Synthesis of 1*H*-Indeno[1,2-*f*]-3,6a-methano-1,3,5-triazocines from *N*,*N'*-Dibenzylidenephenylmethanediamines and 1-Indanone

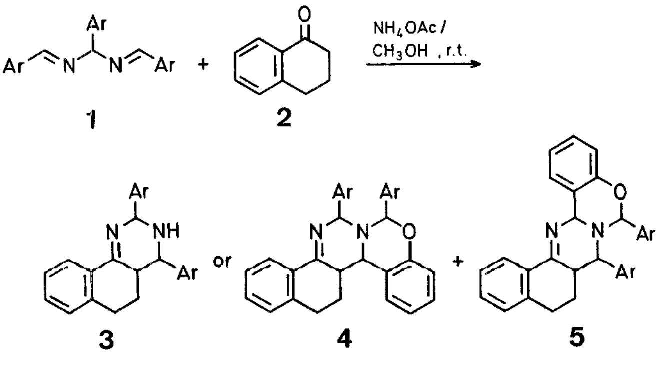
Tokiharu TAKAJO*, Satoshi KAMBE

Oyama National College of Technology, Oyama-shi, Tochigi 323, Japan

Wataru ANDO

Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki 300-31, Japan

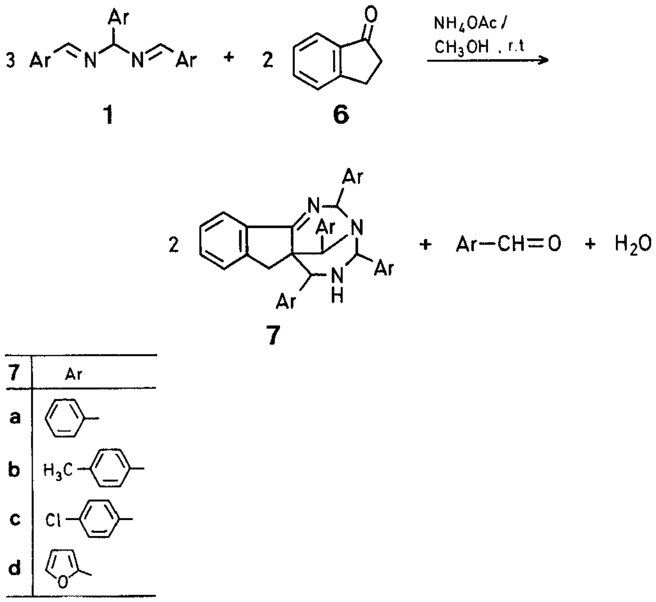
Open chain compounds with double carbon-nitrogen double bonds have potential as convenient reagents for the synthesis of nitrogen-containing heterocycles. Apart from the many systematic studies on carbodiimides[1], which are applied to the synthesis of peptides and azines[2], the other open-chain double Schiff bases have been little used synthetically. On the other hand, cyclocondensation of *N*,*N'*-dibenzylidenephenylmethanediamines (**1**) and α-tetralone (**2**) gave 57–70% yields of the benzoquinazoline (**3**; Ar = C_6H_5, 4-H_3CO—C_6H_4, 4-Cl—C_6H_4, 2-Cl—C_6H_4) or a mixture (2:1 molar ratio) of **4** and **5** (Ar = 2-HO—C_6H_4) (Scheme **A**)[3].



Scheme **A**

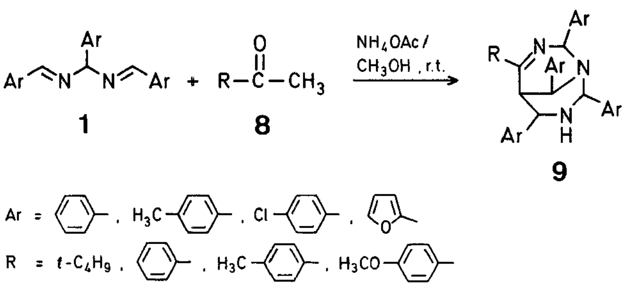
0039-7881/82/1232-1080 $ 03.00

In the present communication, we report the synthesis of novel 1*H*-indeno[1,2-*f*]-3,6a-methano-1,3,5-triazocines (**7**) from **1** and 1-indanone (**6**) by similar treatment (Scheme **B**) of an equimolar mixture of **1**, **6**, and ammonium acetate in methanol at room temperature until no further white precipitate is produced (50-73% yield of **7**).



Scheme **B**

A strikingly parallel example to the formation of **7** is the formation of 1,3,5-triazabicyclo[3.3.1]-3-nonenes **9** from the following condensation of **1** with alkyl or aryl methyl ketone **8** (Scheme **C**)[4].



Scheme **C**

1*H*-Indeno[1,2-*f*]-3,6a-methano-2,4,6,12-tetraphenyl-2,3,4,5,6,6a-hexahydro-1,3,5-triazocine (7a):

A mixture of **1a** ($Ar=C_6H_5$, 1.49 g, 5 mmol), 1-indanone (**6**; 0.66 g, 5 mmol), and ammonium acetate (0.4 g, 5 mmol) in methanol (5 ml) is magnetically stirred at ambient temperature for 10 h, and the mixture allowed to stand overnight. The deposited precipitate is collected and recrystallized from 1:1 tetrahydrofuran/methanol (20 ml) to give **7a** as a white crystalline material; yield: 1.2 g (70%); m.p. 204-205 °C.

$C_{37}H_{31}N_3$	calc.	C 85.85	H 6.04	N 8.12
(517.6)	found	85.59	6.10	8.01

I.R. (nujol): $\nu=3320$ (NH), 1664 (C=N), 755, 701 cm⁻¹.

¹H-N.M.R. ($CDCl_3$): $\delta=8.0$-6.7 (m, 24 H_{arom}); 6.00 (s, 1H, N—C<u>H</u>—N=); 5.26 (d, 1H, NH—C<u>H</u>—N, $J=4$ Hz); 4.79 (d, 1H, NH—C<u>H</u>—C, $J=4$ Hz); 4.28 (s, 1H, N—C<u>H</u>—C); 3.46, 3.00 (2 d, 1H each, <u>H</u>—C—<u>H</u>, $J=16$ Hz); 1.98 ppm (t, 1H, N<u>H</u>, $J=4$ Hz).

1*H*-Indeno[1,2-*f*]-3,6a-methano-2,4,6,12-tetrakis[4-methylphenyl]-2,3,4,5,6,6a-hexahydro-1,3,5-triazocine (7b):

An equimolar (5 mmol) mixture of **1b** ($Ar=4\text{-}H_3C—C_6H_4$), **6**, and ammonium acetate in methanol (5 ml) is treated as above to give **7b** as a white crystalline material; yield: 1.1 g (58%); m.p. 172-174 °C.

$C_{41}H_{39}N_3$	calc.	C 85.82	H 6.85	N 7.32
(573.8)	found	85.60	6.95	7.12

I.R. (nujol): $\nu=3250$ (NH), 1659 (C=N), 814, 770, 736 cm⁻¹.

¹H-N.M.R. ($CDCl_3$): $\delta=7.8$-6.6 (m, 20 H_{arom}); 5.95 (s, 1H, N—C<u>H</u>—N=); 5.23 (s, 1H, NH—C<u>H</u>—N); 4.73 (s, 1H, NH—C<u>H</u>—C); 4.24 (s, 1H, N—C<u>H</u>—C); 3.40, 2.98 (2 d, 1H each, <u>H</u>—C—<u>H</u>, $J=16.5$ Hz); 2.35, 2.30, 2.23, 2.08 (4 s, 3H each, C<u>H</u>₃); 2.00 ppm (s, 1H, N<u>H</u>).

1*H*-Indeno[1,2-*f*]-3,6a-methano-2,4,6,12-tetrakis[4-chlorophenyl]-2,3,4,5,6,6a-hexahydro-1,3,5-triazocine (7c):

An equimolar (5 mmol) mixture of **1c** ($Ar=4\text{-}Cl—C_6H_4$), **6**, and ammonium acetate in methanol (5 ml) is stirred for 19 h and allowed to stand for 1 day. The deposited precipitate is collected and recrystallized from 1:1 tetrahydrofuran/methanol (30 ml) to give **7c** as a white crystalline material; yield: 1.6 g (73%); m.p. 205-206 °C.

$C_{37}H_{27}N_3Cl_4$	calc.	C 67.80	H 4.15	N 6.41
(655.4)	found	67.59	4.01	6.59

I.R. (nujol): $\nu=3230$ (NH), 1661 (C=N), 1100, 1023, 818, 741 cm⁻¹.

¹H-N.M.R. ($CDCl_3$): $\delta=7.9$-6.8 (m, 20 H_{arom}); 5.88 (s, 1H, N—C<u>H</u>—N=); 5.17 (s, 1H, NH—C<u>H</u>—N); 4.72 (s, 1H, NH—C<u>H</u>—C); 4.16 (s, 1H, N—C<u>H</u>—C); 3.36, 3.03 (2d, 1H each, <u>H</u>—C—<u>H</u>, $J=15.5$ Hz); 1.90 ppm (br, 1H, N<u>H</u>).

1*H*-Indeno[1,2-*f*]-3,6a-methano-2,4,6,12-tetrakis[2-furyl]-2,3,4,5,6,6a-hexahydro-1,3,5-triazocine (7d):

An equimolar (5 mmol) mixture of **1d** (Ar = 2-furyl), **6**, and ammonium acetate in methanol (2 ml) is stirred for 7 h and allowed to stand for 1 day. The deposited precipitate is collected and recrystallized from 1:1 tetrahydrofuran/methanol (20 ml) to give **7d** as a white crystalline material; yield: 0.8 g (50%); m.p. 193-194 °C.

$C_{29}H_{23}N_3O_4$	calc.	C 72.94	H 4.86	N 8.80
(477.5)	found	72.77	4.93	8.63

I.R. (nujol): $\nu=3325$ (NH), 3110, 1655 (C=N), 1148, 1010, 808, 758, 736 cm⁻¹.

¹H-N.M.R. ($CDCl_3$): $\delta=8.0$-6.0 (m, 16 H_{arom} and 1H, N—C<u>H</u>—N=); 5.65 (s, 1H, NH—C<u>H</u>—N); 4.89 (s, 1H, NH—C<u>H</u>—C); 4.62 (s, 1H, N—C<u>H</u>—C); 3.31, 2.96 (2 d, 1H each, <u>H</u>—C—<u>H</u>, $J=16.5$ Hz); 2.4 ppm (br, 1H, N<u>H</u>).

Received: June 3, 1982

---

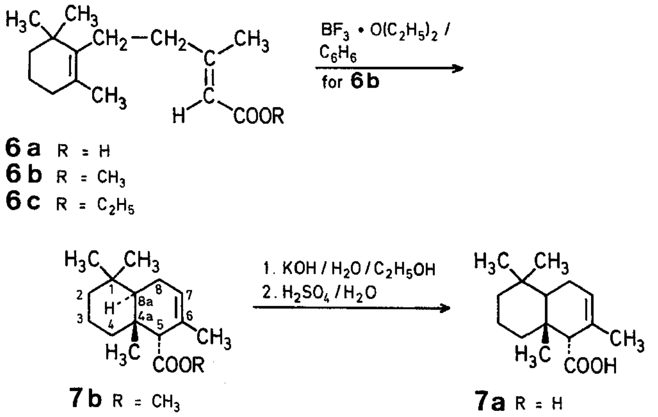
[1] M. Mikołajczyk, P. Kielbasinski, *Tetrahedron* **37**, 233 (1981).
A. Williams, I. T. Ibrahim, *Chem. Rev.* **81**, 589 (1981).

[2] T. Wagner-Jauregg, *Synthesis* **1976**, 349.

[3] T. Takajo et al., *Oyama Kogyo Koto Senmon Gakko Kenkyu Kiyo* **12**, 19 (1980); *C. A.* **94**, 65590 (1981).

[4] T. Takajo, S. Kambe, *Synthesis* **1981**, 151.

C. Schmidt, N. H. Chishti, T. Breining, *Synthesis* **1982** (5), 391-393:
The formula scheme for the reaction **6**→**7** (p. 391) should be:



6a R = H
6b R = CH_3
6c R = C_2H_5

7b R = CH_3

7a R = H

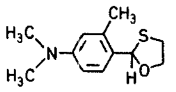
B. A. Arbuzov, N. N. Zobova, *Synthesis* **1982** (6), 433-450:
The correct name for compound **15** (p. 436) is *N'*-benzoyl-*N*,*N*-dimethyl-2-phenyl-2-butenamidine and for compound **30b** (p. 439) is 4-trifluoroacetylimino-2-trifluoromethyl-4*H*, 9a*H*-pyrido[2,1-*b*]-1,3,5-oxadiazine.

Chen-Chu Chan, Xian Huang, *Synthesis* **1982** (6), 452-454:
The last sentence on page 452 should read: However, under the normal conditions [20% aqueous sodium hydroxide in the presence of benzyltriethylammonium chloride (TEBA)] the ring underwent cleavage and the main product was dimethylmalonic acid in the case of methylation.

P. Molina, A. Arques, A. Ferao, *Synthesis* **1982** (8), 645-647:
Compounds **3**,**4**, and **6** are substituted pyrido[2,1-*b*][1,3,4]thiadiazinium salts.

Abstract 6431, *Synthesis* **1982** (9), 801
The correct name for the title compounds **3** is 2-oxoalkanehydroximic chlorides.

B. Burczyk, Z. Kortylewicz, *Synthesis* **1982** (10), 831-832:
In Table 1 (p. 832) the b.p. of product **6a** should be 113-114°C/0.3 torr; the structure and molecular formula of product **7d** should be



and $C_{12}H_{17}NOS$ (223.2); the b.p. and n_D^{20} of product **8a** should be 114-116°C/60 torr and 1.5346, respectively. In Table 2 (p. 832) the second term in the ^{1}H-N.M.R. spectrum of product **7b** should be 1.90 (s, 3H, CH_3).

K. D. Deodhar, A. D. D'Sa, S. R. Pednekar, D. S. Kanekar, *Synthesis* **1982** (10), 853-854:
The correct name for compounds **4a**,**b** (p. 854) is (*E*)- and (*Z*)-6-benzylidene-3-oxo-2,3,4,6-tetrahydro[1,2,4]triazino[3,4-*a*]isoindoles.

L. Lepage, Y. Lepage, *Synthesis* **1982** (10), 882-884:
The correct name for compound **10** (p. 884) is 2-acetyl-1,4-diphenyl-1,2,3,4-tetrahydro-1,4-epithiopentacene-7,12-quinone.

R. R. Schmidt, A. Wagner, *Synthesis* **1982** (11), 958-962:
It should be noted that the numbers in the products **5**-**16c** in Table 1 refer only to the ^{1}H-N.M.R. data in Table 2 and are not identical with the numbering used for the systematic nomenclature of the products.

T. Takajo, S. Kambe, W. Ando, *Synthesis* **1982** (12), 1080-1081:
The compounds **7** should be named 2,4,6,12-tetraaryl-2,5,6,7-tetrahydro-4*H*-3,6a-methanoindeno[1,2-*f*][1,3,5]triazocines.