	Formula	M.P.	Crude Yield, %	Calcd. C	Calcd. H	Calcd. N	Calcd. Ionic Cl	Found C	Found H	Found N	Found Ionic Cl
C_6H_5	CH_3	$C_{14}H_{21}ClN_2O_2$	186–188 dec.	35	59.0	7.4	9.8	12.5	59.2	7.6	9.6	12.7
C_6H_5	C_2H_5	$C_{17}H_{27}ClN_2O_2$	135–136 dec.	47	62.5	8.3	8.6	10.8	62.1	8.2	8.4	10.8
3-ClC_6H_4	CH_3	$C_{14}H_{20}Cl_2N_2O_2$	181–183 dec.	96	52.7	6.3	8.8	11.1	52.5	6.0	8.4	11.2
3-ClC_6H_4	C_2H_5	$C_{17}H_{26}Cl_2N_2O_2$	dec.[b]	47	56.5	7.3	7.8	9.8	56.9	7.0	7.7	9.8

[a] All compounds prepared by *Method A.* [b] Indefinite, softened at 110°, decomposed at 120°.

TABLE V

COMPOUNDS RELATED TO CHOLINE CHLORIDE AND ACETYLCHOLINE HALIDES

$$\overset{\ominus}{X}\ R_3\overset{\oplus}{N}CH_2C{\equiv}CCH_2OZ$$

R	Z	X	Formula	M.P.	Crude Yield, %	Calcd. C	Calcd. H	Calcd. N	Calcd. Ionic X	Found C	Found H	Found N	Found Ionic X
CH_3	H	Cl	$C_7H_{14}ClNO$	95–97 dec.	61	51.4	8.6	8.6	21.7	51.3	8.7	8.2	21.9
C_2H_5	H	Cl	$C_{10}H_{20}ClN_2O_2$	86–93 dec.	68	58.4	9.8	6.8	17.2	58.1	9.5	6.9	17.2
CH_3	CH_3CO	Cl	$C_9H_{16}ClNO_2$	163–65 dec.	72	52.3	7.8	6.8	17.2	52.4	8.0	6.8	17.3
C_2H_5	CH_3CO	Br	$C_{12}H_{22}BrNO_2$	94–96 dec.	52	49.1	7.6	4.8	27.4	49.3	7.6	4.9	27.5

Anal. Calcd. for $C_{13}H_{15}ClN_2O_2$: C, 58.5; H, 5.6. Found: C, 58.7; H, 5.5.

4-Diethylamino-2-butynyl N-(3-chlorophenyl)carbamate was prepared in a manner similar to that above, in benzene. The product was a gummy solid which crystallized on exposure to air. There was obtained a 95% yield of a crude product which was recrystallized from hexane; m.p. 77–78°.

Anal. Calcd. for $C_{15}H_{19}ClN_2O_2$: C, 50.9; H, 3.9. Found: C, 50.9; H, 3.8.

Preparation of 4-[N-(3-chlorophenyl)carbamoyloxy]-2-butynyldimethylethylammonium iodide. A solution of 4-dimethylamino-2-butynyl *N*-(3-chlorophenyl)carbamate (8 g., 0.03 mole) and ethyl iodide (15.6 g., 0.10 mole) in 300 ml. of benzene was allowed to stand at ambient temperature. After 24 hr., 9.2 g. (75%) of crude product was collected by filtration and dried under vacuum. A small portion was recrystallized from an ethanol–ether mixture, m.p. 120–121° dec.

Preparation of 4-[N-(3-chlorophenyl)carbamoyloxy]-2-butenyltriethylammonium chloride. A mixture of 4-chloro-2-butenyl *N*-(3-chlorophenyl)carbamate (20.8 g., 0.08 mole), triethylamine (15.2 g., 0.15 mole) and 150 ml. of dry benzene was stirred at ambient temperature for 24 hr. The benzene was decanted from the reaction mixture and the residue was dissolved in 25 ml. of water. The water solution was added to 150 ml. of benzene and the mixture distilled until the water was removed. The remaining benzene was decanted. The residue, 13.6 g. (47%), solidified after being subjected to vacuum for 24 hr. Recrystallization from ethanol–ether gave 11.5 g. (40%) of product, m.p. 110–120°.

The following procedures were used for the preparation of the compounds in Table V.

Preparation of 4-hydroxy-2-butynyltrimethylammonium chloride. A solution of 4-chloro-2-butyn-1-ol (10.5 g., 0.10 mole) in 200 ml. of dry benzene was saturated with trimethylamine. The reaction mixture was stirred for 18 hr. and the bulk of the solvent was removed from the product by decantation. After removal of residual solvent under reduced pressure there was obtained approximately 10 g. (61% crude) of an amber colored gum. After several recrystallizations from an ethanol–ether mixture there was obtained 1.6 g. (10%) of a white amorphous solid, m.p. 95–97° (sealed tube).

Preparation of 4-acetoxy-2-butynyltrimethylammonium chloride. A solution of 4-chloro-2-butynyl acetate (5.0 g., 0.034 mole) in 100 ml. of dry benzene was saturated with gaseous trimethylamine at ambient temperature. The reaction mixture was agitated for 2 hr., the solid removed by filtration and dried in a vacuum desiccator over phosphorus pentoxide. There was obtained 5.0 g. (72%) of off-white crystals; m.p. 163–165°.

Preparation of 4-acetoxy-2-butynyltriethylammonium bromide. From a mixture of 4-diethylamino-2-butynyl acetate (22.0 g., 0.12 mole), ethyl bromide (32.7 g., 0.03 mole) and 250 ml. of benzene there deposited, after 2 weeks, 4.6 g. (15%) of product; m.p. 94–96° dec. After 2 months another 11.7 g. of product was collected bringing the total to 16.3 g. (52%). The combined solids were washed several times with ether and dried in vacuum over phosphorus pentoxide, m.p. 94–96° dec.

SPENCER CHEMICAL COMPANY
MERRIAM, KAN.

Electronic Effects in the Diels-Alder Reaction between Methyl Phenylpropiolate and Substituted Tetraphenylcyclopentadienones[1]

MICHAEL G. ROMANELLI[2] AND ERNEST I. BECKER[3]

Received August 3, 1961

Previous studies in this laboratory have been concerned with the Diels-Alder reaction between tetracyclone and (1) Y—C≡C—C_6H_5 (Y = CH_3,

---

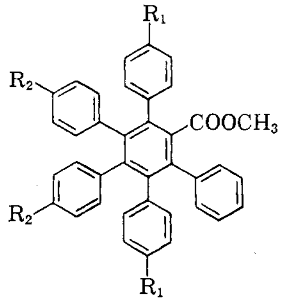
[1] Taken from the thesis submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Bachelor of Science, 1961.

[2] National Science Undergraduate Research Participant, Summer 1960.

[3] To whom inquiries should be sent.

TABLE I

METHYL 2,3,4,5-TETRAKIS(ARYL)-6-PHENYLBENZOATES



R_1	R_2	M.P.	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Chlorine Calcd.	Chlorine Found
Cl	H	329–330	77.95	77.39	4.48	4.38	12.11	11.88
				77.89		4.53		
H	Cl	252–253	77.95	77.46	4.48	4.67	12.11	12.38
Cl	Cl	288–289	69.74	69.96	3.70	3.88	21.67	21.53
CH_3O	H	267–268	83.31	82.98	5.59	5.62		
H	CH_3O	256–257	83.31	83.48	5.59	5.94		
				83.45		5.82		
CH_3O	CH_3O	222–224	79.22	79.30	5.70	5.75		

CH_2OH, CHO, $COOCH_3$, COOH, H)[4] and (2) methyl substituted phenylpropiolates.[5,6] Their conclusion was that electron-withdrawing substituents accelerate the reaction. This investigation was concerned with electronic effects of substituents in the diene using methyl phenylpropiolate in all cases.

EXPERIMENTAL

The starting tetracyclones were synthesized according to literature procedures as indicated.

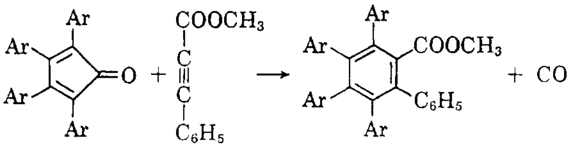
Tetracyclone, m.p. 220–221° (reported,[7] 219–220°); 2,5-bis(4-chlorophenyl)-3,4-diphenylcyclopentadienone, m.p. 236.5–237.5° (reported,[8] 239–240°); 3,4-bis(4-chlorophenyl)-2,5-diphenylcyclopentadienone, m.p. 249.5–250.5° (reported,[8] 253–254°); tetrakis(4-chlorophenyl)cyclopentadienone, m.p. 286.0–287.0° (reported,[8] 297–299°); 2,5-bis(4-methoxyphenyl) - 3,4 - diphenylcyclopentadienone, m.p. 195.2–196.0° (reported,[9] 195.0–195.4°); 3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopentadienone, m.p. 236.5–237.5° (reported,[9] 226.8–227.2°); tetrakis(4-methoxyphenyl)cyclopentadienone, m.p. 247.2–248.2° (reported,[9] 255–256°). Each of the cyclones synthesized here gave no depression with samples of the previously reported compounds.

Phenylcyclohexane, purified according to Corson and Ipatieff,[10] had a boiling point of 108–109° (12.5 mm.), n_D^{21} 1.5265 (reported: n_D^{25} 1.5190,[11] n_D^{25} 1.5254,[12] n_D^{26} 1.5221[5]). Methyl phenylpropiolate boiled at 77° (1 mm.), n_D^{22} 1.5634, n_D^{28} 1.5608 (reported,[13] n_D^{25} 1.5618). On standing, the ester developed a green color which interfered with the kinetic measurements; it was therefore distilled before use.

The reaction was followed by measuring the rate of evolution of carbon monoxide. The kinetic runs and calculations were carried out as before.[5] At the end of each experiment, the products were filtered from the reaction mixtures after cooling. They were recrystallized three times from either xylene or acetic acid (see Table I).

RESULTS AND DISCUSSION

The over-all equation for the reaction is



The reaction displayed second-order kinetics even when carried to 90% completion. The reaction rate constants are given in Table II.

The reaction rate constant for tetracyclone itself agrees within 5% with previous values (1.48×10^{-3} molal^{-1} sec.$^{-1}$ [5] and 1.56×10^{-3} molal^{-1} sec.$^{-1}$ [6]) after correcting for temperature using E_a of 19 kcal.

The rate constants show that chlorine substitution in tetracyclone increases the reaction rate constants while chlorine substitution in the ester also increases the reaction rate constant: for methyl

---

[4] J. J. Dudkowski and E. I. Becker, *J. Org. Chem.*, **17**, 201 (1952).

[5] I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1958).

[6] D. N. Matthews, doctoral dissertation, Polytechnic Institute of Brooklyn, 1961.

[7] J. R. Johnson and O. Grummitt, *Org. Syntheses*, Coll. Vol. III, 806 (1955).

[8] F. J. Thaller, D. E. Trucker, and E. I. Becker, *J. Am. Chem. Soc.*, **73**, 228 (1951).

[9] S. B. Coan, D. E. Trucker, and E. I. Becker, *J. Am. Chem. Soc.*, **77**, 60 (1955).

[10] B. B. Corson and V. N. Ipatieff, *Org. Syntheses*, Coll. Vol. **II**, 151 (1943).

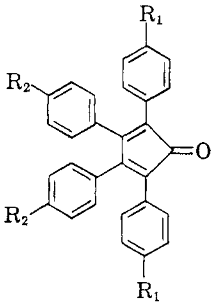
[11] J. F. McKenna and F. J. Sowa, *J. Am. Chem. Soc.*, **59**, 471 (1937).

[12] B. B. Corson and V. N. Ipatieff, *J. Am. Chem. Soc.*, **59**, 645 (1937).

[13] C. Moureu, P. T. Muller, and J. Varin, *Ann. chim.*, [9] **2**, 269 (1914).

TABLE II

REACTION RATE CONSTANTS



Run No.	R_1	R_2	Temp.	$k \times 10^3$ (molal^{-1} sec.$^{-1}$)
7	H	H	176.4	1.58
8	H	H	176.4	1.57
20	H	H	176.3	1.58
21	H	H	176.3	1.62
			Av.	1.59 ± 0.02
11	Cl	H	176.5	2.42
13	Cl	H	176.3	2.53
15	Cl	H	176.3	2.65
16	Cl	H	176.3	2.50
19	Cl	H	176.3	2.57
			Av.	2.53 ± 0.07
10	H	Cl	176.3	2.37
12	H	Cl	176.3	1.93
14	H	Cl	176.3	2.17
17	H	Cl	176.3	2.38
18	H	Cl	176.3	2.07
			Av.	2.18 ± 0.15
28	Cl	Cl	176.3	3.10
30	Cl	Cl	176.3	2.98
31	Cl	Cl	176.3	3.33
32	Cl	Cl	176.3	3.13
33	Cl	Cl	176.3	3.30
			Av.	3.17 ± 0.12
34	CH_3O	H	176.3	2.13
35	CH_3O	H	176.3	2.30
36	CH_3O	H	176.3	2.13
37	CH_3O	H	176.3	2.15
			Av.	2.18 ± 0.07
22	H	OCH_3	176.3	1.23
24	H	OCH_3	176.3	1.19
26	H	OCH_3	176.3	1.12
27	H	OCH_3	176.3	1.19
			Av.	1.18 ± 0.03
38	CH_3O	CH_3O	176.3	1.78
39	CH_3O	CH_3O	176.3	1.93
40	CH_3O	CH_3O	176.3	1.70
			Av.	1.80 ± 0.08

phenylpropiolate, $k = 1.48 \times 10^{-3}$ molal^{-1} sec.$^{-1}$ and for methyl 4-chlorophenylpropiolate, $k = 2.25 \times 10^{-3}$ molal^{-1} sec.$^{-1}$. Methoxy substitution in tetracyclone accelerates the reaction when in the *para* positions of the 2- and 5-phenyls, and in all four *para* positions, but decelerates the reaction when in the *para* positions of the 3- and 4-phenyls, whereas the methoxyl group slows the reaction when in the 4- position of methyl phenylpropiolate ($k = 1.10 \times 10^{-3}$ molal^{-1} sec.$^{-1}$). Thus, for the first time it is noted that a halogen may accelerate the Diels-Alder reaction whether in the dienophile or in the diene. The rate-substituent effects observed here are different from those in other Diels-Alder reactions in which no carbon monoxide is lost. For example, it has been shown that the *p*-chloro group has the expected effect of reducing the rate of reaction of 1-phenylbutadiene with maleic anhydride.[14] On the other hand, in the reaction between tetracyclone and methyl phenylpropargylate, the absence of a wall effect[5,6] has been interpreted to mean that the evolution of carbon monoxide is not the rate-determining step in accordance with the concept of Newman.[15] However, the absence of the wall effect has not been demonstrated for substituted tetracyclones and substituted methyl phenylpropargylates.

It is also noteworthy that substitution in tetracyclone affects the reaction to a different extent depending upon the position of substitution in the diene; that is, substitution in the 2,5-phenyls is more activating than substitution in the 3,4-phenyls. These results and those in the preceding paragraph are not easily understood in the present state of knowledge of the reaction. Further work is under way.

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 1, N. Y.

---

(14) E. J. DeWitt, C. T. Lester, and G. A. Ropp, *J. Am. Chem. Soc.*, **78**, 2101 (1956).

(15) M. S. Newman and E. Coflisch, Jr., *J. Am. Chem. Soc.*, **80**, 830 (1958).

Preparation of Trimethylsilyl Ethers of Hindered 2,4,6-Trialkylphenols

SIDNEY FRIEDMAN, MARVIN L. KAUFMAN, AND
IRVING WENDER

Received August 4, 1961

As part of the development of a procedure for preparing the trimethylsilyl ethers of coal and of phenols, we have recently reported the successful preparation of 2,6-di-*t*-butylphenoxytrimethylsilane, using hexamethyldisilazane and trimethylchlorosilane as reagents and pyridine as solvent.[1] Pyridine was chosen because of its very good solvent action on coal, and the observation that it was necessary for derivative formation in the case of 2,6-di-*t*-butylphenol and for complete reaction of coal.

While most phenols will react readily with hexamethyldisilazane, di-*t*-butylphenol requires the presence of pyridine and trimethylchlorosilane as well. At that time,[1] 2,6-di-*t*-butylphenol was the

---

(1) S. Friedman, M. L. Kaufman, W. A. Steiner, and I. Wender, *Fuel*, **40**, 33 (1961).