

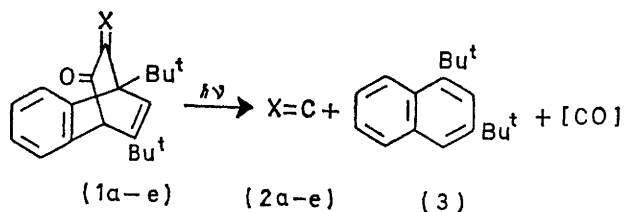
## Isocyanides from Monoimines of a Bicyclo[2,2,2]octadienedione

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**Summary** A photo-cycloreversion of the *N*-*n*-propyl-, *N*-cyclohexyl-, and *N*-phenyl-monoimine derivatives (**1b—d**) of 1,8-di-*t*-butyl-5,6-dioxo-2,3-benzobicyclo-octa-2,7-diene (**1a**) gives the corresponding isocyanides (**2b—d**) and 1,3-di-*t*-butylnaphthalene in good yields.

PHOTO-ELIMINATION of a bridge in 1,8-di-*t*-butyl-5,6-dioxo-2,3-benzobicyclo-octa-2,7-diene (**1a**) (a yellow solid adduct from benzyne and 3,5-di-*t*-butyl-*o*-benzquinone)<sup>1</sup> and its *N*-*n*-propyl- (**1b**), *N*-cyclohexyl- (**1c**) and *N*-phenyl-monoimine (**1d**) and -monoxime (**1e**) derivatives produced 1,3-di-*t*-butylnaphthalene (**3**)<sup>2</sup> in good yields.† Each monoimine



a; X = O, b; X = N-Pr, c; X = N-cyclo-C<sub>6</sub>H<sub>11</sub>, d; X = N-Ph, e; X = NOH.

also gave a good yield of the corresponding *n*-propyl (**2b**), cyclohexyl (**2c**), and phenyl isocyanide (**2d**). No attempt was made to detect either carbon monoxide, presumably a product of each photoreaction as either a concerted or a stepwise process, or fulminic acid expected from the oxime (**1e**).

Each sample in degassed cyclohexane was irradiated with light at 254 nm until starting material could no longer be detected by t.l.c. The mixture was separated on a silica gel column. Products (**2**) and (**3**) (Table 2) gave identical comparison with authentic material. The yield of *n*-propyl

isocyanide was determined after transformation (assumed to be quantitative) into *N*-*n*-propylformamide, identical with an authentic sample.<sup>5</sup>

TABLE 1.

Derivatives of (**1a**) from reactions with amines (RNH<sub>2</sub>).

R	Time, min	( <b>1</b> )	Yield %	m.p. °C	$\nu_{\max}$ cm <sup>-1</sup> C=O, C=N
Pr ..	15	( <b>b</b> )	67	152—153	1740, 1669
cyclo-C <sub>6</sub> H <sub>11</sub>	120	( <b>c</b> )	50	155—156	1740, 1661
Ph ..	180	( <b>d</b> )	51	85—86	1727, 1660
HO ..	240	( <b>e</b> )	69	202—203	1724, 1634

Heating the diketone (**1a**) with an equimolar amount of a primary amine in methanol at reflux containing a few drops of hydrochloric acid gave the corresponding yellow monoimine (**1b—d**) (Table 2). The colourless oxime was obtained from (**1a**) and hydroxylamine hydrochloride in aqueous DMSO (Table 2). Unsuccessful attempts to prepare the di-imine or dioxime derivatives by treating (**1a**)

TABLE 2.

N.m.r. (CDCl<sub>3</sub>) singlets for 1-*t*-Bu<sup>t</sup> in (**1a—e**).

( <b>1</b> )	$\delta$ (integration)	Coalescence temp. °C	$\Delta G^\ddagger$ kcal/mol
( <b>a</b> )	1.36(6), 1.73(3)	110	19.19
( <b>b</b> )	1.36(3), 1.41(3), 1.75(3)	116	19.50
( <b>c</b> )	1.35(3), 1.40(3), 1.72(3)	120	19.71
( <b>d</b> )	1.38(3), 1.43(3), 1.80(3)	126	19.98
( <b>e</b> )	1.37(3), 1.40(3), 1.91(3)	124	19.88

with an excess of an amine or by treating the monoimine or monoxime with the appropriate amine led to the formation of, or recovery of, the monoimine or monoxime.

The imine or oxime function can be assigned to the 6-position and magnetically non-equivalent protons to the *t*-butyl group in the 1-position in (**1b—e**). In the diketone (**1a**) and its derivatives (**1b—e**) one butyl group showed an

† Each new compound and (**1a**) m.p. 135—136° (lit.<sup>1</sup> m.p. 103°) gave satisfactory elemental analyses.

n.m.r. singlet for 9H but the other t-butyl in (**1a**) was split into two singlets (2:1) and into three singlets (1:1:1) in each derivative (Table 3). This is consistent with a hindrance to free rotation for the t-butyl group at the 1-position. Coalescence temperatures were determined and  $\Delta G^\ddagger$  values were calculated using Eyring's equation<sup>6</sup> (Table 3). Each original spectrum was observed on cooling the sample to room temperature.

After heating in xylene (170–180°C, 4 h) the diketone (**1a**) could no longer be detected and 1,3-di-t-butyl-naphthalene (**3**) was isolated (51%). Unresolved product mixtures were obtained from similar treatment of (**1b–e**).

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<sup>1</sup> W. Ried and T. S. Eng, *Annalen*, 1969, **727**, 219.

<sup>2</sup> R. W. Franck and E. G. Leser, *J. Org. Chem.*, 1970, **35**, 3932.

<sup>3</sup> M. H. Guillemand, *Ann. Chim. Phys.*, 1908, **14**, 311.

<sup>4</sup> I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, 'Isonitrile Syntheses' in 'Newer Methods of Preparative Organic Chemistry,' ed. W. Foerst, Academic Press, New York, 1968, p. 37.

<sup>5</sup> P. G. Piquett, W. A. Gersdorff, and S. I. Gertler, U.S. Dept. Agr., A.R.S., *ARS-33-17*, 1956; *Chem. Abs.*, 1955, **50**, 8125d.

<sup>6</sup> H. Kessler, *Angew. Chem. Internat. Edn.*, 1970, **9**, 219.