over a period of several minutes with vigorous stirring. After 30 min the solvent was removed by an aspirator at room temperature and the residue was purified by usual techniques.

Reaction of CC with DCC (1). The residue obtained from CC and DCC (1.03 g, 5 mmol) was dissolved in *n*-hexane and the amorphous pale yellow solid was filtered off. The solution was condensed and kept in a refrigerator to give colorless prisms of **4** (1.85 g, 95%): mp 101 °C; ir 1690 cm^{-1} (C=N); NMR δ 4.41 [1, m, methyne H(a)], 3.70 [1, m, methyne H(b)], 2.30–1.00 (20, m, dicyclohexyl H); *m/e* 389 ($M^{\cdot+}$, 0.0001), 354 ($M^{\cdot+}$ − ·Cl, 0.01), 308 ($M^{\cdot+}$ − cyclohexenyl radical, 0.11).

Anal. Calcd for $C_{16}H_{22}Cl_3N_5$: C, 49.16; H, 5.63; N, 17.97. Found: C, 48.99; H, 5.62; N, 17.91.

Reaction of CC with *N*-Isopropylidenebenzylamine (2). The residue obtained from CC and the imine (735 mg, 5 mmol) was extracted with anhydrous Et_2O under a nitrogen atmosphere. The insoluble solid was dissolved in dry CH_2Cl_2 and anhydrous Et_2O was added to the solution slowly to give colorless needles of **7** (440 mg, 48%): mp 114–118 °C;[9] ir 2630 and 1690 cm^{-1} (C=N+<); NMR δ 7.60–7.10 (5, m, aromatic H), 4.82 (2, s, $-CH_2Ph$), 2.70 and 2.41 [6, s, $(CH_3)_2C$=].

Anal. Calcd for $C_{10}H_{13}N$·HCl:[10] C, 65.39; H, 7.62; N, 7.62. Found: C, 64.13; H, 7.44; N, 7.73.

The ether filtrate was chromatographed by preparative TLC developed with benzene to give two main bands, which were extracted with CH_2Cl_2. The solution from the upper band was distilled to give **5** as a colorless liquid (162 mg, 11%): bp 125–126 °C (0.15 mm);[11] ir (NaCl) 1665 cm^{-1} (C=C); NMR δ 7.27 (5, s, aromatic H), 5.10 and 4.85 (2, d, J = 1.8 Hz, vinylic H), 4.95 (2, s, $-CH_2Ph$), 1.84 (3, s, $-CH_3$); *m/e* 203 ($M^{\cdot+}$ − $\cdot C_7H_7$, 64.2).

Anal. Calcd for $C_{13}H_{12}Cl_2N_4$: C, 52.88; H, 4.06; N, 18.98. Found: C, 52.63; H, 4.09; N, 19.32.

The product from the other band was crystallized from *n*-hexane to give colorless prisms of **6** (484 mg, 38%), identical with an authentic sample.[5]

From 10 mmol of the imine, the compounds **5** (929 mg, 63%), **6** (383 mg, 30%), and **7** (865 mg, 93%) were obtained by the same procedure as above.

Reaction of CC with 2,3,3-Trimethylindolenine (3). The residue obtained from CC and the indolenine (795 mg, 5 mmol) was extracted with anhydrous Et_2O followed by preparative TLC developed with a mixture of *n*-hexane and benzene (3:1 v/v) to give two main bands, which were extracted with CH_2Cl_2 and crystallized from *n*-hexane, respectively. The upper band was assigned as **9** (52 mg, 3.4%): mp 122–123 °C; ir 1650 cm^{-1} (C=C); NMR δ 8.41 (1, m, $C_{7'}$ H), 7.43–7.10 (3, m, aromatic H), 6.37 [1, d, J = 1.0 Hz, olefinic H(b)], 5.80 [1, d, J = 1.0 Hz, olefinic H(a)], 1.43 [6, 3′,3′-$(CH_3)_2$]; *m/e* 306 ($M^{\cdot+}$, 47.6), 291 ($M^{\cdot+}$ − $\cdot CH_3$, 100).

Anal. Calcd for $C_{14}H_{12}Cl_2N_4$: C, 54.72; H, 3.90; N, 18.24. Found: C, 54.80; H, 4.11; N, 18.24.

The other band was assigned as **10** (674 mg, 41%): mp 128–129.5 °C; ir 3485 cm^{-1} (–OH); NMR δ 8.13 (1, m, $C_{7'}$, H), 7.15–7.05 (3, m, aromatic H), 5.75 (1, s, –OH), 1.75 (3, s, 2′-CH_3), 1.39 and 1.22 [6, s, 3′,3′-$(CH_3)_2$]; *m/e* 324 ($M^{\cdot+}$, 27.5), 306 ($M^{\cdot+}$ − H_2O, 17.7), 291 ($M^{\cdot+}$ − MeOH, 96.5).

Anal. Calcd for $C_{14}H_{14}Cl_2N_4O$: C, 51.69; H, 4.30; N, 17.27. Found: C, 51.66; H, 4.39; N, 17.29.

Also, the ether-insoluble solid **11** (488 mg, 50%) was identical with an authentic sample.

From 10 mmol of the indolenine, **9** (1.534 g, 100%) and **11** (977 mg, 100%) were obtained, respectively, calculated on the basis of CC.

Reaction of 2,4-Dichloro-6-methoxy-*s*-triazine with the Indolenine 3. A mixture of the *s*-triazine (980 mg, 5 mmol) and **3** (1.59 g, 10 mmol) in dry CH_3CN (2 ml) was boiled for 1 h. The solvent was removed at room temperature and the residue was extracted with anhydrous Et_2O followed by preparative TLC developed with benzene to give two main bands, which were extracted with Et_2O and crystallized from *n*-hexane, respectively. The upper band was assigned as **14** (362 mg, 24%): mp 81–82 °C; ir 1650 cm^{-1} (C=C); NMR δ 8.60–8.39 (1, m, $C_{7'}$ H), 7.50–7.10 (3, m, aromatic H), 6.39 [1, d, J = 1.8 Hz, olefinic H(b)], 5.02 [1, d, J = 1.8 Hz, olefinic H(a)], 4.10 (3, s, $-OCH_3$), 1.43 [6, s, 3′,3′-$(CH_3)_2$]; *m/e* 302 ($M^{\cdot+}$, 20.1), 287 ($M^{\cdot+}$ − $\cdot CH_3$, 85.4).

Anal. Calcd for $C_{15}H_{15}ClN_4O$: C, 59.53; H, 4.95; N, 18.51. Found: C, 59.49; H, 4.95; N, 18.64.

The other band contained **15** (769 mg, 48%): mp 132–133 °C; ir 3410 cm^{-1} (–OH); NMR δ 8.23–8.03 (1, m, $C_{7'}$ H), 7.32–7.00 (3, m, aromatic H), 6.27 (1, s, –OH), 4.02 (3, s, $-OCH_3$), 1.57 (3, s, 2′-CH_3), 1.39 and 1.22 [6, s, 3′,3′-$(CH_3)_2$]; *m/e* 320 ($M^{\cdot+}$, 49.7), 305 ($M^{\cdot+}$ − $\cdot CH_3$, 52.1), 304 ($M^{\cdot+}$ − CH_4, 38.4).

Anal. Calcd for $C_{15}H_{17}ClN_4O_2$: C, 56.16; H, 5.30; N, 17.47. Found: C, 56.42; H, 5.62; N, 17.65.

The ether-insoluble solid **11** (939 mg, 96%) was identical with an authentic sample. A band close to the baseline on TLC was also extracted with Et_2O and identified as **3** (24 mg, 3%, crude).

Acknowledgment. The authors are indebted to Professor Eugene E. van Tamelen, Stanford University, and his group for giving us the opportunity to use the facilities for this research. We also thank Dr. Roy Neville for his useful discussions of this investigation.

Registry No.—**1**, 538-75-0; **2**, 1197-48-4; **3**, 1640-39-7; **4**, 58502-52-6; **5**, 58502-53-7; **6**, 30369-82-5; **7**, 58502-54-8; **9**, 58502-55-9; **10**, 58502-56-0; **11**, 17790-92-0; **14**, 58502-57-1; **15**, 58502-58-2; CC, 108-77-0; 2,4-dichloro-6-methoxy-*s*-triazine, 3638-04-8.

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(7) The ratio was estimated on the basis of the signals of the olefinic and the hydroxy protons in the NMR spectrum. The ratio was not changed in a NMR sample tube kept for 1 week.
(8) The same manner as ref 7 for the estimation.
(9) The compound was extremely unstable and lost weight during weighing in preparation for the microanalysis owing to atmospheric hydrolysis to benzylamine hydrochloride.
(10) The calculated values for the cyanuric chloride salt, $PhCH_2{}^+N(R)$=$C(Cl^-)(CH_3)_2$·$C_{13}H_{13}Cl_3N_4$, are C, 47.58; H, 3.92; N, 16.89.
(11) The liquid was solidified within 30 min, mp 66–68 °C.

Ethoxycarbonylnitrene Insertion Selectivity. Photolysis of Ethyl Azidoformate in Bicyclo[4.*n*.0]alkanes and in Alkylcyclohexanes

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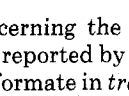
We first observed the influence of halogenated solvents in lowering the insertion selectivity of ethoxycarbonylnitrene (EtOCON) generated by the thermal decomposition of ethyl azidoformate ($EtOCON_3$) toward the C–H bonds of *cis*- and *trans*-decalins.[1] Assuming stabilization of the singlet nitrene by dichloromethane, a possible explanation is that the triplet nitrene inserts into the tertiary C–H bonds of these hydrocarbons.[2] Later, Brinkmann et al.[3] found by the CIDNP technique during the thermolysis of ethyl azidoformate in *trans*-decalin an emission signal indicating the intermediacy of a radical pair. However, the multiplicity of the reactive intermediate, i.e., whether a triplet or a singlet diradical nitrene generates ·NHCOOEt, remained an open question.



Another case concerning the same effect of the dichloromethane has been reported by Belloli et al.[4] for the thermolysis of ethyl azidoformate in *trans*-1,2-dimethylcyclohexane (TDCH). The proportion of tertiary product to other isomers

Table I. Ratio of CH/CH_2 Bonds Reactivity of Hydrocarbons toward Ethoxycarbonylnitrene[a]

Registry no.	Entry	Hydrocarbon	Thermolysis		Photolysis
			CH_2Cl_2	Neat	
493-01-6	1		2.3[b]	2.9[b]	4.5
2207-01-4	2		4.0	4.4	5.0
493-02-7	3		1.3[b]	2.3[b]	3.7
6876-23-9	4		2.0	2.5[c]	3.2
4551-51-3	5		2.8[b]	3.0[b]	3.1
286-08-8	6		0.4[b]	0.5[b]	0.5
108-87-2	7		2.6	3.1	4.1

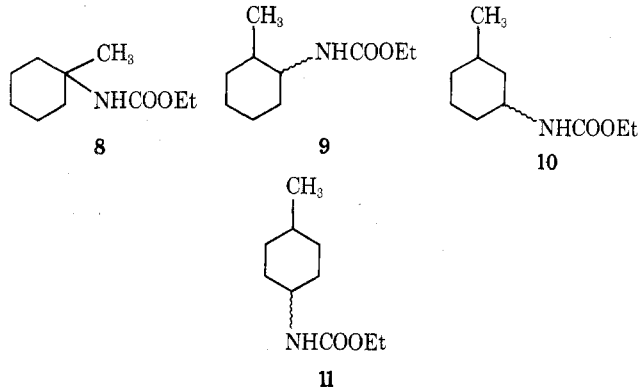
[a] The average deviation of these values is 0.15. [b] Reference 2. [c] This value is in good agreement with that found by Belloli et al. (ref 4) for the same reaction (2.4).

dropped from 38.7% for neat TDCH to 22.6% for 8.1 mol of TDCH in CH_2Cl_2.

We now report on the results obtained for the photolysis of $EtOCON_3$ (Hanovia medium-pressure 100-W lamp, room temperature, 6–8 h) in neat *cis*- and *trans*-bicyclo[4.4.0]decanes (decalins) (**1** and **3**), *cis*-bicyclo[4.3.0]nonane (hydrindane) (**5**), *cis*-bicyclo[4.1.0]heptane (norcarane) (**6**), *cis*- and *trans*-1,2-dimethylcyclohexanes (CDCH and TDCH) (**2** and **4**), and methylcyclohexane (**7**). Repeated experiments and careful integration of peak areas gave the results shown in Table I. The data clearly show that the photolysis of $EtOCON_3$ in *cis* and *trans*-decalins, in *cis*- and *trans*-1,2-dimethylcyclohexanes, and in methylcyclohexane gave an increased insertion selectivity, while no change was observed for the other substrates. The analogous behavior found for both *cis*-decalin and CDCH and *trans*-decalin and TDCH was to be expected from the similar steric situation of such pairs of hydrocarbons. An interesting point is the parallel between the solvent effect previously noted in the thermolysis and the increase in insertion selectivity found in the photolysis, namely, the same hydrocarbons which suffered solvent influence on insertion selectivity during the thermolysis gave also higher selectivity ratio in the photolysis.

On the basis of experimental evidence[5] it is commonly assumed that about 30% of ethoxycarbonylnitrene is generated in the triplet state by the photolysis of ethyl azidoformate. On account of this, the present data might give further support to our assumption that the triplet nitrene is reactive in particular cases where high stable tertiary alkyl radicals are involved in a process of hydrogen abstraction–recombination.[6] Probably the radical stability is more important than the above-mentioned steric factor. From this point of view the data concerning the thermolysis and the photolysis of $EtOCON_3$ in bicyclo[4.1.0]heptane are consistent with the low stability of the tertiary radical derived from **6**, as shown by the behavior of the radical chlorination of this hydrocarbon,[7] while the high stability of the tertiary decalyl radical is well established.[8] However, on this basis, we are unable to rationalize the behavior of bicyclo[4.3.0]nonane for which the stability of the tertiary radical is comparable. On the other hand, the high selectivity displayed by triplet methylene[9] or triplet oxygen[10] in insertion reactions on C–H bonds is well known. Nevertheless, we do not exclude the intervention of the singlet diradical nitrene as recent LCAO–MO–SCF calculations[11] suggest for the reaction between EtOCON and C–H bonds.

Chart I. Tertiary and Secondary Insertion Products of EtOCON on Methylcyclohexane



Experimental Section

Analytical VPC was carried out by a Carlo Erba Fractovap GI gas chromatograph using an Emulphor capillary column (60 m × 0.29 mm). Infrared spectra were obtained on a Perkin-Elmer 257 Infracord instrument. ^1H NMR spectra were recorded on a Perkin-Elmer R32 90-MHz spectrometer. Mass spectra were obtained on a AEI-MS12 spectrometer at an ionization potential of 70 eV. Photolyses were carried out in a quartz vessel using a medium pressure Hanovia PCR lamp. The volume ratio of ethyl azidoformate to hydrocarbon (to dichloromethane) was 1:10 (:100). Irradiation time was 6–8 h.

Ethyl azidoformate was prepared from ethyl chloroformate and sodium azide.[12] *cis*-Bicyclo[4.1.0]heptane was obtained from WBL. Pure *cis*-bicyclo[4.3.0]nonane was obtained by spinning band distillation of commercial cis, trans mixture (Koch-Light). All other hydrocarbons are available from Fluka. The C–H insertion products (carbamates) for *cis*- and *trans*-bicyclo[4.4.0]decanes, *cis*-bicyclo[4.3.0]nonane, and *cis*-bicyclo[4.1.0]heptane were previously reported.[2] For the isomeric *cis*- and *trans*-1,2-dimethylcyclohexanes carbamates we found the same order of elution as observed by Belloli et al.[4] Identification of the eight isomeric methylcyclohexane carbamates was made by comparison of VPC retention times and spectra with those of independently synthesized compounds. The order of elution was a first peak for the tertiary C–H insertion product, followed by six partially overlapping peaks for the secondary insertion products, and finally a peak for the primary insertion product.

Ethyl *N*-(2-Methylcyclohexyl)carbamates (9). A solution of 500 mg (3.5 mmol) of *o*-toluidine hydrochloride in 5 ml of absolute ethanol was hydrogenated at 55 °C (1 atm) in the presence of 50 mg of PtO_2 Adams. The filtrate was evaporated and the residue dissolved in NaOH (2 N) and extracted with ether. To the organic layer, washed with saturated NaCl solution, 5 ml of water and, at 5 °C with stirring, 540 mg (5 mmol) of ethyl chloroformate were added. The stirring was continued for 30 min and the ether layer was separated, washed with saturated NaCl solution, dried over anhydrous sodium sulfate, and evaporated to dryness. Quantitative yield of the two isomers was obtained (74% of the shorter retention time product): ir (CCl_4) 3460 (NH) and 1730 cm^{-1} (CO); NMR (CCl_4) δ 1.25 (t, CH_3 of Et), 0.9 (d, CH_3), 3.4 (m, NCH), 4.05 (q, CH_2 of Et), 4.5 (broad, NH); *m/e* 185 (parent), 128 (base peak).

Ethyl *N*-(3-Methylcyclohexyl)carbamates (10). Two isomers (36% of the shorter retention time product) were obtained with the procedure described above starting from *m*-toluidine hydrochloride: ir (CCl_4) 3450 (NH) and 1730 cm^{-1} (CO); NMR (CCl_4) δ 1.2 (t, CH_3 of Et), 0.9 (d, CH_3), 4.0 (q, CH_2 of Et), 4.6 (broad, NH); *m/e* 185 (parent), 142 (base peak).

Ethyl *N*-(4-Methylcyclohexyl)carbamates (11). Two isomers (80% of the shorter retention time product) were obtained with the procedure described above starting from *p*-toluidine hydrochloride: ir (CCl_4) 3450 (NH) and 1730 cm^{-1} (CO); NMR (CCl_4) δ 1.25 (t, CH_3 of Et), 0.95 (d, CH_3), 4.05 (q, CH_2 of Et), 4.8 (broad, NH), 3.8 (m, NCH); *m/e* 185 (parent), 128 (base peak).

Ethyl *N*-(1-Methylcyclohexyl)carbamate (8). A mixture of 2.5 ml of glacial acetic acid, 2.28 g (0.02 mol) of 2-methylcyclohexanol (BDH), and 1.15 g of NaCN was added under stirring to a solution of 2.5 ml of 90% H_2SO_4 in 2.5 ml of glacial acetic acid over a period of 30 min. The temperature was maintained at 50–60 °C. The reaction mixture was then allowed to stand at room temperature overnight;

afterwards it was cooled and 8.5 g of ice and 11 g of NaOH in 21 ml of water were added. The mixture was then refluxed for 4 h. The cooled solution was extracted with ether. The ether layer was then extracted with 2 N HCl. The amine was extracted with ether from the water layer made alkaline. Treatment with ethyl chlorocarbonate afforded 1.95 g of carbamate: ir (CCl_4) 3450 (NH) and 1730 cm^{-1} (CO); NMR (CCl_4) δ 1.25 (t, CH_3 of Et), 1.1 (s, CH_3), 3.95 (q, CH_2 of Et), 4.25 (broad, NH); *m/e* 185 (parent), 142 (base peak).

Acknowledgment. We are grateful to the Italian Research Council (CNR), Rome, for partially supporting this work.

Registry No.—**8**, 1837-74-7; *cis*-**9**, 58486-01-4; *trans*-**9**, 58486-02-5; *cis*-**10**, 58486-03-6; *trans*-**10**, 58486-04-7; *cis*-**11**, 58486-05-8; *trans*-**11**, 58486-06-9; *o*-toluidine HCl, 636-21-5; ethyl chloroformate, 541-41-3; *m*-toluidine HCl, 638-03-9; *p*-toluidine HCl, 540-23-8; ethyl azidoformate, 817-87-8.

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Some Reactions of Chlorotrialkyl-1,3-cyclobutanediones

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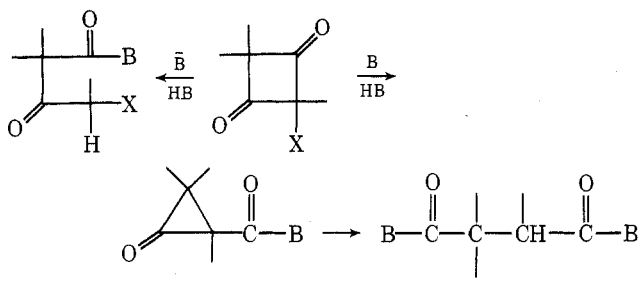
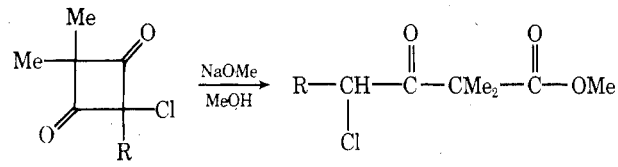
The base-catalyzed ring contraction of α-halocyclobutanones to cyclopropyl derivatives is a very useful and well-documented reaction.[1,2] Tetraalkyl-1,3-cyclobutanediones undergo ring opening reactions in the presence of base to yield β-keto esters.[3] 1,2-Cyclobutanedione has been prepared and shown to undergo ring contraction to hydroxycyclopropanecarboxylic acid.[4] In view of these considerations, the halotrialkyl-1,3-cyclobutanediones provide an interesting system for study. It would appear that such compounds could undergo



a ring contraction reaction and/or a ring opening reaction. The cyclopropanone would be expected to undergo ring opening in the presence of base to yield a succinic acid derivative. Consequently, the purpose of this paper is to investigate the reaction of chlorotrialkyl-1,3-cyclobutanediones with sodium methoxide in methanol and also to examine some chemistry of these diones as related to tetraalkylcyclobutanediones.

The chlorotrialkyl-1,3-cyclobutanediones are readily available from the mixed dimerizations of dimethylketene and alkylhaloketenes.[5] The treatment of several chlorotrialkyl-1,3-cyclobutanediones with sodium methoxide in methanol



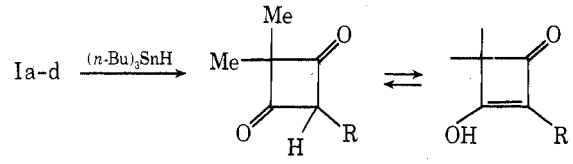
Ia, R = Me
b, R = Et
c, R = *i*-Pr

IIa, R = Me
b, R = Et
c, R = *i*-Pr

yielded the ring opened products, β-keto esters. Although two β-keto esters are possible, only the expected γ-chloro-β-keto ester was found. There was no evidence of the cyclopropanone derivative or the diester of succinic acid.

Apparently, the strain associated with the cyclopropanone ring system prohibits this ring contraction pathway from being followed. The formation of only the γ-chloro-β-keto ester is consistent with the chloro substituent stabilizing the carbanionic character in the transition state to a greater degree than the methyl substituents. The ring opening reaction of tetramethyl-1,3-cyclobutanedione requires a much longer reaction time than the chlorotrialkyl-1,3-cyclobutanedione. This further supports the stabilizing influence of the chloro substituent. The rate of the reaction decreases as the size of R increases from methyl to isopropyl as expected. When R is *tert*-butyl, ring opening does not occur; the dione is completely recovered.

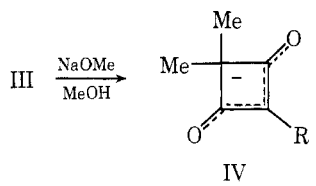
The chlorotrialkyl-1,3-cyclobutanediones (I) react with tri-*n*-butyltin hydride to yield the corresponding trialkyl-1,3-cyclobutanediones (III), which exist as the dione in the



IIIa-d

solid state, but the enol form is the predominant form in solution as evidenced by infrared. Conversion of the chlorotrialkyl-1,3-cyclobutanediones to the trialkyl-1,3-cyclobutanediones could also be accomplished by treatment with sodium borohydride in methanol.

The trialkyl-1,3-cyclobutanediones (III) did not undergo ring opening reactions. Apparently, the well-delocalized enolate, IV, is immediately produced in the basic media, and the reaction is terminated at this stage.



IV

The peracid oxidation of tetramethyl-1,3-cyclobutanedione occurs smoothly and in good yield to the expected lactone.[6,7] This Baeyer–Villiger oxidation of Ia and Ib gives the ring expansion product, V, in good yield. No other ring expansion product could be detected. The structure of V was assigned on the basis of the NMR data, i.e., the chemical shift of the geminal methyl groups in V is comparatively downfield