100° isothermal. The second column was a 0.125 in. × 6 ft 20% DEGS–2% H_3PO_4 on Chromosorb W. Temperature requirements were similar to those above. A 0.125 in. × 6 ft SE-30 column was sufficient to resolve 1,2-dibromocycloalkanes, bromocycloalkanes, and 3-bromocyclohexene in the distillation fractions. Bromodichloronitromethane may possess severe toxic properties. All reactions and distillations should be performed in a well-ventilated hood. Protective goggles and gloves must be worn during all operations. Thus, precautions should parallel those of chloropicrin.[9]

Bromodichloronitromethane. The procedure was essentially that of Burk and Davis.[10] Halogenation of nitromethane (73 g) with a mixture of Cl_2 (230 g) and Br_2 (160 g) afforded a 95% total yield of the mixed trihalonitromethanes. Fractional distillation in vacuo through a 12-in. column packed with 0.25 in. glass helices yielded 50 g (20%) of bromodichloronitromethane of 99.5% purity (GLC) having d^{25} 2.073 and bp 52° (22 Torr), together with 84 g (28%) of chlorodibromomethane of 98% purity, d^{25} 2.398, bp 67–69° (22 Torr).

1-Bromo-2-(dichloronitromethyl)cyclohexane (I), Photoinitiation. A solution, containing 20.5 g (0.25 mol) of cyclohexene and 52.3 g (0.25 mol) of bromodichloronitromethane in 500 ml of benzene, was placed in an Ace 500-ml photochemical reactor equipped with a 450-W Hanovia lamp and a Pyrex absorption sleeve. The solution was then sparged with purified nitrogen for 30 min followed by irradiation for 8 hr at 25°. The olefin was monitored by GLC until its disappearance, which usually required 8 hr. The solvent was removed under vacuum at 40°. No residue or tar was present at this stage of isolation. Final fractionation was achieved through a short path column under vacuum. The distillation was terminated when the distilling flask temperature reached 120°. Tar formation was quite evident during this distillation. A total of 9.4 g (13% yield) of I was recovered. Analysis indicated its purity to be 95%. NMR data for I indicated that it was a mixture (40:60) of cis and trans isomers: by 90–92° (0.2 Torr); $n^{20}D$ 1.5369; ir 1590 (asymmetric NO_2) and 1320 cm^{-1} (symmetric NO_2); NMR ($CDCl_3$) δ 2.83 ($HCCl_2NO_2$, cis isomer), 3.24 ($HCCl_2NO_2$, trans isomer), 4.01 (HCBr, trans isomer), and 4.72 (HCBr, cis isomer). Elemental analysis was consistent with the assigned structure.

1-Bromo-2-(dichloronitromethyl)cyclopentane (II), Photoinitiation. A solution containing 17 g (0.25 mol) of cyclopentene and 52.3 g (0.25 mol) of bromodichloronitromethane in 500 ml of benzene was treated in a manner similar to I. Maximum tar formation was also noted above 120° during the final distillation. A total of 12.5 g (18% yield) of II was recovered. Analysis indicated its purity to be 95%. NMR data for II indicated that it was a trans isomer: bp 89–91° (0.5 Torr); $n^{20}D$ 1.5230; NMR δ 3.78 ($HCCl_2NO_2$) and 4.38 (HCBr). Elemental analysis was consistent with the assigned structure.

I and II by Redox-Transfer. A solution containing 0.25 mol of cyclic olefin and 0.25 mol of bromodichloronitromethane was placed in a 250-ml three-neck flask equipped with stirrer, thermometer, and dry ice condensor. A solution of 0.55 g (0.005 mol) of diethylamine hydrochloride and 0.45 g (0.02 mol) of cupric chloride in 20 ml of acetonitrile was added to the reagents. This solution was heated to 80° for 20 hr. Upon cooling the reaction mixture was washed twice with 200 ml of 2 *M* hydrochloric acid followed by a 500-ml water wash. The solution was dried over anhydrous sodium sulfate. It was then distilled through a Vigreux column to remove unreacted reagents and solvent. Final fractionation was achieved utilizing a short-path column. A total of 18.2 g (25% yield) of I and 18.0 g (26%) of II were recovered from the respective reactions. Analytical values of these compounds were identical with those obtained previously.

***trans*-1-Bromo-2-(dichloronitromethyl)cyclohexane.** After distillation of I, 25 g of the high-purity fraction (95%) was placed in a 25-ml flask and allowed to stand in a dry ice–dichloromethane bath for 8 hr. Small crystals were formed after this treatment. The mixture was allowed to stand at 0° for 7 days. The liquid remaining was removed by micropipette. The crystals were washed with 5 × 5 ml of hexane (cooled in dry ice) and dried. Only 1 g of 95% purity *trans*-I was recovered, mp 33–35°.

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Registry No.—*cis*-I, 57049-75-9; *trans*-I, 57049-76-0; *trans*-II, 57049-77-1; cyclohexene, 110-83-8; bromodichloronitromethane, 918-01-4; cyclopentene, 142-29-0.

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Reactions of Azines with Diphenylketene

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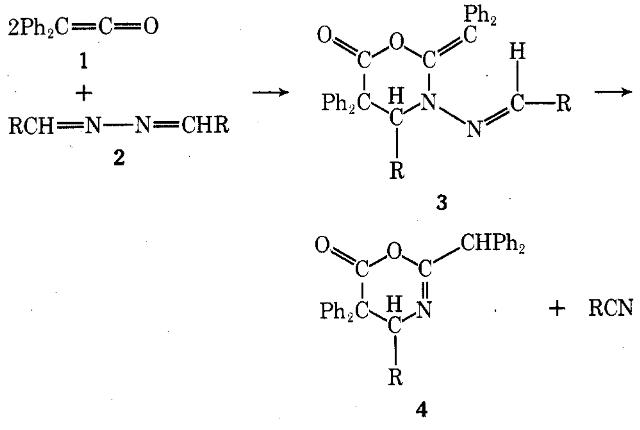
In contrast to extensive studies on the cycloaddition reactions of diphenylketene (1) with alkenes, imines, alkadienes, or heterocumulenes,[1] the reaction of 1 with nitrogen analogues of conjugated dienes has been reported[2,3] only with N=C–C=N compounds as dienes. We now report some cycloaddition reactions of 1 with aldehyde azines, RCH=N–N=CHR.

The reaction of 1 with acetaldehyde azine (2a) was carried out in refluxing ether for 5 hr, and a white, crystalline product was obtained in a good yield. On the basis of elemental analysis and spectral data shown in Table I, the reaction product was assumed to be 4-methyl-5,5-diphenyl-2-diphenylmethyl-4,5-dihydro-1,3-oxazin-6-one (4a), formed by the elimination of 1 mol of acetonitrile from the adduct (3a) of 2 mol of 1 and 1 mol of 2a. At lower temperature (−20°), the expected cycloadduct 3a was obtained. Compound 3a was unstable, and decomposed to 4a and acetonitrile on heating at about 100° or refluxing in ether.



2–4a, R = Me; **b**, R = Et; **c**, R = *i*-Pr

Other aliphatic aldehyde azines, propionaldehyde azine (**2b**) and isobutyraldehyde azine (**2c**), also reacted with **1** to

Table I[a]
4-Alkyl-5,5-diphenyl-2-diphenylmethyl-4,5-dihydro-1,3-oxazin-6-one (4)

Compd	R	Yield, %	Mp, °C	Formula	Mass M^+	Ir (KBr), cm^{-1} C=O	C=N	C–O–C	NMR (CCl_4), δ
4a	Me	70	156–157	$C_{30}H_{25}NO_2$	431	1775	1655	1120 1070	7.50–6.64 (m, 20 H), 4.79 (s, 1 H), 4.30 (q, 1 H), 1.00 (d, 3 H)
4b	Et	75	135–138	$C_{31}H_{27}NO_2$	445	1770	1660	1120 1090	7.61–6.65 (m, 20 H), 4.84 (s, 1 H), 4.18 (t, 1 H), 1.24 (m, 2 H), 0.87 (t, 3 H)
4c	*i*-Pr	55	146–148	$C_{32}H_{29}NO_2$	459	1775	1670	1120 1095	7.58–6.73 (m, 20 H), 4.91 (s, 1 H), 4.33 (d, 1 H), 1.33 (m, 1 H), 0.91 (d, 3 H), 0.67 (d, 3 H)

[a] Satisfactory analytical values (±0.35% for C, H, N) for all compounds in this table and Table II were submitted for review. Ed.

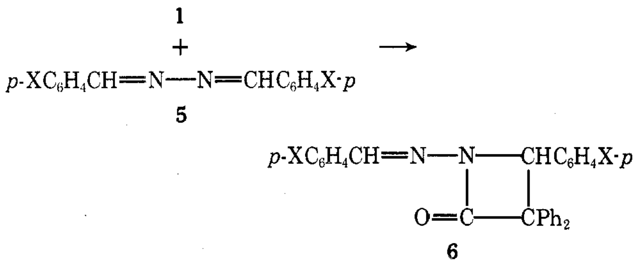
Table II
1-(*p*-X-Benzylideneamino)-4-(*p*-X-phenyl)-3,3-diphenyl-2-azetidinone (6)

Compd	X	Yield, %	Mp, °C	Formula	Mass M^+	Ir, cm^{-1} C=O	C=N	NMR (CCl_4), δ	Uv (EtOH), nm λ_{max}	Log ε
6a	H	53	186–187	$C_{28}H_{22}N_2O$	402	1750	1650	7.88 (s, 1 H) 7.80–6.92 (m, 20 H) 5.89 (s, 1 H)	286 296 308	4.31 4.33 4.17
6b	Me	62	197–199	$C_{30}H_{26}N_2O$	430	1755	1645	7.72 (s, 1 H), 7.69–6.70 (m, 18 H) 5.82 (s, 1 H), 2.23 (s, 3 H) 2.12 (s, 3 H)	291 302 314	4.46 4.48 4.36
6c	MeO	74	187–188	$C_{30}H_{26}N_2O_3$	462	1760	1645	7.72 (s, 1 H), 7.68–6.50 (m, 18 H) 5.80 (s, 1 H), 3.68 (s, 3 H) 3.60 (s, 3 H)	300 312 322	4.50 4.55 4.46
6d	Cl	30	160–161	$C_{28}H_{20}N_2OCl_2$	470 472	1750	1650	7.85 (s, 1 H) 7.77–6.84 (m, 18 H) 5.87 (s, 1 H)	292 304 315	4.49 4.50 4.37

give 4-ethyl- (**4b**) and 4-isopropyl-5,5-diphenyl-2-diphenylmethyl-4,5-dihydro-1,3-oxazin-6-one (**4c**), respectively.

Aromatic aldehyde azines such as benzaldehyde azine (**5a**), *p*-methyl- (**5b**), *p*-methoxy- (**5c**), and *p*-chlorobenzaldehyde azine (**5d**) were allowed to react with **1** in refluxing xylene for 5 hr. Analyses and mass spectra indicated that the products were the adducts of 1 mol of **1** and 1 mol of **5**. The structures of the adducts were confirmed by ir, NMR, and uv spectra (Table II) to be the 2-azetidinone derivatives **6a**, **6b**, **6c**, and **6d**. When the reaction was carried out in refluxing ether or benzene, the yields were lower than those in xylene.

The reactions of **1** with ketone azines gave no adducts, and the starting materials were recovered.



5, 6a, X = H; b, X = Me; c, X = OMe; d, X = Cl

Experimental Section

The ir spectra were recorded on a Hitachi EPI-G2 spectrophotometer, the NMR spectra were taken on a Varian A-60 instrument with tetramethylsilane as an internal standard, the mass spectra were obtained on a Hitachi RMU-7M mass spectrometer, and the uv spectra were determined with a Hitachi EPS-3T spectrophotometer.

4-Alkyl-5,5-diphenyl-2-diphenylmethyl-4,5-dihydro-1,3-oxazin-6-one (4). To a refluxing solution of 0.05 mol of **2** in 100 ml of dried ether, 0.1 mol of **1** was added. After refluxing for 5 hr under a nitrogen atmosphere, the reaction mixture was cooled, and the precipitate thus obtained was recrystallized from CCl_4 to give **4**. The results are shown in Table I.

Intermediates 3a and 3b. To a solution of 4.2 g (0.05 mol) of **2a** in 100 ml of dried ether, 19.4 g (0.1 mol) of **1** was added at −20°, and the mixture was stirred for 2 hr at the same temperature. The precipitate was filtrated under cooling and washed with cold dried ether to give 16.6 g (70%) of **3a**.

When 14.2 g (0.03 mol) of **3a** was heated at about 100°, 1.0 g of colorless liquid distilled, boiling at 80°, which was identified as MeCN by ir spectrum. The solid residue was recrystallized from CCl_4 to give 11.2 g (87%) of **4a**.

Similarly, 18.5 g of **3b** was obtained from 0.05 mol of **2b** and 0.1 mol of **1**, yield 74%, decomposed at about 90° to give **4b** and EtCN.

3a: ir (KBr) 1770, 1630, 1120, 1090 cm^{-1}; NMR (CCl_4) δ 7.48–6.82 (m, 20 H), 6.76 (q, 1 H), 4.90 (q, 1 H), 1.15 (d, 3 H), 1.05 (d, 3 H).

Anal. Calcd for $C_{32}H_{28}N_2O_2$: C, 81.33; H, 5.97; N, 5.93. Found: C, 81.08; H, 6.22; N, 6.07.

3b: ir (KBr) 1760, 1635, 1140, 1125 cm^{-1}; NMR (CCl_4) δ 7.52–6.85 (m, 20 H), 6.67 (t, 1 H), 4.68 (t, 1 H), 2.51 (m, 4 H), 1.08 (t, 3 H), 0.56 (t, 3 H).

Anal. Calcd for $C_{34}H_{32}N_2O_2$: C, 81.57; H, 6.44; N, 5.60. Found: C, 81.33; H, 6.63; N, 5.44.

1-(*p*-X-Benzylideneamino)-4-(*p*-X-phenyl)-3,3-diphenyl-2-azetidinone (6). A mixture of 0.1 mol of **1**, 0.1 mol of **5**, and 100 ml of dried xylene was refluxed for 5 hr under a nitrogen atmosphere, and the solvent was removed by distillation under reduced pressure. The reddish residue was added to ether to precipitate the crude product. Recrystallization from CCl_4 gave **6**. The results are summarized in Table II.

Registry No.—**1**, 525-06-4; **2a**, 592-56-3; **2b**, 15601-98-6; **2c**, 18300-78-2; **3a**, 56930-54-2; **3b**, 56930-55-3; **4a**, 56930-56-4; **4b**, 56930-57-5; **4c**, 56930-58-6; **5a**, 588-68-1; **5b**, 4702-76-5; **5c**, 2299-73-2; **5d**, 3510-48-3; **6a**, 56930-59-7; **6b**, 56930-60-0; **6c**, 56930-61-1; **6d**, 56930-62-2.

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