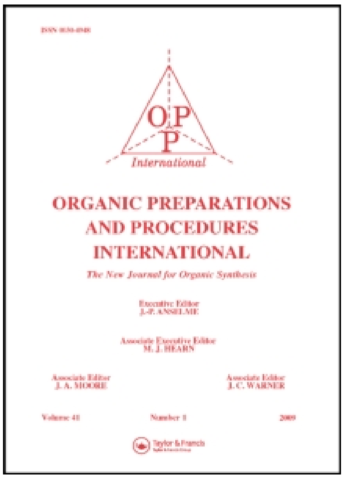

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PHASE-TRANSFER CATALYZED DOUBLE MICHAEL CONDENSATION. PREPARATION OF 7,11-BISARYLSPIRO[5,5]UNDECANE-1,9-DIONES

D. Loganathan[a]; T. Varghese[ab]; G. K. Trivedi[a]
[a] Department of Chemistry, Indian Institute of Technology, Bombay, INDIA [b] Instruments Laboratory (R and D), Asian Paints (India) Ltd., Bombay

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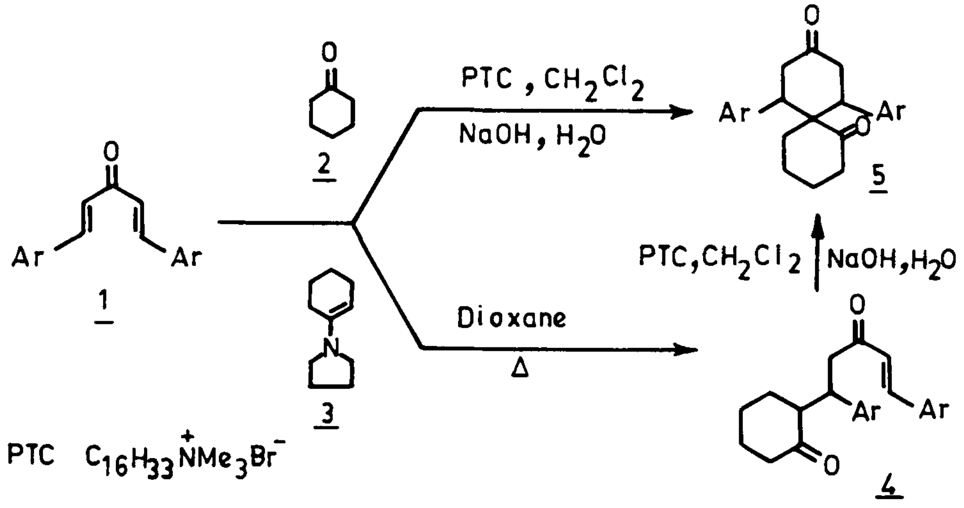
OPPI BRIEFS

PHASE-TRANSFER CATALYZED DOUBLE MICHAEL CONDENSATION.
PREPARATION OF 7,11-BISARYLSPIRO[5,5]UNDECANE-1,9-DIONES

Submitted by D. Loganathan, T. Varghese+ and G. K. Trivedi*
(11/01/83)
Department of Chenmistry, Indian Institute of Technology
Powai, Bombay 400 076, INDIA

Double Michael condensation involving the reaction of cyclohexane-1,3-dione with a cross-conjugated α,β-unsaturated ketone and catalyzed by sodium ethoxide in ethanol, first reported by De Jongh and Wynberg[1] as an elegant and single-pot preparation of spiro compounds, has been used by Stork[2] for the ingenious synthesis of the antibiotic griseofulvin and by Hamanaka and co-workers[3] for the preparation of a synthon for spiro prostaglandins. The usefulness of this reaction as a general method for spiroannulation has been limited by its low yield, particularly when extended to cyclohexanone and cyclopentanone (yields 5.3% and 0% respectively).[4] Even though the yield was improved (40-50%) by employing the corresponding enamines,[4,5] followed by an intramolecular Michael addition,



the advantages of a single-pot synthesis were lost in the bargain.

We now report that the title compounds (5) may be obtained in fair to good yields from the single-pot reaction of cyclohexanone with substituted 1,4-pentadien-3-one-1,5-bisaryls (1) in dichloromethane-aqueous sodium hydroxide biphasic system catalyzed by cetyltrimethylammonium bromide at room temperature. Physical constants, yields and spectral data of these spirodiones are presented in the Table. Attempts to isolate the 1,5-bisaryl-5-(2-oxo-cyclohexyl)pent-1-ene-3-ones (4) from the reaction media using a variety of phase-transfer conditions failed. However, 4b and 4c independently prepared by enamine method,[4] were converted in near quantitative yields to 5b and 5c respectively under phase-transfer conditions.

EXPERIMENTAL SECTION

The substituted 1,4-pentadien-3-one-1,5-bisaryls were obtained by the condensation of appropriate aryl aldehyde and acetone according to the procedure of Vogel.[6] 1-N-Pyrrolidinocyclohex-1-ene (3) was prepared according to Ref. 7. Cetyltrimethylammonium bromide was purchased from E. Merck. Cyclohexanone of Analar grade and all solvents of commercial grade were distilled once before use. Yields mentioned are of isolated pure products and not optimized. Melting points were determined by the open capillary method and are uncorrected. Infrared spectra were obtained in nujol on a Perkin-Elmer 237B spectrophotometer. Ultraviolet spectra were determined with a Varian SuperScan 3 spectrophotometer. Proton nmr spectra were recorded at 100 MHz on a Varian XL-100A spectrometer in $CDCl_3$ with TMS as internal standard.

7,11-Bisarylspiro[5,5]undecane-1,9-diones (5). General Procedure.- A solution of 1,4-pentadien-3-one-1,5-bisaryl (1) (1 mmol) and cetyltrimethylammonium bromide (109 mg, 0.3 mmol) in dichloromethane (15 ml) was stirred vigorously with a mixture of cyclohexanone (2 107.8 mg, 1.1 mmol) and 5% aqueous sodium hydroxide (12 ml, 2.5 mmol) at room temperature for 23-24 hrs. The two phases were then separated and the dichloromethane layer washed with water (3 x 5 ml), dried over sodium sulphate and the solvent removed under vacuum. The crude product was purified by column chromatography on silica gel using petroleum ether-ethyl acetate (50:1) as

TABLE. 7,11-Bisarylspiro[5,5]undecane-1,9-diones (5)

Cmpd	Ar	Yield	mp. (lit. mp.) MS(M+) m/e	UV [EtOH] λ max(nm) (ε)	IR ν[cm^{-1}]	^{1}H-NMR δ(ppm)
5a	C_6H_5	77% 23 hrs	173-174° (173-176°)[4] 332	253(309), 260(374), 265(335), 300(109)	1695,1600, 1375,1220, 750,700	1.30-3.00(m,11H); 3.16 (dd, 1H, J = 12Hz, 5Hz), 3.74(dd, 1H, J = 16Hz, 12Hz), 3.90 (t, 1H), J = 5Hz, 5Hz), 7.22(bs, 5H, H_{arom}), 7.30(bs, 5H, H_{arom}).
5b	p-MeOC_6H_4	66% 24 hrs	183-184° (182-183°)[5] 392	213(3678), 230(18650), 278(2728), 284(2556)	1710,1605, 1375,1250, 1025,825	1.30-3.00(m, 11H), 3.08 (dd, 1H, J = 12Hz, 5Hz), 3.50-4.00 (m, 2H), 3.80 (s, 3H), 3.84 (s, 3H), 6.70-7.20 (m, 8H, H_{arom}).
5c	Piperonyl	34% 34 hrs	190-191° 420	242(3290), 246(3463), 289(8486)	1690,1600, 1370,1245, 920,790	1.30-2.90 (m, 11H), 3.10(dd, 1H, J = 12Hz, 5Hz), 3.68 (dd, 1H, J = 16Hz, 12Hz), 3.80 (t, 1H, J = 5Hz, 5Hz), 5.86 (s, 2H), 6.00 (s, 2H), 6.40-6.80 (m, 6H, H_{arom}).
5d	P-ClC_6H_4	52% 26 hrs	159-160° 401	223(22985), 227(23315)	1700,1610 1375,1075, 1010,820	1.30-3.00 (m, 11H), 3.08 (dd, 1H, J = 12Hz, 5Hz), 3.67 (dd, 1H, J = 16Hz, 12Hz), 3.90 (t, 1H, J = 5Hz, 5Hz), 7.00-7.40 (m, 8H, H_{arom}).

Anal. 5c: Calcd. for $C_{25}H_{24}O_6$: C, 71.41; H, 5.75. Found: C, 71.52; H, 5.87

5d: Calcd. for $C_{25}H_{22}O_2Cl_2$: C, 68.83; H, 5.52. Found: C, 68.70; H, 5.79.

eluent (Table).

1,5-Bisaryl-5-(2-oxo-cyclohexyl)pent-1-ene-3-ones (4b-c).- Prepared from the corresponding 1,4-pentadien-3-one-1,5-bisaryls by reaction with 1-N-pyrrolidinocyclohex-1-ene (3) according to Ref. 4.

4b: 63% yield, mp. 135-136°, lit.[5] mp. 135-136°.

4c: 50% yield, the compound was crystallized from ethanol, mp. 175-178°; IR: 1696, 1637, 1600, 1496, 1370, 1250, 1165, 975 cm^{-1}; nmr: δ 1.50-3.20 (m, 11 H), 3.60 (ddd, 1H, J = 10 Hz, 10 Hz, 4 Hz), 5.92 (s, 2H), 6.02 (s, 2H), 6.46 (d, 1H, J = 16 Hz), 6.60-7.20 (m, 6H, H_{arom}), 7.46 (d, 1H, J = 16 Hz).

Anal. Calcd. for $C_{25}H_{24}O_6$: C, 71.41; H, 5.75

Found: C, 71.20; H, 5.39

Spirodiones 5b-c from 4b-c. General Procedure.- A mixture of 4b or 4c (1 mmol), cetyltrimethylammonium bromide (109 mg, 0.3 mmol) in aqueous 5% sodium hydroxide (12 ml, 2.5 mmol) and dichloromethane (15 ml) was stirred vigorously for nearly 25 hrs. The organic layer was then separated, washed with water (3 x 5 ml) and dried over sodium sulphate. Evaporation of the solvent under vacuum gave crude 5b or 5c which was purified by column chromatography on silica gel using petroleum ether-ethyl acetate (50:1) as eluent. Yields were nearly quantitative.

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A SYNTHESIS OF THE SIDEROPHORE

1,3,5-TRIS(N,N',N"-2,3-DIHYDROXYBENZOYL)AMINOMETHYLBENZENE

Submitted by (10/28/83) Paul F. Schuda[*+], Catherine M. Botti[+] and Michael C. Venuti[++]

[+]Department of Chemistry, University of Maryland
College Park, MD 20742

[++]Syntex Research Corporation
Institute of Bioorganic Chemistry
Palo Alto, CA 94303

Enterobactin (1) is a potent iron chelator ($K_f = 10^{52}$). Although two routes[1,2] of the enterobactin mimic 2 have been reported, the difficulties encountered in scale-up and reproduction of one of the procedures and the fact that experimental details for reference 2 are missing leads us to