very small. Furthermore, the steric inhibition of resonance of the *ortho*-isocyanato group by the methyl group is considered to be negligible. Hence, the m-σ value that is used in the evaluation of the reactivity of the *para*-isocyanato group by the *ortho*-isocyanato group is unaffected by the presence of the methyl group. Therefore, the calculated k/k_0 value for the *para* group is 2.75 using the determined value of ρ and the appropriate σ values from Table II. The k/k_0 value for the *ortho* group is 1.03, using the average of the experimental data of compounds I-6 and V-3 (or 0.93 using the data from the "ortho" line of Fig. 1). Thus, the expected initial k/k_0 value for 2,4-tolylene diisocyanate is 3.78. A comparison of the experimental log k/k_0 values to the calculated one is shown in Table III.

TABLE III

VALUES OF RELATIVE RATE CONSTANTS FOR 2,4-TOLYLENE DIISOCYANATE

log k/k_0	Source
0.577	Calculated
0.688	Cmpd. I-9
0.631	Cmpd. V-2
0.562	Cmpd. VI-2

The agreement between the calculated and experimental values, which were derived under various conditions, is rather striking and within 0.1 log units which is the accepted limit of accuracy for this type of correlation. Thus, it is concluded that the ratio of reactivity of the *para* to the *ortho* group is about 2.67 to 1. The difference in reactivity of one order of magnitude that has been previously assumed does not apply to these groups, but is the ratio of the sum of the reactivities of both isocyanato groups compared to that of the *ortho*-isocyanato group when the *para*-substituent is a carbamide and not an isocyanato group.

Further corroboration for this approach lies in the similar explanation of the value for the rate constant of 4-chloro-1,3-diphenylene diisocyanate (compound VI-3). The difference between the experimental and calculated log k/k_0 values of 4,6-dichloro-1,3 phenylene diisocyanate (compound VI-4) is taken as the steric effect due to an *ortho*-chloro group. Hence, the expected k/k_0 values for the *para*- and *ortho*-isocyanato groups of compound VI-3 are 13.0 and 10.8, respectively, resulting in an initial relative rate constant of 23.8 (1.377 log units) *vs.* the experimental value of 36.5 (1.562 log units). Considering the scarcity of applicable data in this series, the agreement is quite good and again emphasizes the fact that the two isocyanato groups have reactivities of the same order of magnitude.

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Bisacylation of 4-Pyrones

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In a recent paper[1] a method describing the acylation of 4-pyrones under the catalytic influence of trifluoroacetic acid has been described. This contribution represents an elaboration of that method in which bisacylation is accomplished. The procedure, although relatively simple, produces the diketones in high yield and remarkably free of polymerized contaminants.

Bisacylation of 4-pyrones in the presence of trifluoroacetic acid appears to be nonspecific in the orientation and the acyl groups are apparently put on any position available on the pyrone nucleus.

The bisacylated compounds, I-A–G, are given in Table I. Several derivatives of compound I-A, a relatively simple substance and illustrative of the nature of this type of compound, are given in confirmation of its generalized structure as compounds III and IV.

Included in this communication are several instances in which either acid anhydrides or *p*-bromo phenacyl bromide have been induced to react with pyrones. These compounds are listed in Table II as the II-A–C Series.

Attempted reduction of compounds I-B, -D, -E, and -F under the conditions of the Meerwein-Pondorf-Verley reaction failed in every case. The analytical results indicated that the pyrone had been fragmented and the pyrone structure destroyed.

Reduction of compounds I-A, -D and -E and II-A and -B with potassium borohydride in absolute ethanol was fairly successful in that compounds I-D and II-B were reduced as expected. The three other compounds gave analytical results which could not be justified. Infrared data are given for most of the new compounds listed in Tables I and II in Table III.

EXPERIMENTAL[2]

Preparation of compounds I-A–G *series.* A mixture consisting of 0.2 mol. of the acyl halide, except in the case of I-E in which 0.3 mol. of benzoyl chloride was used, 0.1 mol. of the pyrone and 35 ml. trifluoroacetic acid was refluxed for 30 min. or sufficiently longer so that hydrogen chloride was no longer evolved. The mixture was then diluted with 150 ml. of water, cooled, and filtered. The sample was dried in air and the analytical sample obtained by recrystallizing the compound once from boiling heptane.

The isolation of compound I-G was handled somewhat differently in that after the reaction mixture was diluted with water the solution was neutralized with sodium bicarbonate and extracted with benzene. The substance was

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[1] L. L. Woods and P. A. Dix, *J. Org. Chem.* **24**, 1126 (1959).

[2] All analyses were performed by Dr. Carl Tiedcke, Teaneck, N. J. All melting points were determined on a Fisher-Johns melting point assembly.

TABLE I

Pyrone	Acyl Halide	Yield %	M.P.°	Formula	Calculated C	Calculated H	Found C	Found H
I-A 2,6-Dimethyl-4-pyrone	*p*-Tolyl chloride	96	177–178	$C_{23}H_{20}O_4$	76.64	5.59	76.29	5.29
I-B 2,6-Dimethyl-4-pyrone	Cinnamoyl chloride	85	120	$C_{25}H_{20}O_4$	78.10	5.24	77.64	5.51
I-C 2,6-Dimethyl-4-pyrone	Benzoyl chloride	99	111–113	$C_{21}H_{16}O_4$	75.89	4.85	76.11	4.98
I-D Kojic acid diacetate	Benzoyl chloride	100	119–120	$C_{24}H_{18}O_8$	66.35	4.17	66.09	4.35
I-E α-Chloro-α-deoxy kojic acid	Benzoyl chloride	100	110	$C_{27}H_{17}ClO_6$	68.57 Chlorine	3.59 7.49	68.87 7.27	3.38
I-F Benzodihydro-4-pyrone	Benzoyl chloride	61	115–117	$C_{23}H_{16}O_4$	77.51	4.52	77.07	4.74
I-G Kojic acid diacetate	Acetyl chloride	17	121	$C_{14}H_{14}O_8$	54.19	4.54	53.94	4.29

TABLE II

Pyrone	Anhydride or Phenacyl halide	Yield, %	M.P.°	Formula	Calculated C	Calculated H	Found C	Found H
II-A 2,6-Dimethyl-4 pyrone	Phthalic anhydride	60	133.5	$C_{15}H_{12}O_6$	66.17	4.44	66.42	4.12
II-B Kojic acid diacetate	Benzoic anhydride	96	144–145	$C_{17}H_{14}O_7$	61.81	4.27	61.57	4.40
II-C 2,6-Dimethyl 4-pyrone	*p*-Bromo phenacyl bromide	90	113	$C_{15}H_{13}O_3Br$	56.09	4.07	56.47	4.27

TABLE III
INFRARED DATA[a]

Sample	Wave Number cm.$^{-1}$[b]
I-A	2985, 2857, 1661 (B), 1610, 1577, 1422, 1319, 1282, 1183, 1117
I-B	3077 (VB), 1761, 1675 (B), 1621, 1488, 1445, 1418, 1339, 1307, 1282, 1222, 1070
I-D	2778 (VB), 1681 (B), 1600, 1577, 1449, 1418, 1321, 1290 (B), 1183, 925.
I-E	3067–2757 (VB), 1733 = shoulder, 1689 (B), 1603, 1449, 1422, 1321, 1285 (B), 1263, 1248, 1202, 934
I-F	3376, 3106, 2817, 2667, 2538, 1675 (B), 1600, 1580, 1449, 1420, 1321, 1287 (B), 1179, 935
II-A	2008, 1848, 1754 (VB), 1695 = shoulder, 1613, 1462, 1353, 1255 (B), 1109, 869
II-B	3067, 1730, 1661, 1631, 1597, 1431 = shoulder, 1427, 1370, 1333, 1252 (VB), 1215, 1143, 1053, 1021

[a] Significant absorption bands of some of the compounds listed in Tables I and II measured in wave number cm.$^{-1}$ on a Beckmann IR-5 instrument using KBr pellets. [b] B = broad, VB = very broad.

obtained by removal of the solvent over a steam bath then recrystallized twice from heptane.

Preparation of compounds of II-A–C *series.* The reactants were mixed in the same mol. proportions along with 25 ml. of trifluoroacetic acid. The reflux period for compounds II-A and -B was 1 hr. and for II-C was 5 hr. The procedure for the purification of the substances was accomplished by recrystallization first from ethanol then from heptane.

2,6-Dimethyl-3,5-di(p-tolyl)-4-pyridone (III). Four grams of I-A was placed in 15 ml. absolute alcohol and warmed to dissolve the compound. To this mixture 10 ml. of concentrated ammonium hydroxide was added. Storage of the solution overnight in the refrigerator produced crystals which were filtered, dried in air, and recrystallized once from heptane, m.p. 158–159.

Anal. Calcd. for $C_{23}H_{21}NO_3$: C, 76.02; H, 5.88; N, 3.89. Found: C, 76.24; H, 5.69; N, 3.67.

Malononitrile derivative of I-A (IV).[3] Three grams of I-A along with 1.5 g. malononitrile was refluxed for 1 hr. in 25 ml. acetic anhydride then poured into 400 ml. of ice water. The precipitate, when dried in air, was recrystallized twice from heptane, m.p. 160.

Anal. Calcd. for $C_{32}H_{20}N_6O$: N, 16.65. Found: N, 16.49.

Reduction of compounds I-D *and* II-B *with potassium borohydride.* Three grams of the acylated compound was mixed with 30 ml. of ethanol and then 3 g. powdered potassium borohydride was gradually sifted in while the mixture was magnetically stirred. The retaining flask was then loosely stoppered with a cotton plug. After standing overnight the mixtures were each treated with 50 ml. of water to which 10 ml. of concentrated hydrochloric acid had been added. The mixtures were stored in the freezer overnight to produce a precipitate which when dried in air weighed 1.3 g. for II-B. Sample I-D did not form a precipitate, so the solution was extracted with ethyl acetate and the solvent removed over a steam bath to give nearly 4 g. of brown crystals. Both samples were purified by recrystallizing the crude compounds from boiling heptane: m.p. I-D, 112.5–114, m.p. II-B 153–155.

Anal. Calcd. for $C_{24}H_{22}O_8$ compound I-D: C, 65.74; H, 5.05. Found: C, 65.49; H, 4.82. Calcd. for $C_{17}H_{18}O_7$ compound II-B: C, 61.44; H, 4.85. Found: C, 61.27; H, 4.59.

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(3) L. L. Woods, *J. Am. Chem. Soc.*, **80**, 1440 (1958).