described above under A to give crude product residues. The unchanged esters and acetylacetone were removed from the crude residues by fractional distillation, and the remaining product residues were fractionated *in vacuo* to give triketones Ie and If.

The pot residue remaining after the fractionation of triketone If was recrystallized from ethanol–hexane to give about 0.2 g. (1–2%) of dipropionamide, m.p. 155–155.5°, reported m.p. 152–153°.[23]

Anal. Calcd. for $C_6H_{11}NO_2$ (dipropionamide): C, 55.78%; H, 8.54%. Found: C, 55.87%; H, 8.77%.

(C) Acetylation of 2-Acetylcyclohexanone.—To a stirred suspension of 0.3 mole of lithium amide was added 14.0 g. (0.1 mole) of 2-acetylcyclohexanone[24] in 75 ml. of anhydrous ether to produce a grayish white mixture of dilithio-2-acetylcyclohexanone and lithium amide. After stirring for 1 hr., a solution of 17.6 g. (0.2 mole) of ethyl acetate in 75 ml. of anhydrous ether was added during 1–2 min. The resulting reaction mixture was stirred for 1 hr., and then worked up as described under A to give crude residue, which was recrystallized directly to give triketone II.

Benzoylation of Propionylacetone.—Propionylacetone was prepared by alkylating disodioacetylacetone with methyl iodide in liquid ammonia.[25] The product boiled at 68–70° at 36 mm.[26]

A solution of 11.4 g. (0.1 mole) of propionylacetone in 100 ml. of anhydrous ether was added to a stirred suspension of 0.3 mole of lithium amide in 600 ml. of liquid ammonia to give a grayish-white mixture of dilithiopropionylacetone and lithium amide. After stirring for 30 min., a solution of 27.2 g. (0.2 mole) of methyl benzoate in 75 ml. of anhydrous ether was added, and the stirring continued for 30 min. The reaction mixture was worked up essentially as described above for the propionylation of benzoylacetone to give 8 0 g. (37% or 49% based on the β-diketone used minus that recovered) of triketone Ib, b.p. 117–119° at 0.1 mm., which agrees with the boiling point of this compound prepared by the method described above (see Table I).

A 1.66-g. sample of this product was cyclized with ammonia in ethanol (see below) to give 1.06 g. (70%) of pyridone Xb, m.p 152–153°. This melting point was not depressed on admixture of this product with a sample of Xb prepared as described below, and the infrared spectra of the two samples were identical (see Tables V and VI).

Cyclizations of 1,3,5-Triketones with Sulfuric Acid to Form 4-Pyrones (Tables III and IV).—A 1-g. sample of the triketone was dissolved in 10 ml. of concentrated sulfuric acid at 0°. After swirling for 10 min. at this temperature, the solution was poured into ice–water and worked up by one of the procedures described below.

In the cyclization of triketone Ia the solid hydrate which precipitated[5] was filtered and shaken in a separatory funnel with hot hexane and saturated sodium bicarbonate solution. The layers were separated. Cooling of the hexane solution precipitated pyrone VIIIa. A mixed melting point of VIIIa with authentic 2-methyl-6-phenyl-4*H*-pyran-4-one[3] showed no depression, and the infrared spectra of the two compounds were identical.

In the cyclizations of triketones Ib–d the cold, aqueous solution was extracted with ether. The extract was washed with water, followed by saturated sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. The solvent was removed and the residue recrystallized from an appropriate solvent (Table III).

In the cyclizations of triketones Ie–f and II the cold, aqueous solution was first neutralized with saturated sodium bicarbonate solution, then extracted with ether and worked up as described above in the cyclizations of triketones Ib–d.

Cyclizations of 1,3,5-Triketones with Ammonia to Form 4-Pyridones (Tables V and VI).—To 1 g. of the triketone dissolved in 50 ml. of absolute ethanol in a 125-ml. erlenmeyer flask was added commercial, anhydrous liquid ammonia until the flask became cold. The solution was evaporated to dryness on a steam bath, and the entire process was repeated with the residue. The pyridone was isolated by one of the procedures described below.

Pyridones Xa and XI were isolated by direct recrystallization of the residue from an appropriate solvent (Table V).

Pyridones Xb and Xe were isolated by washing the residues with ether and hexane, respectively to remove impurities before recrystallization from an appropriate solvent (Table V).

In the preparation of pyridone Xc the residue was an oil which solidified on treatment with ether–hexane accompanied by cooling and scratching. Attempts to recrystallize Xc from various solvents gave oils. The product was finally purified by dissolving the oil in absolute ethanol, filtering to remove any solid impurities, evaporating to dryness, and washing the remaining, crushed solid several times with ether (see footnote *d*, Table V).

In the preparation of pyridone Xd the residue was first crystallized from ether–petroleum ether (b.p. 30–60°) and then recrystallized from acetone–water.

In the cyclization of triketone If crude pyridone Xf precipitated during the second treatment with absolute ethanol and liquid ammonia. The solid was filtered, placed overnight in a vacuum desiccator at 1 mm., and recrystallized from acetone after treatment with Norite.

(23) R. Otto and J. Troeger, *Ber.*, **23**, 759 (1890).

(24) For the preparation of this β-diketone see reference in footnote 8, p. 131.

(25) The details of this method will be published soon by K. G. Hampton, T. M. Harris, and C. R. Hauser. Similar alkylations have been described previously; see ref. 2 and R. B. Meyer and C. R. Hauser, *J. Org. Chem.*, **25**, 158 (1960).

(26) For other methods for preparing this compound see reference in footnote 8, pp. 122–124.

Synthesis of Some Spirobarbiturates

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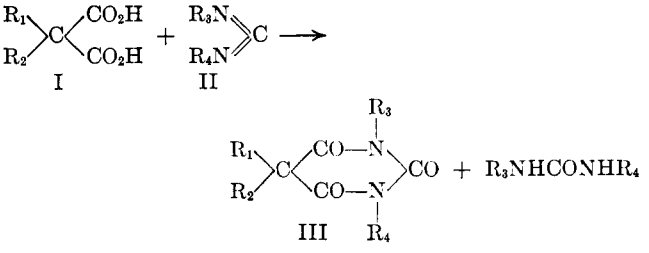
Received October 25, 1962

The synthesis of several spirobarbiturates by a recent new method is described. Some electronic and steric factors affecting this synthesis are discussed.

Recently, a new method was described[2] for the synthesis of barbituric acids (III) which involves the reaction between malonic acid (I) and carbodiimides (II). The scope of this reaction has now been extended by the preparation of spirobarbiturates—a class of compounds known for their interesting physiological activity.[3]



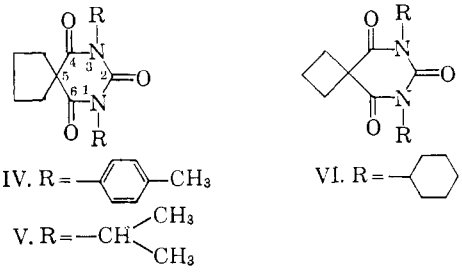
The reaction of 1,1-cyclobutanedicarboxylic acid and 1,1-cyclopentanedicarboxylic acid with different carbo-

(1) National Science Foundation Undergraduate Research Participant.

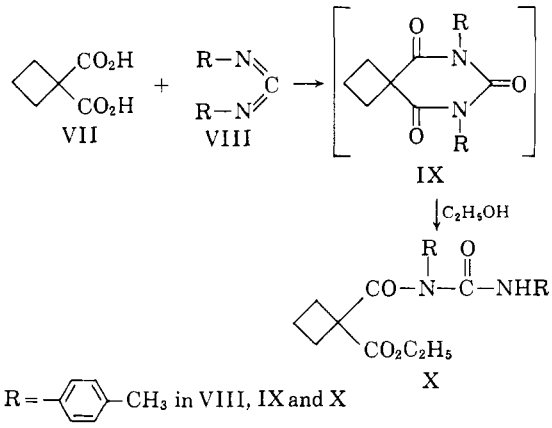
(2) A. K. Bose and S. Garratt, (a) *J. Am. Chem. Soc.*, **84**, 1318 (1962); (b) *Tetrahedron*, in press.

(3) A. Burger, "Medicinal Chemistry," Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1951, p. 129.

diimides was studied. Spirobarbiturates IV, V, and VI were obtained in good yield under mild conditions. The structure of these compounds was confirmed by their elemental analysis and n.m.r. spectra.

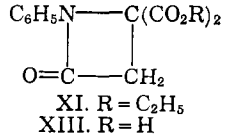


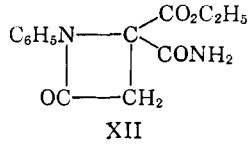
When 1,1-cyclobutanedicarboxylic acid (VII) was allowed to react with di-*p*-tolylcarbodiimide (VIII) in tetrahydrofuran solution, di-*p*-tolylurea was formed, but the other product of the reaction after crystallization from alcohol was found to be not the expected spirobarbiturate IX. On the basis of analytical data and the n.m.r. spectrum, this compound was shown to possess the structure X. Evidently the spirobarbiturate IX was cleaved by ethyl alcohol although under parallel conditions IV, V, or VI suffered no noticeable cleavage.

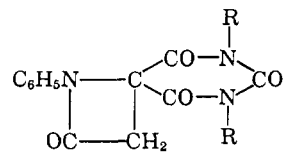


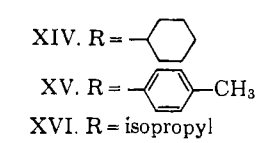
The condensation of 1,1-cyclobutanedicarboxylic acid with *N,N'*-diisopropylcarbodiimide afforded diisopropylurea and a yellow oil which from its n.m.r. spectrum was found to be a mixture of compounds. The reaction was not pursued further.

Attempts to prepare a spirobarbiturate by the condensation of 1-phenyl-4,4-dicarbethoxyazetidin-2-one (XI) with urea or thiourea under standard reaction conditions[4] failed. The only product isolated in a very small yield from the thiourea reaction was XII. Application of the carbodiimide method of synthesis to the β-lactam dicarboxylic acid XIII, however, produced the









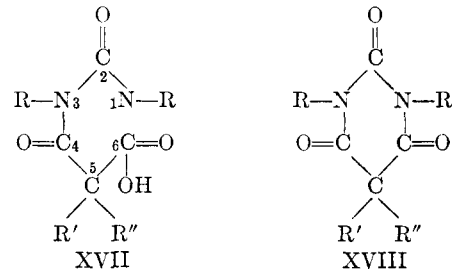
(4) E. Fischer and A. Dilthey, *Ann.*, **335**, 334 (1934).

spirobarbiturates XIV, XV, and XVI. The presence of some extra peaks of low intensity in the n.m.r. spectrum of a sample of XV crystallized from alcohol indicated that cleavage of the barbiturate had taken place to a small extent (*cf.* X).

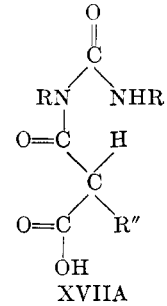
There do not appear to be any *N,N'*-disubstituted spirobarbiturates reported previously.[3] The carbodiimide method for the synthesis of spirobarbiturates gives higher yields under milder reaction conditions than the other known methods.[5]

It has been noted previously[2] that *N,N'*-di-*p*-tolylcarbodiimide did not form barbiturates with unsubstituted or monosubstituted malonic acids, whereas barbiturates were formed with disubstituted malonic acids. The facile formation of the spirobarbiturates IX and XV is in keeping with this pattern. *N,N'*-Diisopropylcarbodiimide produces barbiturates with equal facility from substituted and unsubstituted malonic acids.

The difference between aromatic and aliphatic carbodiimides in the reaction with malonic acids is striking.[6] This difference may in part be due to electronic factors associated with the resonance involving the nitrogen and the aromatic ring. In all probability, however, steric factors play a more important role in the cyclization to barbiturates. Examination of molecular models shows that when R is an aryl group in the intermediate XVII, the molecule is much more crowded than when R is an alkyl group or the cyclohexyl group. Furthermore, in the least hindered conformation of XVII, the least bulky group on C_5 will be nearest to N_1. Thus, when R′ = R″ = H, the carboxyl group will be in an unfavorable position for ring closure (see XVII A). A



similar situation will prevail when R′ = H and R″ = C_2H_5. However, when R′ = R″ = C_2H_5, the substituents on C_5 will be roughly of comparable size



and the carboxyl group will more readily approach N_1 within bond-forming distance. The "*gem*-dimethyl" effect may also assist the formation of the barbiturate

(5) J. A. Starfield and P. M. Daugherty, *J. Am. Chem. Soc.*, **81**, 5169 (1959) and references cited therein.

(6) It should also be noted that the *N*-*p*-tolylbarbiturates IX and XV undergo cleavage by alcoholysis during recrystallization, while their aliphatic analogs VI, XIV, and XVI fail to do so under comparable conditions.

ring (XVIII) when disubstituted malonic acids are used.

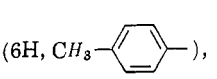
Experimental[7]

General Method for Synthesis of Barbiturates.—A solution of the carbodiimide in tetrahydrofuran was added to a stirred solution of the dicarboxylic acid in tetrahydrofuran at room temperature. In most cases immediate reaction took place and a urea precipitated. In some cases warming on a steam bath for a few minutes was necessary to initiate the reaction. After standing at room temperature for 1 hr., the urea was filtered, washed with tetrahydrofuran, and dried. The combined filtrates were evaporated under reduced pressure yielding the crude barbiturate which usually was purified by recrystallization from alcohol.

1,3-Di-*p*-tolylspiro(cyclopentane-1′,5-barbituric Acid) (IV).—A tetrahydrofuran solution of 1.09 g. of 1,1-cyclopentyldicarboxylic acid and 3.11 g. of *N,N′*-di-*p*-tolylcarbodiimide gave 1.6 g. of di-*p*-tolylurea, m.p. 265°, and the barbiturate IV which was recrystallized from aqueous ethanol, 1.3 g. (52%), m.p. 154–156°.

Anal. Calcd. for $C_{22}H_{22}N_2O_3$: C, 72.91; H, 6.12; N, 7.73. Found: C, 72.75; H, 6.46; N, 7.94.

N.m.r. peaks: 7.15 τ



multiple peaks centered at 3.03 τ (8H, aromatic protons), multiple peaks at 7.80–8.21 τ (protons in the cyclopentane ring).

1,3-Diisopropylspiro(cyclopentane 1′,5-barbituric Acid) (V).—The reaction of 0.88 g. of cyclopentyldicarboxylic acid and 1.41 g. of *N,N′*-diisopropylcarbodiimide in tetrahydrofuran solution gave 0.75 g. of *N,N′*-diisopropylurea, m.p. 190–191°, and crude barbiturate which was recrystallized from ethanol, 0.92 g. (65%), m.p. 42–45°, which had a satisfactory n.m.r. spectrum.

Anal. Calcd. for $C_{14}H_{22}N_2O_3$: C, 63.13; H, 8.33; N, 10.52. Found: C, 63.21; H, 8.62; N, 10.52.

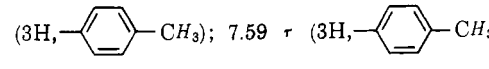
1,3-Dicyclohexylspiro(cyclobutane 1′,5-barbituric Acid) (VI).—A tetrahydrofuran solution of 1.0 g. cyclobutyldicarboxylic acid and 2.9 g. of *N,N′*-dicyclohexylcarbodiimide reacted to give *N,N′*-dicyclohexylurea (1.5 g., m.p. 231–232°) and an oil which crystallized from aqueous ethanol yielding 0.6 g. (26.1%) of the barbiturate, VI, m.p. 87–89°, which had a satisfactory n.m.r. spectrum.

Anal. Calcd. for $C_{19}H_{28}N_2O_3$: C, 68.64; H, 8.49; N, 8.43. Found: C, 69.26; H, 8.80; N, 8.24.

The Reaction of 1,1-Cyclobutanedicarboxylic Acid with *N,N*-Di-*p*-tolylcarbodiimide.—To 1 g. of 1,1-cyclobutanedicarboxylic acid (VII) dissolved in 20 ml. of tetrahydrofuran was added with stirring a solution of 3.1 g. of *N,N′*-di-*p*-tolylcarbodiimide in 25 ml. of tetrahydrofuran. After 30 min. a white solid started to separate. Stirring was continued for another hour and the precipitated urea was removed by filtration. On evaporating the filtrate a white solid was obtained which was crystallized from ethanol to give 1 g. of the compound X, m.p. 128–129.5°.

Anal. Calcd. for $C_{23}H_{26}N_2O_4$: C, 70.03; H, 6.64; N, 7.10. Found: C, 70.24; H, 6.68; N, 7.10.

N.m.r. peaks: triplet centered at 8.71 τ (3H, $-CH_2CH_3$); multiple peaks centered at 8.04 τ (protons on cyclobutane ring); 7.67 τ



broad peak centered at 6.67 τ (1H, —N—*H*); quartet centered at 5.86 τ (2H, $-CH_2-CH_3$), multiple peaks centered at 2.85 τ (aromatic protons).

The Reaction of 1-Phenyl-4,4-dicarbethoxyazetidin-2-one (XI) with Thiourea.—Following in general the standard method[8] for barbiturate synthesis, an alcohol solution of 1.32 g. of XI was added to sodium ethoxide (from 0.1 g. of sodium) in ethanol. An alcoholic solution of thiourea (0.35 g.) was next added and the mixture heated under reflux for 6 hr. After cooling, the reaction mixture was diluted with water and then acidified to pH 2. The reddish brown oil that separated was digested with dilute acid on a steam bath for 30 min. The oil then was extracted with ether. The ether solution was washed with water, dried, and the solvent was removed when there was obtained an oil that crystallized partially on standing. The crystalline material, XII, was recrystallized from ethanol, 0.054 g., m.p. 147–150°. An analytically pure sample of 1-phenyl-4-carbethoxy-4-carboxamidoazetidin-2-one (XII) had the m.p. 149–149.5°.

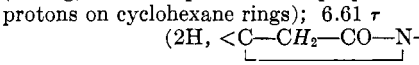
Anal. Calcd. for $C_{13}H_{14}N_2O_4$: C, 59.53; H, 5.38; N, 10.68. Found: C, 59.65; H, 5.36; N, 10.79.

1-Phenyl-4,4-dicarboxyazetidin-2-one[9] (XIII).—A solution of 34.8 g. of 1-phenyl-4,4-dicarbethoxyazetidin-2-one in the minimum amount of dioxane was cooled in an ice bath and to it was added two equivalents of sodium hydroxide solution (about 1 *N*). The reaction mixture was allowed to warm to room temperature and then set aside for 14 hr. by which time the pH of the mixture assumed a constant value. The mixture then was extracted with ether and the aqueous layer was acidified with cold concentrated hydrochloric acid when a thick oil separated. This oil was extracted with benzene and the extract was dried by distilling about one-half of the benzene under ordinary pressure; the rest of the benzene was removed under reduced pressure and the residual solid was washed twice with warm benzene and then dried. The product (25.7 g.), m.p. 168° dec. [lit.,[9] m.p. 171–172° dec.], so obtained was of adequate purity for carrying out subsequent reactions.[10]

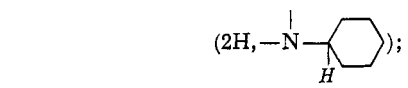
1,3-Dicyclohexylspiro[(1′-phenylazetidin-2′-in)-4′,5-barbituric Acid] (XIV).—1-Phenyl-4,4-dicarboxyazetidin-2-one (XIII) (1.0 g., 0.004 mole) and *N,N′*-dicyclohexylcarbodiimide (2.0 g., 0.009 mole) in tetrahydrofuran solution gave *N,N′*-dicyclohexylurea (0.96 g., 0.004 mole) and a crude product (1.8 g.), which on recrystallization from ethyl acetate gave the spirobarbituric acid, XIV (0.79 g., 44%), m.p. 234–235°.

Anal. Calcd. for $C_{24}H_{29}N_3O_4$: C, 68.06; H, 6.90; N, 9.92. Found: C, 68.10; H, 7.00; N, 9.98.

λ_{max}^{nujol}: 5.53 μ (weak), 5.64 μ (strong), 5.81 μ (weak), 5.92 μ (strong). N.m.r. peaks: multiple peaks centered at 8.47 τ (20H, protons on cyclohexane rings); 6.61 τ



multiple peaks centered at 5.50 τ

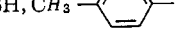


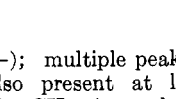
multiple peaks centered at 2.78 τ (5H, aromatic protons).

1,3-Di-*p*-tolylspiro[(1′-phenylazetidin-2′-one)-4′,5-barbituric Acid](XV).—The reaction of 2.0 g. of 1-phenyl-4,4-dicarboxyazetidin-2-one with 3.8 g. of *N,N′*-di-*p*-tolylcarbodiimide in tetrahydrofuran gave 2.0 g. dicyclohexylurea, m.p. 270°, and the barbiturate XV which was recrystallized from ethanol (2.55 g., 63%), m.p. 210°.

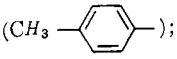
Anal. Calcd. for $C_{26}H_{21}N_3O_4$: C, 71.06; H, 4.82; N, 9.56. Found: C, 71.26; H, 4.82; N, 9.42.

N.m.r. peaks: 7.73 τ





6.54 τ (2H, $-C-CH_2-$); multiple peaks at 2.50–3.0 τ (13H, aromatic protons). Also present at low intensity: triplet centered at 8.85 τ (CH_3-CH_2-); multiple peaks centered at 6.50 τ (CH_3-CH_2-O-); 7.95 τ



8.58 τ. These low intensity peaks are probably due to an analog of X produced by ring cleavage by ethanol during crystallization.

1,3-Diisopropylspiro[(1′-phenylazetidin-2′-one)-4′,5-barbituric Acid] (XVI).—1-Phenyl-4,4-dicarboxyazetidin-2-one (1.0 g., 0.004 mole) and *N,N′*-diisopropylcarbodiimide (1.07 g., 0.008 mole) in tetrahydrofuran solution gave *N,N′*-diisopropylurea (0.4 g., 0.003 mole) and a crude crystalline solid which recrystal-

(7) Microanalyses were performed by Alfred Bernhardt, Mülheim, West Germany. Melting points are uncorrected.

(8) See, for example, J. B. Dickey and A. R. Gray, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York N. Y., 1948, p. 60.

(9) J. C. Sheehan and A. K. Bose, *J. Am. Chem. Soc.*, **72**, 5158 (1950).

(10) This procedure was developed by Dr. T. M. Jacob and Dr. B. N. Ghosh-Mazumdar in our laboratory.

lized from absolute ethanol to give the spirobarbituric acid XVI (0.19 g., 14%), m.p. 222–223°.

Anal. Calcd. for $C_{18}H_{21}N_3O_4$: C, 62.96; H, 6.16; N, 12.24. Found: C, 63.35; H, 5.88; N, 12.12.

λ_{max}^{nujol}: 5.6 μ (strong), 5.66 μ (strong), 5.9 μ (strong). The n.m.r. spectrum was satisfactory.

Acknowledgment.—This research was supported in part by a grant (MY-3930) from the National Institutes of Health, U. S. Public Health Service. We are thankful to Dr. E. R. Malinowski and Paul H. Weiner[1] for the n.m.r. data.

The Synthesis of 5-Diphenylmethylene-2(5*H*)-thiophenone and Related Compounds[1,2]

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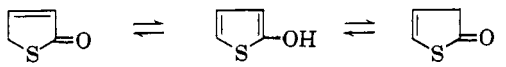
Received March 6, 1962

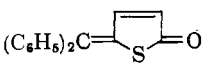
A general reaction leading to 5-substituted methylene-2(5*H*)-thiophenones is described. The mechanism, scope, and limitations of the reaction are discussed.

A number of 2(5*H*)-thiophenone derivatives have been reported[4]; they have been produced, for the most part, by ring closure methods leading to substituted thiolactone–thienol systems,[5] although two compounds possessing this structure have been reported as stemming from reactions involving 2-methoxythiophene.[6] The related compound, 2-thienol, II, has been prepared and characterized by Hurd and Kreuz[7]; evidence was also obtained indicating the existence of the tautomer 2(5*H*)-thiophenone, I, and possibly 2(3*H*)-thiophenone, III.



I II III

During the course of some work directed toward the preparation of potential antimetabolites of the estrogens, an attempt was made to prepare a 2-methoxythienyl analog of triphenyl carbinol through the reaction of benzophenone with 5-methoxy-2-thienyllithium. Instead of the expected carbinol, 5-diphenylmethylene-2(5*H*)-thiophenone, IV, was obtained in 72% yield.



IV

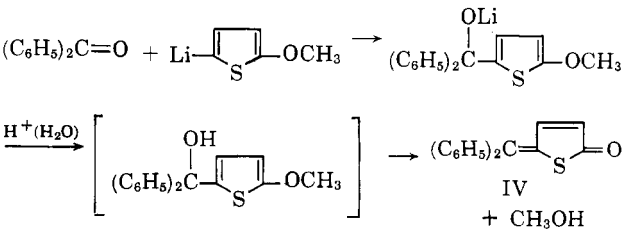
It was found on further study that the reaction is general and leads to 5-diarylmethylene-2(5*H*)-thiophenones in good yield; the corresponding 5-dialkylmethylene and 5-alkarylmethylene derivatives are also accessible but in poorer yield.

The key reactant in our procedure was 2-methoxythiophene which was first characterized by Hurd and Kreuz[7]; it was not until the work of Sicé, however, that this thiophene derivative became readily available.[8] Using the latter method with minor modifications, it was possible to convert thiophene by way of 2-iodothiophene to 2-methoxythiophene in 69% yield. The reaction of 2-methoxythiophene with either phenyl or, more conveniently, with *n*-butyllithium produced the reagent, 5-methoxy-2-thienyllithium.

When benzophenone was treated with the lithium reagent followed by hydrolysis, a bright yellow crystalline product melting at 112° was obtained. This compound failed to show either the expected hydroxyl absorption in the vicinity of 3560 cm.$^{-1}$ or absorption at 1205 cm.$^{-1}$ which is characteristic of the 2-methoxythienyl group; it did absorb strongly, however, at 1675 cm.$^{-1}$ which is consistent with an α,β-unsaturated thiolactone structure.[7] The ultraviolet spectrum was consistent with a highly conjugated carbonyl system, exhibiting bands at 251.5 and 358 mμ (Fig. 1). An analysis of the compound indicated the formula, $C_{17}H_{12}OS$, and oxidation of the compound with potassium permanganate in acetone produced benzophenone. All of the experimental observations are consistent with the structure of 5-diphenylmethylene-2(5*H*)-thiophenone, IV.

Although spectral evidence was never obtained for an intermediate carbinol stage in the case of the benzophenone reaction, even when the hydrolysis step was carried out in cold water, hydroxyl absorption was observed in subsequent runs with other carbonyl compounds, and it seems probable that the initial reaction of the lithium reagent occurs normally to first form the lithium salt of the carbinol.

The over-all reaction with benzophenone may be represented by the following equation.



Although a study of the demethylation rearrangement mechanism is still under way, it now seems probable that a resonance stabilized carbonium ion, V, is in-

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(2) Presented in part at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(3) Department of Chemistry, University of Washington, Seattle, Wash.

(4) Although compounds of this type are indexed by *Chemical Abstracts* as thiolactones of the corresponding acids, they are cross indexed as 2(5*H*)-thiophenones; for convenience, the latter names are used here. These compounds may also be named as substituted 3-thiolen-2-ones and 3-thiacyclopenten-5-ones, although these two methods of naming have not gained general acceptance.

(5) P. Friedlander and V. Kielbasinski, *Ber.*, **45**, 3389 (1912); H. Paal, *ibid.*, **19**, 556 (1886). For a general discussion of thiolactone–thienol tautomerism see H. D. Hartough, "Thiophene and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 292.

(6) W. Herz and L. Tsai, *J. Am. Chem. Soc.*, **77**, 3529 (1955).

(7) C. D. Hurd and K. L. Kreuz, *ibid.*, **72**, 5543 (1950).

(8) J. Sicé, *ibid.*, **75**, 3697 (1953).