Table II. Physical Data for Compounds 7

compd[a]	R	yield, %	mp, °C
7a	C_6H_5	80	110-111
7b	o-$CH_3C_6H_4$	70	67-68
7c	p-BrC_6H_4	85	129-131
7d	p-$CH_3C_6H_4$	90	120-121
7e	p-$NO_2C_6H_4$	85	128-130

[a] Elemental analyses (C, H, N) were submitted for review and agree well with the theoretical values.

to the proposed structure of compounds **5**. The amidoxime derivatives **7** are accessible by reacting the parent amidoximes **6** with ethyl chloroformate in the presence of triethylamine.

Compounds **7** show two N-H stretching bands at 3260-3495 cm^{-1}, in addition to a strong C=O stretching at 1745-1760 cm^{-1} (Table II). The ^{1}H NMR spectra of compounds **7** exhibit, besides the aromatic protons, a broad singlet at about δ 5 ppm (2 H), attributed to the NH_2 protons. The ethoxy hydrogens appear as a quartet centered at about δ 4.2-4.4 ppm (2 H) and a triplet at about 1.3-1.4 ppm (3 H).

Experimental Section

Melting points were determined on a Philip-Harris melting point apparatus and are uncorrected. The IR spectra (KBr) were measured on a Perkin Elmer 577 spectrophotometer. A Varian T-60A spectrometer was used to obtain the ^{1}H NMR spectra, with tetramethylsilane as the internal reference. The mass spectra were recorded on a Varian MAT 112 spectrometer using the direct inlet technique (EI, 70eV).

Hydroxamoyl chlorides were prepared by direct chlorination of aldoximes as described elsewhere (*4*). Amidoximes were synthesized from the corresponding nitriles and hydroxylamine hydrochloride following literature (*7-9*) procedures.

***3-Aryl-1,2,4-oxadiazol-5(4H)-ones* (*5*).** (a) Potassium cyanate (15 mmol) and the particular hydroxamoyl chloride (10 mmol) were stirred in dry acetone (about 20 mL) overnight at room temperature. Water (50 mL) was then added and the precipitate was collected by filtration and crystallized from acetone-petroleum ether (bp 40-60 °C); yields were in the range of 50-65%.

(b) To a stirred solution of the *O*-carbethoxyamidoxime **7** (10 mmol) in absolute ethanol (20 mL), sodium (15 mmol) was added portionwise over a period of 10 min. The solvent was then removed in vacuo, and the residue acidified with 5% hydrochloric acid. The precipitate was filtered, air-dried, and crystallized.

***O-Carbethoxyamidoximes* (*7*).** To a stirred solution of the amidoxime (20 mmol) in chloroform (40 mL) was added at room temperature a solution of ethyl chloroformate (22 mmol) in chloroform (10 mL). To this reaction mixture, triethylamine (30 mmol) was then added dropwise. The resulting mixture was finally stirred for 1 h at room temperature and then washed twice with water (2 × 50 mL). The organic layer was dried (anhydrous sodium sulfate) and the solvent evaporated. The solid residue was crystallized from chloroform-petroleum ether (bp 40-60 °C).

Registry No. **1a**, 698-16-8; **1b**, 74467-03-1; **1c**, 29203-58-5; **1d**, 36288-37-6; **1e**, 1011-84-3; **1f**, 33512-94-6; **5a**, 1456-22-0; **5b**, 26925-60-0; **5c**, 16672-19-8; **5d**, 31827-28-8; **5e**, 19932-97-9; **5f**, 24011-15-2; **6a**, 613-92-3; **6b**, 40312-14-9; **6c**, 19227-14-6; **6d**, 19227-13-5; **6e**, 1613-86-1; **7a**, 54752-10-2; **7b**, 104849-77-6; **7c**, 104849-78-7; **7d**, 31827-21-1; **7e**, 104849-79-8; potassium cyanate, 590-28-3; ethyl chloroformate, 541-41-3.

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A Convenient Synthesis of N,N'-Acylated Perimidones

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

In the course of our study of the conformational analysis of 5- and 6-membered heterocyclic rings fused to benzene ring, we have reported the synthesis of several diacyl and diaroyl derivatives of benzimidazolone (*1*), benzimidazole (*2*), and tetrahydroquinoxaline (*3*). To extend the study, it was necessary to synthesize monoacylated and diacylated perimidone derivatives (II and III). No detectable yields were obtained with classical methods of acylation (*2*, *3*) except with the dibenzoyl derivative (*4*) (III; R = phenyl). However, good to excellent yields are obtained with the use of *n*-butyllithium. *n*-Butyllithium deprotonates the perimidone and renders the nitrogen atom more nucleophilic to react with the corresponding acid chloride or anhydride. The reaction pathway is shown in Scheme I. The structures and the physical properties of the

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Table I. Structure, Physical Properties, and NMR Data of Perimidone and Its Derivatives

compd	R	mp, °C	yield, %	crystllg solvent	^{1}H NMR(δ)[a,b]
I		304–05			6.68 (m, 2 H)[c] 7.21 (m, 4 H) 9.13 (b, 2 H)
IIa	H	245–46	49	EtOH	7.00 (m, 1 H) 7.45 (m, 5 H) 8.64 (bs, 1 H) 9.79 (s, 1 H)
IIb	CH_3	273–74	65	$EtOH/H_2O$	2.77 (s, 3 H) 6.69 (bs, 1 H) 7.18 (m, 5 H) 9.14 (bs, 1 H)
IIc	$(CH_3)_2CH$	179–81	72	$EtOH/H_2O$	1.22 (d, 6 H) 3.48 (septet, 1 H) 6.62 (m, 1 H) 6.85 (m, 1 H) 7.28 (m, 4 H) 9.50 (bs, 1 H)
IIIa	CH_3	146–48	84	$EtOH/H_2O$	2.69 (s, 6 H) 7.41 (m, 6 H)
IIIb	H_3CCH_2	103–04	79	$EtOH/H_2O$	1.25 (t, 6 H) 3.06 (q, 4 H) 7.03 (m, 2 H) 7.38 (m, 4 H)
IIIc	$(H_3C)_3C$	95–96	74	$EtOH/H_2O$	1.42 (s, 18 H) 6.50 (m, 2 H) 7.43 (m, 4 H)
IIId	o-$CH_3C_6H_4$	185–86	89	EtOH	2.60 (s, 6 H) 6.95 (d, 2 H) 7.24 (m, 10 H) 7.98 (d, 2 H)
IIIe	*o*-$CH_3OC_6H_4$	209–11	93	EtOH	3.65 (s, 6 H) 7.10 (m, 4 H) 7.44 (m, 8 H) 7.92 (m, 2 H)
IIIf	*o*-NO_2-C_6H_4	188–90	51	EtOH	7.76 (m, 12 H) 8.10 (m, 2 H)

[a] NMR spectra were recorded in acetone-d_6 and Me_4Si was used as internal standard. [b] bs means broad singlet. [c] The chemical shift of the aromatic protons on the ortho carbon.

Scheme I

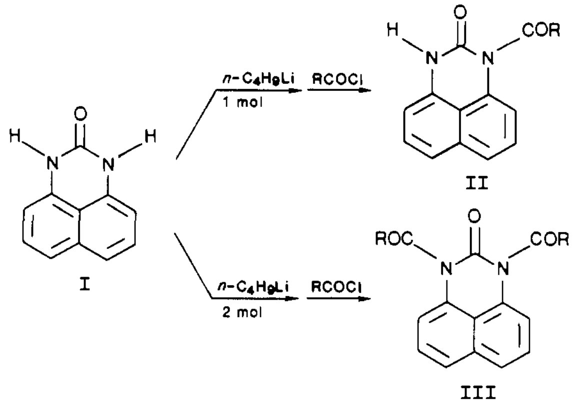

Table II. Elemental Analysis[a]

compd	% C	% H	% N
IIa	67.93 (67.73)	3.77 (4.00)	13.21 (13.16)
IIb	69.03 (69.18)	4.42 (4.39)	12.39 (12.45)
IIc	70.87 (70.76)	5.51 (5.50)	11.02 (11.05)
IIIa	67.16 (67.10)	4.48 (4.64)	10.45 (10.59)
IIIb	68.90 (68.58)	5.40 (5.34)	9.50 (9.85)
IIIc	71.59 (71.60)	6.82 (6.89)	7.95 (8.04)
IIId	77.10 (76.86)	4.80 (5.04)	6.67 (6.65)
IIIe	71.68 (71.51)	4.43 (4.65)	6.20 (6.26)
IIIf	62.24 (61.83)	2.9 (2.61)	11.62 (11.86)

[a] Calculated (found).

perimidone derivatives are shown in Table I.

Experimental Section

The IR spectra, as KBr disks, were recorded on a Pye-Unicam SP 300 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 (Table II).

***Acylation Procedure*.** The acylation of perimidone 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. Perimidone (5 mmol) was introduced in the flask and dissolved in dried tetrahydrofuran (30 mL). The tetrahydrofuran was purified prior to use by distillation over sodium benzophenone ketyl. The flask was then immersed in an ice bath and 10.5 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 (5 mmol for monoacylated and 10 mmol for diacylated perimidones). 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: 3210, 1715, and 1600 cm^{-1}; II: 3200, 1710–1660, and 1590 cm^{-1}; III: 1725 and 1660 cm^{-1}.

Registry No. I, 5157-11-9; IIa, 105335-85-1; IIb, 105335-86-2; IIc, 105335-87-3; IIIa, 105335-88-4; IIIb, 105335-89-5; IIIc, 105335-90-8;

IIId, 105335-91-9; IIIe, 105335-92-0; IIIf, 105335-93-1.

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Reaction of 1-Benzyl-1*H*-triazole-4,5-dicarboxaldehyde with Cyclic Ketones

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Three 4-hydroxy-1-benzyl-4,5-dihydro-5,7-polymethyleno-6(2*H*)-cycloheptatriazolones (IVa–c) and 1-benzyl-5,7-dodecano-6(2*H*)-cycloheptatriazolone (III) were synthesized by the aldol-type condensation reaction of 1-benzyl-1*H*-triazole-4,5-dicarboxaldehyde (I) with cyclododecanone (IIa), cycloundecanone (IIb), cyclododecanone (IIc), and cyclopentadecanone (IId), respectively.

Azides have been considered as one of the most important precursors for the synthesis of triazoles by their reactions with substituted acetylenes. As part of our continuous interest in the syntheses and reactions of triazole derivatives (*1*, *2*). I report here details of the condensation reaction of 1-benzyl-1*H*-triazole-4,5-dicarboxaldehyde (I) with cyclic ketones (IIa–d) to form polymethylene-bridged 1-benzylcycloheptatriazolones. Bridged cycloheptatriazolone (III) was obtained when I was condensed under aldol condensation reaction condition with cyclopentadecanone (IId). But when I was condensed with IIa–c under the same condition, the corresponding hydroxycycloheptatriazolones (IVa–c) were obtained (Scheme I). This I:I cyclic addition is closely analogous to known cycloaddition between phthalaldehyde and cyclic ketones (*3*, *4*).

Scheme I

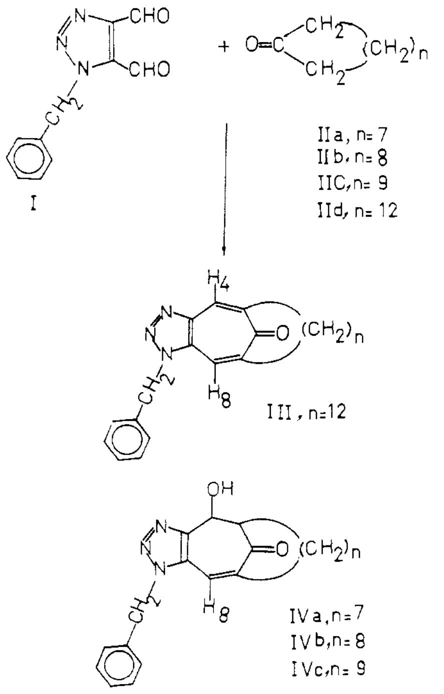

Table I. Physical Data and NMR Spectra of Prepared Compounds[a]

compd	mp, °C	reflux time, h	yield, %	¹H NMR[b] ppm	¹H NMR[b] assignments
III	205–207	8	60	7.75	(H_4, H_8, 2 H, S)
				7.22	(C_6H_k–, 5 H, S)
				5.75	(C_6H_5–CH_2–, 2 H, m)
				2.60–3.0	($C{=}C{-}CH_2$, 4 H, m)
				0.85–1.65	(–CH_2–, 20 H, m)
IVa	197–199	9	54	7.28	(C_6H_5–, 5 H, S)
				6.85	(H_8, 1 H, S)
				5.70	(–*OH*, 1 H, S)
				5.55	(C_6H_5–CH_2–, 2 H, S)
				4.80	(>C(OH)H, 1 H, m)
				3.15	(H_5, 1 H, m)
				0.9–1.90	(–CH_2–, 14 H, m)
IVb	205–207	2.5	72	7.27	(C_6H_5–, 5 H, S)
				6.90	(H_8, 1 H, S)
				5.68	(–*OH*, 1 H, S)
				5.52	(C_6H_5–CH_2–, 2 H, S)
				4.60	(>C(OH)H, 1 H, m)
				3.17	(H_5, 1 H, m)
				2.36–2.63	(–CH_2–, 2 H, m)
				2.0–2.20	(–CH_2–, 2 H, m)
				1.0–1.35	(–CH_2–, 12 H, m)
IVc	217–218	2	71	7.20	(C_6H_5–, 5 H, S)
				6.90	(H_8, 1 H, S)
				5.70	(–OH, 1 H, S)
				5.57	(C_6H_5–CH_2–, 2 H, S)
				4.68	(>C(OH)H, 1 H, m)
				3.25	(H_5, 1 H, m)
				2.45–2.65	(–CH_2–, 2 H, m)
				2.11–2.20	(–CH_2–, 2 H, m)
				0.90–1.30	(–CH_2–, 14 H, m)

[a] Elemental analysis, (C, H, N) in agreement with theoretical values were obtained and submitted for review. [b] $CDCl_3$–Me_2SO-d_6 was used as the NMR solvent for all compounds except $CDCl_3$ used for compound III. 4-Hydroxy-1-benzyl-4,5-dihydro-5,7-heptano-6(2*H*)-cycloheptatriazolone (IVa). 4-Hydroxy-1-benzyl-4,5-dihydro-5,7-octano-6(2*H*)-cycloheptatriazolone (IVb). 4-Hydroxy-1-benzyl-4,5-dihydro-5,7-nonano-6(2*H*)-cycloheptatriazolone(IVc).

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