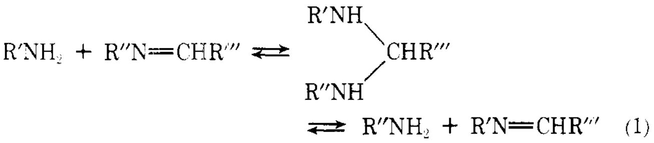
between **2** and **3** via aminals as shown below in eq 1. After standing for about 24 h at room temperature, the trans isomer content of **2** increased to ~65%. Separation of the resulting **2** and **3** was not attempted but should be possible by distillation or fractional crystallization. Repeated equilibration with trans-enriched samples of **2** and **3c** would even further increase the trans content of **2**.



$$\mathrm{R'NH_2} + \mathrm{R''N{=}CHR'''} \rightleftarrows \begin{matrix}\mathrm{R'NH}\\ \mathrm{R''NH}\end{matrix}\!>\!\mathrm{CHR'''} \rightleftarrows \mathrm{R''NH_2} + \mathrm{R'N{=}CHR'''} \quad (1)$$

R' = cis-R; R'' = trans-R; R''' = C_6H_5

The isomer distribution in all samples of amine **2** and imine **3** can be measured from the ^{13}C-NMR spectra of the samples. Use of ^{13}C rather than H NMR for the analysis is desirable as shift reagents are needed to separate coincident peaks in the proton spectra of the isomer mixtures.[9] Table I lists the ^{13}C chemical shifts of the compounds studied. The chemical shifts of several carbon positions, especially C-5, differ sufficiently to determine the isomer distribution by integration of peak areas.

Experimental Section[10]

Starting Materials. The required isomeric bis(4-benzylideneaminocyclohexyl)methanes **3a**, **3b**, and **3c** were prepared by heating benzene (or toluene) solutions of the corresponding amine **2a**, **2b**, or **2c** with 2 mol of benzaldehyde. The reaction flask is connected to a water separator and heating is continued until water separation is completed. Evaporation of solvent yields the imines in colorless crystals. Samples are recrystalized for analysis from chloroform–methanol (**3a** and **3c**) or methanol–water (**3b**); ^{13}C-NMR data are listed in Table I. **3a:** mp 132–133 °C; colorless plates; IR ($CHCl_3$) 1635 cm^{-1} (C=N). Anal. Calcd for $C_{27}H_{34}N_2$: C, 83.89; H, 8.87; N, 7.25. Found: C, 83.69; H, 9.02; N, 7.07. **3b:** mp 98–99 °C; colorless crystals; IR ($CHCl_3$) 1635 cm^{-1} (C=N). Anal. Calcd for $C_{27}H_{34}N_2$: C, 83.89; H, 8.87; N, 7.25. Found: C, 83.94; H, 8.83; N, 71.4. **3c:** mp 153–154 °C; colorless needles; IR ($CHCl_3$) 1635 cm^{-1} (C=N). Anal. Calcd for $C_{27}H_{34}N_2$: C, 83.89; H, 8.87; N, 7.25. Found: C, 84.00; H, 8.71; N, 7.19.

Cis–Trans Isomerization of 3a to 3c. (a) With Potassium *tert*-Butoxide. A 3.0-g sample of **3a** is suspended in 6 mL of 1,2-dimethoxyethene (DME). After adding 0.6 g of potassium *tert*-butoxide the mixture is stirred for 64 h under a blanket of nitrogen at room temperature, after which the thick suspension is diluted with water (ca. 40–50 mL). Colorless or nearly colorless crystals are left undissolved which are filtered off and after being washed with water are dried at 70 °C; yield 3.0 g, ^{13}C-NMR analysis gives an overall cis–trans ratio of 7:93. Stirring of the crude product with methanol and filtration leaves essentially pure **3c**.

(b) With Potassium Hydroxide–18-Crown-6. A mixture of 5.0 g of isomeric imines **3** with a cis–trans ratio of 72:28, 1.0 g of powdered potassium hydroxide, and 0.2 g of 18-crown-6 is suspended in 10 mL of DME and stirred for 95 h at room temperature in a nitrogen atmosphere. The resulting suspension is diluted with 50–60 mL of water, filtered, and dried at 70 °C, 5.0-g yield. ^{13}C NMR shows the crude material to contain more than 95% trans imine. Similar experiments with about 2–4 wt % Kryptofix 222 instead of 18-crown-6 give comparable results.

Hydrolysis of 3c. A solution of 10.0 g of **3c** in 100 mL of 2 N hydrochloric acid is kept at 50 °C for ca. 60 min. Hydrolysis is indicated by separation of droplets of benzaldehyde. The resulting mixture is extracted with methylene chloride (4 × 10 mL) after cooling. Drying the extracts with sodium sulfate and evaporation of solvent lead to quantitative recovery of benzaldehyde.

On adjusting the pH of the aqueous phase to 9–10 by adding 30% sodium hydroxide solution the *trans,trans*-amine **2c** is separated in fine droplets, which crystalize on scratching. Extraction with methylene chloride (4 × 10 mL) gives 5.5 g (quantitative) of crude **2c** after evaporation of solvent, mp (hexane) 63 °C (Lit.[11] 64–64.4 °C), identical in IR comparison with authentic **2c**.

Equilibration between 3c and an Isomer Mixture of 2. A mixture of isomers of **2** (1.05 g, 0.005 mol), having an overall cis–trans ratio of 71:29, is dissolved in 6 mL of methylene chloride together with 1.93 g (0.005 mol) of **3c**. ^{13}C-NMR analysis of the mixture after 24 h reveals a change of the cis–trans ratio of the amine **2** to 33:66 and of the imine **3** to 35:65.

Registry No.—**1**, 101-77-9; benzaldehyde, 100-52-7.

References and Notes

(1) W. J. Farrissey, Jr., and F. F. Frulla (to Upjohn Co.) German Offen. 1 948 566 (1970); Chem. Abstr., **72**, 132163b (1970); T. H. Chung, M. L. Dillon, and G. L. Lines (to Upjohn Co) German Offen. 2 423 639 (1975); Chem. Abstr., **82**, 139514g (1975).

(2) The two cyclohexene rings are linked equatorially to the bridging methylene group at C-1 and C-1'. With amino groups on C-4 and C-4' the cis,cis isomer **2a** has therefore a,e–e',a', the cis,trans isomer **2b** a,e–e',e', and the trans,trans isomer **2c** e,e–e',e' conformation.

(3) A. Sieglitz and O. Wulff (to Farbwerke Hoechst A.-G.) German Patent 875 653 (1953); *Chem. Abstr.*, **52**, 9201 (1958); E. Runne and H. Bestian (to Farbwerke Hoechst A.-G.) German Patent 748 457 (1952); *Chem. Abstr.*, **52**, 5459 (1958); E. Runne and F. Sinn (to Farbwerke Hoechst A.-G.) German Patent 909 456 and 909 457 (1954); *Chem. Abstr.*, **52**, 11123 (1958).

(4) M. Takamatsu, T. Sakurai, and M. Shiozaki (Teijin Ltd.) Japan 71 16 979; *Chem. Abstr.*, **75**, 35245j (1971); W. J. Arthur (to E. I. DuPont) German Patent 1 768 427 (1972); *Chem. Abstr.*, **77**, 47944r (1972); R. J. Kallal (to E. I. DuPont) German Offen. 2 301 106 (1973); *Chem. Abstr.*, **79**, 91683r (1973).

(5) W. J. Arthur (to E. I. DuPont) U.S. Patent 3 347 917 (1967); *Chem. Abstr.*, **69**, 18699u (1968); Y. Koneko, M. Shimada, and H. Yasuda (Asahi Chemical Industry Co., Ltd) Japan 73 34 735; *Chem. Abstr.*, **80**, 120389 (1974).

(6) E. I. DuPont de Nemours & Co., Netherlands Appl. 6 607 949 (1966); *Chem. Abstr.*, **67**, 21498s (1967); Imperial Chemical Industries Ltd., French Demande 2 012 261 (1970); *Chem. Abstr.*, **73**, 130691n (1970); W. Mesch (to BASF A.-G.) German Offen. 1 810 924 (1970); *Chem. Abstr.* **73**, 66133j (1970); K. Adam, H. I. Joschek, and H. Hoffmann (to BASF A.-G.) German Offen. 2 038 023 (1972); *Chem. Abstr.*, **76**, 112790h (1972); S. Kosaka and S. Wakamatsu (to Toray Industries, Inc.) Japan 72 38 438 (1972); *Chem. Abstr.*, **78**, 15647a (1973); Y. Hirai, K. Miyata, and K. Watanabe (to Mitsui Toatsu Chemicals Inc.) Japan Kokai 75 37 760 (1975); *Chem. Abstr.*, **83**, 131229t (1975).

(7) Related isomerizations involving carbanion formation have been reported: J. C. Clark, G. H. Phillipps, and M. R. Steer, *J. Chem. Soc., Perkin Trans. 1*, 475 (1976); R. D. Guthrie and J. L. Hedrick, *J. Am. Chem. Soc.*, **95**, 2971 (1973).

(8) J. C. Richer and D. Perelman, *Can. J. Chem.*, **48**, 570 (1970).

(9) H. V. Brederode and W. G. B. Huysmans, *Tetrahedron Lett.*, 1695 (1971).

(10) Elemental analyses were by Galbraith Laboratories, Knoxville, Tenn; IR were determined using a Beckman Acculab 4 and Perkin-Elmer 625 spectrophotometer; ^{13}C NMR spectra were determined with a Varian CFT 20 (in $CDCl_3$ with Me_4Si as interal standard). All melting points are uncorrected.

(11) A. E. Barkdoll, H. W. Gray, and W. Kirk, Jr., *J. Am. Chem. Soc.*, **73**, 741 (1951).

Intramolecular Aldol Condensation of 2,2'-Dimethylbenzil

Gerald J. Boudreaux and Ernest I. Becker*

Department of Chemistry, University of Massachusetts at Boston, Boston, Massachusetts 02125

Byron H. Arison

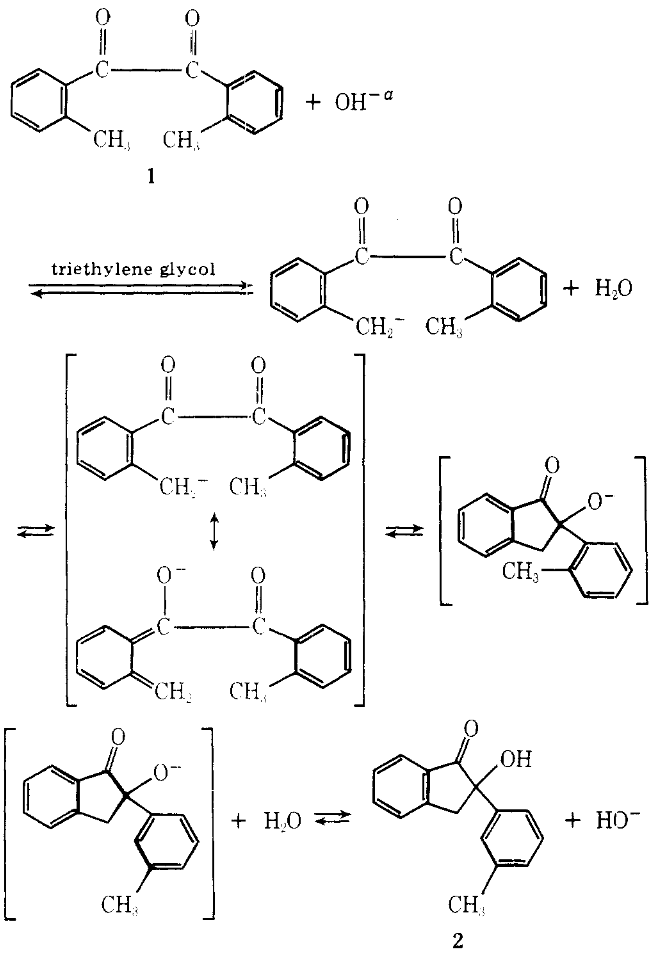
Research Laboratories, Merck, Sharp & Dohme, Rahway, New Jersey 07065

Received October 19, 1977

During the base-catalyzed condensation of 2,2'-dimethylbenzil (**1**) with 1,3-diphenyl-2-propanone to prepare the reddish-black 2,5-diphenyl-3,4-bis(*o*-tolyl)cyclopentadienone,[1] a crystalline, colorless side product (**2**) was isolated in 9% yield, mp 155–157 °C. Ultimate analysis agreed with the formula $C_{16}H_{14}O_2$, identical with that of the starting material, 2,2'-dimethylbenzil. **2** was insoluble in aqueous alkali. Treatment of **2** with alkali in alcohol restored a yellow color. The infrared spectrum showed the following peaks: 3400 (s, tertiary OH), 1700 cm^{-1} (s, C=O), 1602 (m, Ar), 1210 (s, C—O, C=O), 1055 (s, CO), 960 (w, Ar), and 745, 730, and 715 cm^{-1} (ortho-disubstituted Ar). The 300-MHz NMR spectrum ($CDCl_3$) revealed peaks at δ 2.348 (3 H, s, $ArCH_3$), 2.86 (1 H, s, OH), 3.58 (2 H, s, $ArCH_2$), 7.16 (1 H, m, tolyl H_3), 7.24 (2 H,

0022-3263/78/1943-1827$01.00/0

Scheme I



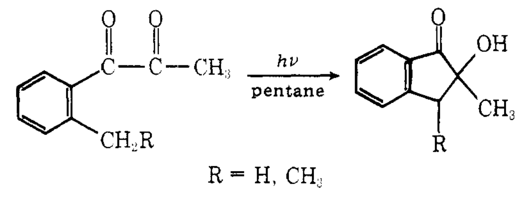
[a] From Triton B: PhCH$_2$N$^+$(CH$_3$)$_3$OH$^-$.

m, tolyl H$_4$, H$_5$), 7.37 (1 H, d, J = 8.0 Hz, tolyl H$_6$), 7.47 (1 H, d, J = 7.5 Hz, indanone H$_4$), 7.48 (1 H, t, J = 7.5 Hz, indanone H$_6$), 7.70 (1 H, d, t, J = 1.3, 7.5 Hz, indanone H$_5$), and 7.94 (1 H, d, J = 7.5 Hz, indanone H$_7$). Mass spectral analysis exhibited peaks at 238, 220, 119, and 91. These data are in agreement with 2-hydroxy-2-(*o*-tolyl)-1-indanone as the structure of **2**.

2 may be envisaged as forming from **1** via an intramolecular aldol condensation (Scheme I). The reversible arrows, characteristic of the aldol condensation, rationalize the formation of a yellow color [1?] when **2** is treated with alcoholic alkali.

The peaks in the mass spectrum may be rationalized by decomposition as shown in Scheme II. The peak at 220 might be accounted for by dehydration of **2** to the corresponding indenone in a parallel reaction. Cleavage of benzil to benzoyl in the mass spectrometer has been previously reported.[2]

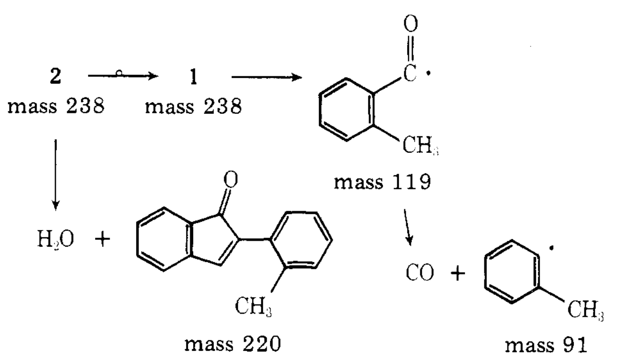
To the authors' knowledge this kind of rearrangement of a methylated benzil under basic conditions has not been reported. However, a photochemical reaction producing an analogous indanone has been observed[3,4] (eq 1). Therefore **1**



(1)

was subjected to photochemical conditions. In the presence of ultraviolet light in carbon disulfide, **1** afforded **2** in 60% yield. It thus became necessary to ascertain whether light was important in the base-catalyzed reaction. In the dark the base-catalyzed reaction was shown to produce **2**, thus suggesting that the base-catalyzed reaction and photochemical reaction are distinctly different reactions.

Scheme II



Experimental Section

2-Hydroxy-2-(*o*-tolyl)-1-indanone and 2,5-Diphenyl-3,4-bis(*o*-tolyl)cyclopentadienone. A solution of 0.224 g (0.94 mmol) of 2,2′-dimethylbenzil and 0.237 g (1.13 mmol) of 1,3-diphenyl-2-propanone in 1.0 mL of triethylene glycol was heated to 95 °C. Triton B (0.4 mL) was added and the solution was kept at 95–100 °C for 20 min. The solution turned dark purple upon addition of the catalyst. After cooling to room temperature, about 10 mL each of benzene and water were added. Separation of the benzene layer and distillation of the benzene at about 100 mm left a thick, purple oil, which was stored in a vacuum desiccator. After 1 h of standing, crystals formed, which were washed with about 3 mL of cyclohexane–benzene (95:5) and filtered quickly. Washing the crystals with a few drops of cold methanol afforded 0.020 g (9.0%) of **2**, mp 155–157 °C. Anal. Calcd for C$_{16}$H$_{14}$O$_2$: C, 80.65; H, 5.92. Found: C, 80.54; H, 6.21.

The purple liquid remaining after filtration of **2** was evaporated to dryness in vacuo, dissolved in a small amount of cyclohexane–benzene (95:5), and chromatographed on a column of neutral alumina (14 × 2.5 cm) using the same solvent as eluant. A yellow and a purple band separated. The column was cut and the alumina containing the purple band was extracted in a Soxhlet apparatus with 125 mL of benzene until the alumina was colorless. Distillation of the benzene left 0.027 g of purple crystals, which were recrystallized from 3 mL of methanol to give 0.015 g (3.9%) of purple-black product, mp 205–207.5 °C (lit.[5] mp 203–204 °C).

2-Hydroxy-2-(*o*-tolyl)-1-indanone. A. Base Catalyzed. A solution of 0.0687 g (0.288 mmol) of 2,2′-dimethylbenzil in 1.0 mL of triethylene glycol was heated in an oil bath to 100–105 °C. Addition of 0.4 mL of Triton B turned the solution red. After 20 min the solution was green and it was heated 5 min more. Benzene (15 mL) was added and the solution was washed with three 5-mL portions of water at which stage the solution was amber. The benzene layer was distilled slowly leaving brown crystals which turned colorless upon washing with cyclohexane–benzene (19:1): 7.2 mg (0.0302 mmol, 10.6%); mp 155–157 °C.

B. Photochemical. A solution of 0.050 g (0.210 mmol) of 2,2′-dimethylbenzil in 17 mL of carbon disulfide was irradiated at room temperature for 5 h using a Curtis Lighting light fixture holding a GE Bulb UA-3GE360W attached to a G. W. Gates & Co. Power Supply, Model 420-U1. Concentration of the solution and cooling afforded 0.030 g (0.126 mmol, 60%) of colorless **2**, mp 154–156 °C.

Acknowledgments. We wish to thank Merck and Co. for the use of the NMR and MS facilities. We also wish to thank Mr. Jack Smith for the determination and interpretation of the mass spectrum.

Registry No.—**1**, 2048-07-9; **2**, 65311-24-2; 2,5-diphenyl-3,4-bis(*o*-tolyl)cyclopentadienone, 65375-82-8; 1,3-diphenyl-2-propanone, 102-04-5.

References and Notes

(1) B. H. Arison, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1967 (Now the Polytechnic Institute of New York).
(2) J. H. Bowie, R. G. Cooks, and G. E. Gream, *Aust. J. Chem.*, **21**, 1247 (1968).
(3) R. Bishop and N. K. Hamer, *J. Chem. Soc. D*, 804 (1969).
(4) R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, 1193 (1970).
(5) Reference 1, p 71.