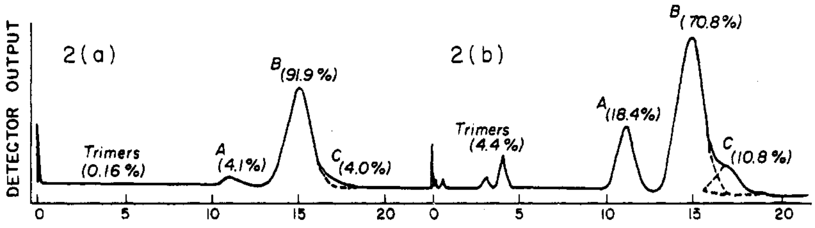
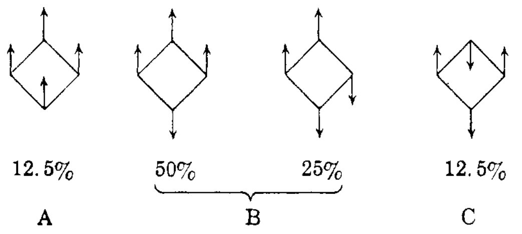


Fig. 2. (a) Methyl phenyl tetramer solid. (b) Methyl phenyl tetramer liquid

2 ft. Apiezon L; temperature, 290°

are single isomers while components B represents two isomers.

The following isomers are possible in the methyl phenyl cyclic tetramer system



Each silicon atom has one phenyl and one methyl substituent and in the above diagrams the arrows represent the phenyl substituent. The per cent composition for each isomer at equilibrium was calculated statistically discounting any energy differences. The assignments indicated above were made by analogy with the trimer system and on the basis of the observed peak areas.

The chromatogram in Figure 3 is included to show that rather extensive rearrangements have occurred in the highest boiling fraction. This fraction contains a large amount of trimer in addition to pentamer with smaller amounts of tetramer and other unidentified products. The rather large amount of trimer is of considerable interest and explains the observation of Young *et al.*[2] . . . "If the column was placed on total reflux at any time, the head temperature would drop to 155-160°." This temperature corresponds to the trimer fraction.

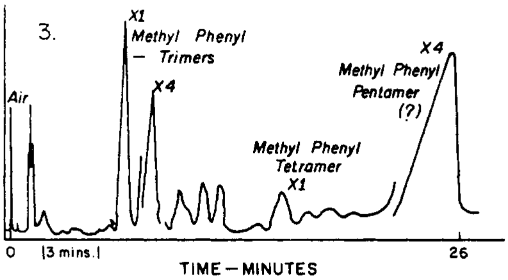


Fig. 3. Methyl phenyl cyclics

Distillation cut, 19-4305; 2 ft. silicone rubber; temperature program, 5.6° min.

It is conceivable that a complete separation of the cyclic tetramer isomers will be possible by gas chromatography. Although a number of stationary liquid phases were studied such as carbowax, silicone grease, and a mixed methyl phenyl silicone, the best separations were obtained with an Apiezon L column.

EXPERIMENTAL

Gas Chromatography. A Model 500 F and M linear programmed gas chromatograph was equipped with a two-foot column of either silicone rubber or Apiezon L grease on chromosorb. The hot-wire detector was maintained at a constant temperature of 305°, the injection port temperature was 300 ± 5° and the helium flow rate was 67 ml. per minute.

Preparation of siloxanes. The methyl phenyl cyclic tri- and tetrasiloxanes were prepared according to the method of Young *et al.*[2] Liquid samples (2 µl.) were injected directly into the chromatograph while the solid samples were used in a dilute benzene solution.

Acknowledgment. The authors are indebted to Dr. J. R. Ladd for the siloxane preparations used in this investigation.

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Synthesis of 1,5-Diphenyl- and 1,1,5,5-Tetraphenyl-2,4-pentanedione

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In connection with another study, moderate quantities of 1,5-diphenyl-2,4-pentanedione (I) were required

$$C_6H_5CH_2COCH_2COCH_2C_6H_5 \quad \text{I}$$

This β-diketone has previously been prepared from phenylacetyl chloride and vinyl acetate by aluminum chloride,[2] and from the magnesium chloride derivative of sodium phenylacetate (Ivanov reagent) and malonyl chloride,[3] but the yields were only 1 and 5%, respectively. Two other

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(1) National Science Foundation Predoctoral Fellow, 1958-1961.

(2) A. Sieglitz and O. Horn, *Chem. Ber.*, **84**, 607 (1951).

(3) D. Ivanov and N. Marekov, *Compt. rend. acad. bulgare sci.*, **4**, 41 (1953); *Chem. Abstr.* **49**, 978h (1955).

methods also have been employed,[4,5] but the yields were not reported.

In the present investigation several methods were considered. The common basic and boron fluoride methods of acylation did not appear suitable for I since the required methyl ketone, phenylacetone, tends to undergo preferential acylation at the methylene rather than the methyl group.[6] Attempts were made to prepare I from malonyl chloride and three molecular equivalents of benzylmagnesium chloride at low temperature[7] and from malononitrile and excess of this Grignard reagent in tetrahydrofuran, but they were unsuccessful. In the latter experiment a relatively insoluble magnesium derivative was formed.[8] However, two successful methods were developed. One of them involved the phenylacetylation of ethyl γ-phenylacetoacetate, followed by decarbethoxylation by means of phenylacetic acid, magnesium oxide and copper acetate (Equation 1).

$$C_6H_5CH_2COCH_2COOC_2H_5 \xrightarrow[2.\ C_6H_5CH_2COCl]{1.\ Na\ (benzene)}$$

$$\underset{II}{(C_6H_5CH_2CO)_2CHCOOC_2H_5} \xrightarrow[MgO,\ Cu(C_2H_3O_2)_2]{C_6H_5CH_2COOH} I \quad (1)$$

The yield of the copper chelate of intermediate II was 58%, and that of the chelate of I, 33%. Intermediate II was also hydrolyzed and decarbethoxylated with acid but the yield of I was only 13%.

The second method, which is probably the preferred one, involved treatment of phenylacetic anhydride and malonic ester with magnesium oxide and copper acetate, β-diketone I being obtained in 57% yield (Equation 2).

$$2(C_6H_5CH_2CO)_2O + CH_2(COOC_2H_5)_2 \xrightarrow[Cu(C_2H_3O_2)_2]{MgO}$$

$$I + 2\ C_6H_5CH_2COOC_2H_5 + 2\ CO_2 \quad (2)$$

This method is an extension of that of Bränström,[9] who used it with malonic ester and purely aliphatic anhydrides such as propionic and butyric anhydrides. Whereas the completion of these reactions was indicated when no more monocarboxylic ester distilled or when the evolution of carbon dioxide ceased, the present reaction (Equation 2) could be followed only by the cessation of evolution of carbon dioxide, since the by-product ethyl phenylacetate boils higher than malonic ester.

Similarly β-diketone III was synthesized from diphenylacetic anhydride and malonic ester, the yield of III being 28%.

$$\underset{III}{(C_6H_5)_2CHCOCH_2COCH(C_6H_5)_2}$$

EXPERIMENTAL[10]

Synthesis of 1,5-diphenyl-2,4-pentanedione (I). *A. According to Equation 1.* Ethyl γ-phenylacetoacetate, b.p. 113–115° at 0.9 mm., was prepared from ethyl acetoacetate and phenylacetyl chloride essentially as described by Zaugg.[11]

To a solution of 30 g. (0.145 mole) of this β-keto ester in 500 ml. of dry benzene was added 3.35 g. (0.145 g.-atom) of sodium metal. After heating at slow reflux for 12 hr., 29.2 g. (0.193 mole) of phenylacetyl chloride was added during 0.25 hr. with stirring to the hot solution of the sodio salt (much heat evolved). After refluxing with stirring for 22 hr., 200 g. of crushed ice was added to the cooled reaction mixture. The layers were separated, and the benzene layer was combined with two benzene extracts of the aqueous layer. Removal of the solvent gave 54.9 g. of residual oil which was added with rapid stirring to a suspension of copper ammonium sulfate, prepared by addition of 26 ml. of concd. ammonium hydroxide to a solution of 28.6 g. of copper sulfate in 100 ml. of water. The resulting chelate was collected, transferred to a beaker, and washed with 100 ml. of ethanol, then recollected. This washing process was repeated three more times to give 35.6 g. of blue chelate which was dissolved in boiling ethyl acetate. After filtering to remove a pale green precipitate, the solvent was distilled from the filtrate to give 30.0 g. (58%) of the copper chelate of ethyl α-(phenylacetyl)-γ-phenylacetoacetate (II), m.p. 175.5–176° and 179.3–179.7° after several recrystallizations from ethyl acetate.

Anal. Calcd. for $C_{40}H_{38}O_8Cu$: C, 67.64; H, 5.53; Cu, 8.95. Found: C, 67.45; H, 5.25; Cu, 8.69.

The chelate of II (30.0 g.) was decomposed in a mixture of dilute sulfuric acid and ether[12] to give 23.3 g. (85%) of II (yellow oil). On attempted distillation of a sample of II, decomposition occurred.

A mixture of 11.2 g. (0.0346 mole) of crude II, 4.72 g. (0.346 mole) of phenylacetic acid, 0.1 g. of magnesium oxide, and 0.05 g. of copper acetate was heated at 190° for 2 hr., at the end of which time the evolution of gas had essentially ceased. After cooling, the reaction mixture was shaken with ether. The ethereal solution was washed with saturated sodium bicarbonate solution and then stirred with saturated aqueous copper acetate solution.[12] The resulting precipitate was collected and washed with ether to give 3.31 g. (33%) of the copper chelate of 1,5-diphenyl-2,4-pentanedione (I), m.p. 213.5–214.2° dec. and 217.5–218.5° dec. after recrystallization from ethyl acetate. This melting point was not depressed on admixture with a sample of this chelate prepared as described below.

A 10.3-g. sample of crude II was refluxed with a mixture of 25 ml. of glacial acetic acid, 25 ml. of water, and 1 g. of 18*M* sulfuric acid for 24 hr. The solvent was removed *in vacuo* on a water bath, and the residue was stirred with 200 ml. of ether. The ethereal solution was washed with saturated sodium bicarbonate solution and dried over magnesium sulfate. The solvent was removed, and the residue was shaken with a saturated aqueous copper acetate solution[12] to give 1.2 g. (13%) of the copper chelate of I, m.p. 212.0–212.5° dec. and 218–218.5° dec. after recrystallization from ethyl acetate. A 1-g. sample of this chelate was decomposed

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(4) M. N. Tilichenko, *Zhur. Obshchei Khim.*, **25**, 2503 (1955); *Chem. Abstr.* **50**, 9327a (1956).

(5) P. Cordier, *Compt. rend.*, **225**, 388 (1947).

(6) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **8**, 59 (1954).

(7) See M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954, Chapt. IX.

(8) See J. L. E. Erickson and M. M. Barnett, *J. Am. Chem. Soc.*, **57**, 560 (1935).

(9) A. Brändström, *Arkiv. Kemi*, **3**, 365 (1951).

(10) Melting points were taken on a Mel-Temp capillary melting point apparatus. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(11) H. E. Zaugg, *J. Am. Chem. Soc.*, **68**, 2492 (1946).

(12) See ref. 6, pp. 122–123.

with 5 ml. of 12N hydrochloric acid and 35 ml. of ether to give 0.84 g. (94%) of I, m.p. 64–65°, reported m.p. 66°.[2]

B. According to Equation 2. Phenylacetic anhydride, m.p. 71.5–72° (reported m.p. 72.5°[13]) was prepared from phenylacetyl chloride and anhydrous sodium phenylacetate in dry benzene as described previously.[14]

A mixture of 101.5 g. (0.4 mole) of this anhydride, 32 g. (0.2 mole) of diethyl malonate, 0.2 g. of magnesium oxide, and 0.1 g. of copper acetate was combined in a flask fitted with an air condenser and a gas inlet tube reaching to the center of the flask. Oxygen-free nitrogen was passed through the reaction flask for 0.5 hr., then the flask was heated at 190° for 2.5 hr. After cooling, the mixture was shaken with 400 ml. of ether, then washed with 5% sodium hydroxide solution to remove phenylacetic acid (β-diketone I was found not to be appreciably soluble in 5% alkali). The ether was removed, and the residue was treated with saturated copper acetate solution. The resulting precipitate was collected and washed with water, followed by petroleum ether (b.p. 30–60°) until the washes were essentially colorless. There was obtained 35.7 g. (63%) of the gray-blue chelate of I, m.p. 219.0–219.5° dec., which was not depressed on admixture with a sample of the chelate of I prepared by method A.

This chelate was decomposed with 12N hydrochloric acid (see above) to give 28.4 g. (90%) of 1,5-diphenyl-2,4-pentanedione (I), m.p. 65.2–66.5° after several recrystallizations from methanol.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.40. Found: C, 80.96; H, 6.22.

This product gave a red enol test with alcoholic ferric chloride.

Synthesis of 1,1,5,5-tetraphenyl-2,4-pentanedione. Diphenylacetic anhydride, m.p. 96.2–97° (reported m.p. 98°[15]) was prepared from diphenylacetic acid and acetic anhydride as described previously.[15]

A mixture of 81.2 g. (0.2 mole) of this anhydride, 16 g. (0.1 mole) of diethyl malonate, 0.2 g. of magnesium oxide, and 0.1 g. of copper acetate was heated at 230° for 2.5 hr., and the reaction mixture worked up essentially as described above for I (under *B*) to give 15.3 g. (35%) of the copper chelate of III, m.p. 230.7–233.5° dec.

Decomposition of 14.7 g. of this chelate with 12N hydrochloric acid and ether gave 10.9 g. (80%) of 1,1,5,5-tetraphenyl-2,4-pentanedione (III), m.p. 135–136.5° after recrystallization from ethanol.

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.11; H, 5.98. Found: C, 86.02; H, 6.03.

This β-diketone gave a red enol color with ethanolic ferric chloride solution.

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[14] J. A. King and F. H. McMillan, *J. Am. Chem. Soc.*, **73**, 4911 (1951).

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The Reactions of Pyrones with Carboxylic Acids, Esters, and Chloromethyl Ether

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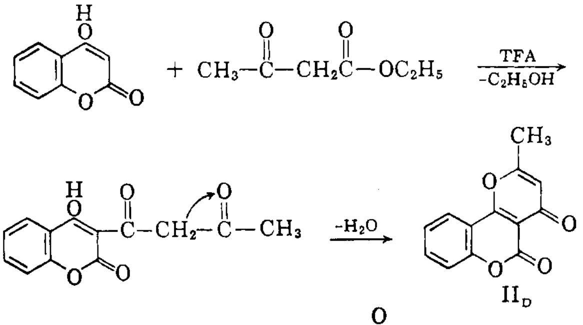
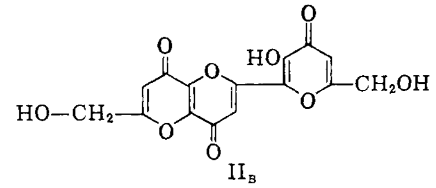
In the recent months investigations of the reaction of 4-pyrones with acyl halides, anhydrides,[1,2] and lactones[3] have been shown to take place in the presence of trifluoroacetic acid to form ketones. Therefore, experiments were designed to ascertain if acids could be used as acylating agents of the several pyrones by using trifluoroacetic acid as a catalyst. When the reaction was tried under the conditions described for the preparation of the compounds of the Ia–f series, good results were obtained.

In order to evaluate the procedure 6-benzoylkojic acid was used as the model compound, as it had been prepared previously and its properties determined.[4] Compound Ic, produced by the action of benzoic acid on kojic acid in the presence of trifluoroacetic acid, gives a melting point within experimental error of that recorded for 6-benzoylkojic acid and it gives the proper carbonyl absorption at 1718 cm.$^{-1}$ The other members of the Ia–f series also give the expected carbonyl absorption frequencies[5] when chelation and other displacement factors are considered.

As carboxylic acids were found to react with pyrones under the conditions related above, esters were tried to determine if they, too, could be induced to react under similar conditions. In this instance, also, 6-benzoylkojic acid was used as the model compound to evaluate the acylation of pyrones by esters. Not only were the expected results realized but a novel condensation was uncovered. The compounds formed by this method are given as the IIa–e series in Table II. The structure for 2-hydroxymethyl-6-(2′-hydroxymethyl-5′-hydroxy-4′-pyrone-6′-pyranyl[3,2-*b*]pyran-4,8-dione is given as is the equation for the preparation of 8-methylbenzopyranyl[3,2-c]pyran-2,10-dione (IId). Compound IIe is formed similarly by the same novel



II$_D$



II$_E$

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