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Synthesis of N,N′-Diacylated 2,2′-Biphenyleneurea

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Several N,N′-diacylated 2,2′-biphenyleneureas were synthesized by quenching the intermediate resulting from the reaction between 2,2′-biphenyleneurea and *n*-butyllithium with the corresponding acylating reagent. The reactions were carried out under inert atmosphere in dried tetrahydrofuran at 0 °C. The prepared derivatives were identified on the basis of their NMR, IR, and elemental analysis data.

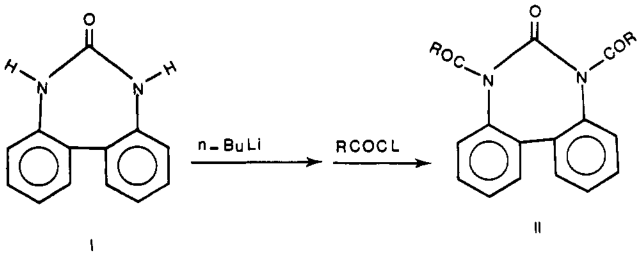
In continuation of our earlier conformational analysis and synthesis (*1*–*3*) of 5- and 6-membered heterocyclic rings fused to the benzene ring, we now report herein the synthesis of several new diacyl and diaroyl derivatives of 2,2′-biphenyleneurea (I). No detectable yields were obtained with classical methods of acylation (*1*, *2*). However, reasonable yields are obtained with the use of *n*-butyllithium (*3*). The reaction pathway is shown in Scheme I. The structures and the physical properties of the 2,2′-biphenyleneurea derivatives are shown in Table I.

Experimental Section

The IR spectra, as KBr disks, were recorded on a Pye-Unicam SP300 spectrophotometer. The ^{1}H NMR spectra were recorded, in acetone-d_6, on a Bruker WP 80-SY spectrometer. Me_4Si was used as internal standard. The elemental analyses (C, H, N) were performed by M-H-W Laboratories, Phoenix, AZ. Melting points were taken on an electrothermal melting point apparatus. The elemental analysis is in agreement with the calculated values and was submitted for review.

Preparation of 2,2′-Biphenylenediamine. 2,2′-Biphenylenediamine was prepared by the reduction of 2,2′-dinitrobiphenyl as described by Dieteren and Koningsberger (*4*).

Scheme I



Preparation of 2,2′-Biphenyleneurea. A mixture of 2,2′-biphenylenediamine (122 mmol), urea (122 mmol), and *n*-amyl alcohol (100 mL) was refluxed with stirring until no more ammonia was evolved. The product precipitates as it is formed. After the reaction mixture was cooled, the product was filtered and then recrystallized from acetic acid (*5*).

Acylation Procedure. The acylation of 2,2′-biphenyleneurea was carried out as follows: A round-bottom flask fitted with a stir bar, septum, gas inlet valve, and mercury bubbler was flame-dried while a stream of nitrogen was flowing through the system. 2,2′-Biphenyleneurea (4 mmol) was introduced in the flask and dissolved in dried tetrahydrofuran (40 mL). The tetrahydrofuran was purified prior to use by distillation over sodium benzophenone ketyl. The flask was then immersed in an ice bath and 8.5 mmol of a 1.6 M aliquot of *n*-butyllithium in hexane was added. The reaction mixture was stirred for 10 min and the corresponding acid chloride or anhydride was added (8 mmol). The ice bath was then removed and the reaction mixture was left with stirring for 15 min. Then, the solvent was removed under reduced pressure. The residue was washed with distilled water and then recrystallized from the appropriate solvent.

The IR spectra (KBr disks) show the following: I: 3200, 1710, and 1600 cm^{-1}; II: 1730–1750, 1695–1710, and 1600 cm^{-1}. These values are averages for series of compound II.

Table I. Structure, Physical Properties, and NMR Data of 2,2′-Biphenyleneurea and Its Derivatives

compd	R	mp, °C	yield, %	crystllg solvent	^{1}H NMR (δ)[a,b]
I		314–18[c]			7.0–7.5 (m, 8 H); 8.8 (s, 2 H)
IIa	H_3CCO	180–82	65	$EtOH-H_2O$	2.24 (s, 6 H); 7.49–7.81 (m, 8 H)
IIb	H_3CCH_2CO	140–42	72	$EtOH-H_2O$	0.93 (t, 6 H); 2.57 (m, 4 H); 7.5–7.7 (m, 8 H)
IIc	$(CH_3)_2CHCO$	131–33	61	$EtOH-H_2O$	0.70 (d, 6 H); 1.11 (d, 6 H); 3.24 (septet, 2 H); 7.5–7.75 (m, 8 H)
IId	$(CH_3)_3CCO$	103–05	57	petroleum ether	1.03 (s, 18 H); 7.50–7.86 (m, 8 H)
IIe	C_6H_5CO	201–02	66	EtOH	7.28–7.64 (m, 10 H); 7.72–8.04 (m, 8 H)
IIf	*o*-$CH_3C_6H_4CO$	235–36	72	EtOH	2.16 (s, 6 H); 6.56 (m, 2 H); 7.11 (m, 6 H); 7.74 (m, 8 H)
IIg	*o*-$CH_3OC_6H_4CO$	237–38	66	EtOH	3.38 (s, 6 H); 6.74–6.95 (m, 4 H); 7.12–7.42 (m, 4 H); 7.54–7.85 (m, 8 H)
IIh	*o*-$NO_2C_6H_4CO$	325–27	65	pyridine	7.60–7.75 (m, 14 H); 8.10 (m, 2 H)

[a] NMR spectra of all derivatives were recorded in acetone-d_6 and Me_4Si was used as internal standard. [b] NMR spectrum of compound I was recorded in deuteriated dimethyl sulfoxide for solubility reason. [c] Reported value in ref *5* is 315–320 °C.

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Registry No. I, 22719-62-6; IIa, 111190-33-1; IIb, 111190-34-2; IIc, 111190-35-3; IId, 111190-36-4; IIe, 2306-35-6; IIf, 111190-37-5; IIg, 111190-38-6; IIh, 111190-39-7; 2,2'-$H_2NC_6H_4C_6H_4NH_2$, 1454-80-4; H_2N-$CONH_2$, 57-13-6; H_3CCOCl, 75-36-5; H_3CCH_2COCl, 79-03-8; $(H_3C)_2CHCOCl$, 79-30-1; $(H_3C)_3CCOCl$, 3282-30-2; C_6H_5COCl, 98-88-4; 2-$H_3CC_6H_4COCl$, 933-88-0; 2-$H_3COC_6H_4COCl$, 21615-34-9; 2-$O_2NC_6H_4COCl$, 610-14-0.

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Synthesis of Some 12-Substituted 9,10-Dimethyldibenz[*b*,*g*]indolizine-8,11-diones

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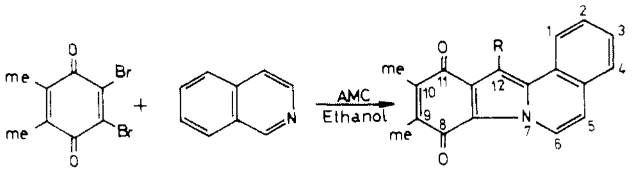
The synthesis of some 12-substituted 9,10-dimethyldibenz[*b*,*g*]indolizine-8,11-diones using 2,3-dibromo-5,6-dimethyl-1,4-benzoquinone with active methylene compounds and isoquinoline has been described.

Recently, we reported (*1*) the synthesis of some 7-substituted 9,10-dimethyldibenz[*b*,*e*]indolizine-8,11-diones using 2,3-dibromo-5,6-dimethyl-1,4-benzoquinone with active methylene compounds and quinoline. We report herein the synthesis of some 12-substituted 9,10-dimethyldibenz[*b*,*g*]indolizine-8,11-diones using isoquinoline instead of quinoline.

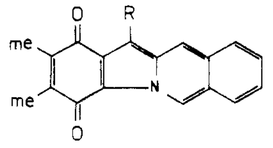


(I -VI)

I R = H
II R = CH_3
III R = CO CH_3
IV R = $CO_2C_2H_5$
V R = CO Ph
VI R = CN

The route employed is analogous to that reported by Pratt et al. (*2*) for synthesizing benzo[*g*]naphth[2,3-*b*]indolizine-8,13-diones.

Considering a similar mechanism to that of the pyridine series (*3*), the formation of compounds I-VI, and not the isomeric form (A), is favored by the fact that the proton in the 1-position in the isoquinoline ring is more acidic than the proton in the 3-position; thus position 1 will be more susceptible to neucleophilic attack to give the desired products which will be stabilized through aromaticity.



(A)

Experimental Section

Melting points were determined by using a Gallenkamp heated block apparatus.

IR spectra were recorded on a Perkin-Elmer 337 spectrometer using KBr disks.

^1H NMR spectra were recorded on a Jeol C-60 HL high-resolution NMR spectrometer using TMS as internal standard.

Microanalyses were carried out by the Analytical Department at the Iraqi National Oil Co. Elemental analyses (C, H, N) were obtained and submitted for review and were within ∓0.4% of the theoretical value (Table I).

Synthesis of 12-Substituted 9,10-Dimethyldibenz[*b*,*g*]indolizine-8,11-diones

General Method. A mixture of 2,3-dibromo-5,6-dimethyl-1,4-benzoquinone (0.0017 mol), which was prepared by fol-

Table I. Characterization Data of 12-Substituted 9,10-Dimethyldibenz[*b*,*g*]indolizine-8,11-diones

compd[a,b]	AMC used	yield, %	mp, °C	^1H NMR (δ, ppm)[c]
I	CH_3NO_2	13	275 (decomp)	2.2 (d, 6 H), 7.7 (m, 5 H), 8.4 (m, 2 H)
II	$C_2H_5NO_2$	21	>320	2.0 (d, 6 H), 2.85 (s, 3 H), 7.5 (m, 4 H), 8.35 (m, 1 H), 9.0 (d, 1 H)
III	$CH_3COCH_2COCH_3$	46	276–8	2.25 (s, 6 H), 3.05 (s, 3 H), 7.7 (m, 6 H)
IV	$CH_3COCH_2CO_2C_2H_5$	65	239–41	1.7 (t, 3 H), 2.2 (s, 6 H), 4.7 (q, 2 H), 7.5 (m, 4 H), 8.4 (m, 2 H)
V	CH_3COCH_2COPh	48	>290 (decomp)	2.25 (d, 6 H), 7.6 (m, 11 H)
VI	$NCCH_2CO_2C_2H_5$	50	>300 (decomp)	2.25 (s, 6 H), 7.7 (m, 5 H), 9.25 (d, 1 H)

[a] Compounds I–V were obtained as deep-red crystals or needles and compound VI as an orange powder. [b] The IR spectra of I to VI exhibited $\nu_{C=O}$ at 1640–1720 cm^{-1} besides the characteristic peaks. Compound VI also exhibited $\nu_{C\equiv N}$ at 2210 cm^{-1}. [c] The ^1H NMR spectra were all recorded in CF_3COOH except for compound V which was recorded in DMSO.

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