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SYNTHESIS OF HETEROCYCLICS VIA ENAMINES—IX[1]

REACTIONS OF 1-SUBSTITUTED-4,4,6-TRIMETHYL-1,4-DIHYDROPYRIMIDINE-2(3H)THIONE DERIVATIVES WITH DIHALOCARBENES.

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Abstract—Dichloroarbene with 1-substituted-4,4,6-trimethyl-1,4-dihydropyrimidine-2(3H) thione derivatives (**2**) formed 7,7-dichloro-3-[(dichloromethyl)thio]-2-substituted-1,5,5-trimethyl-2,4-diazabicyclo[4,1.0] hept-3-ene (**3**) and 7,7-dichloro-2-substituted-1,5,5-trimethyl-2,4-diazabicyclo [4.1.0] heptane-3-thione (**4**). On heating as such or under acidic or basic conditions, **3** changed to the corresponding **4** quantitatively. Diiodocarbene with **2** (R = CH_3,Ph) formed mainly the corresponding 1-substituted-4,4,6-trimethyl-1,4-dihydropyrimidine-2(3H) one **7** (R = CH_3,Ph). **7** (R = CH_3).

For procuring modified nucleosides, ring transformations of biological pyrimidines (**1**) have attracted considerable attention.[2,3] These pyrimidines invariably possess C_5,C_6-enamine double bond[4] and majority of their transformations reported are the outcome of their reactions at the enamine chromophore with electrophiles and nucleophiles.[5] The addition of a methylene bridge across C_5,C_6-double bond of uracil[6–8] and uridine[8] derivatives has been performed with CH_2I_2Zn[6,7] and carbenes,[8] and some of these adducts have been converted to diazepine derivatives.[7]

The ring transformations of such pyrimidine derivatives possessing an additional functionality would be of added interest as the incorporation of such pyrimidines and their ring interconversions in nucleosides would provide modified nucleosides of biological interest. 1-Substituted-4,4,6-trimethyl-1,4-dihydropyrimidine-2(3H)thiones (**2**) constitute one such category possessing a thione functionality at C_2 and hence we became interested in their ring transformations.[1] Here are reported their reactions with dihalocarbenes.

RESULTS AND DISCUSSION

1,4,4,6-Tetramethyl-1,4-dihydropyrimidine-2(3H)thione (**2**, R = CH_3) with dichlorocarbene gave two products, R_f 0.9 and 0.5, in the ratio which varied with the mode of generation of dichlorocarbene. Under catalytic-two-phase conditions using 50% aqueous sodium hydroxide and triethylbenzylammonium chloride as catalyst, the product, R_f 0.9, was the major product and its amount increased with time, at the cost of the product, R_f 0.5.

The component, R_f 0.9, in its mass spectrum showed the parent ion peak at $M^{+\cdot}$ *m/e* 334 indicating that two dichlorocarbene units were added to the parent molecule ($M^{+\cdot}$ *m/e* 170). The loss of $CHCl_2$ and $SCHCl_2$ from the parent ion to form peaks at *m/e* 251 and 219 respectively showed that one dichlorocarbene unit was attached at thioureido sulphur to constitute-$SCHCl_2$. The second dichlorocarbene unit added across the enamine double bond as in the ^1H NMR spectrum of the product, the chemical shift of the enamine-C_5 H of the precursor shifted upfield and appeared at δ2.00 and in its uv spectrum, the absorption band at λ_{max} 257-characteristic for these pyrimidines was also absent. Hence, this component was assigned the structure 7,7-dichloro-3-[(dichloromethyl)thio] 1,2,5,5-tetramethyl-2,4-diazabicyclo [4.1.0] hept-3-ene (**3**, R = CH_3, X = Cl) which was further supported by the fact that in its ^1H NMR spectrum the two gemdimethyl groups which appeared as a singlet at δ1.25 in the precursor, now appeared at δ1.7 and 1.18 indicating the non-planarity of the ring.

The second component, R_f 0.5, showed the parent ion peak at $M^{+\cdot}$ *m/e* 252, indicating that only the dichlorocarbene unit had been added to the parent molecule. In its mass spectrum the absence of peaks formed by the loss of $CHCl_2$ and $SCHCl_2$ showed the absence of -$SCHCl_2$. It was further supported by the presence of a signal at δ176.31 (>C = S)[1] in its ^{13}C NMR spectrum, in which the only olefinic carbon (= C_5H–, δ 110.63) of the precursor had changed to an sp^3 carbon and appeared at δ43.68. Unlike the parent compound, it did not show any absorption band at λ_{max} 257 in its UV spectrum. In the ^1H NMR spectrum, again gemdimethyl formed two signals at δ1.42 and 1.5, indicating the non-planarity of the ring and the C_6–H appeared upfield at δ1.75 (s). Hence, this component was assigned the structure 7,7-dichloro-1,2,5,5-tetramethyl-2,4-diazabicyclo [4.1.0] heptane-3-thione (**4**, R = CH_3, X = Cl).

On monitoring the progress of the reaction, it was found that initially, **4** (X = Cl) was formed and then **3** (X = Cl) started forming. Thus, dichlorocarbene added at C_5,C_6-enamine double bond of 1-substituted-4,4,6-trimethyl-1,4-dihydropyrimidine-2(3H)thione (**2**) to form **4** (X = Cl). Subsequently the anion **5** (X = Cl) and dichlorocarbene formed the anion **6** (X = Cl) which gave the product **3** (X = Cl).

Here also, as reported by Nicoletti,[9] the use of 33% aqueous sodium hydroxide avoided the formation of side products and **4** (X = Cl) was formed as the major product. When dichlorocarbene was generated from chloroform-potassium t-butoxide or from sodium trichloroacetate by refluxing in DME or under catalytic-two-phase conditions using TEBACl, **4** (X = Cl) was formed as the major products.

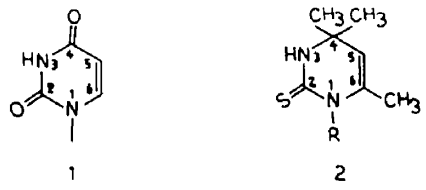
In order to check the generality of cycloadditions of dichlorocarbene with 1-substituted-4,4,6-trimethyl-1,4-dihydropyrimidine-2(3H) thione derivatives, the reactions of **2** (R = Et, C_6H_5, *p*-tolyl) with dichlorocarbene were studied. In case of **2** (R = Et) under catalytic-two-phase conditions the corresponding **4** (X = Cl) was formed as the major product and **3** (X = Cl) as minor product whereas in the case of **2** (R = C_6H_5, *p*-tolyl) the corresponding **3** was formed as major and **4** as minor product. But when dichlorocarbene was generated from chloroform and potassium t-butoxide in all these cases, **4** was formed as the major product because **3** changed quantitatively to **4** under basic conditions.

On heating as such at 100–110° and in the presence of a base or strong mineral acid, derivatives of **3** changed quantitatively to the corresponding **4**. Thus in a single pot experiment the crude product mixtures were heated as such in sulphuric acid on a water bath and the corresponding **4** was obtained in 90–93% yield, providing a convenient method for the synthesis of derivatives of **4**.

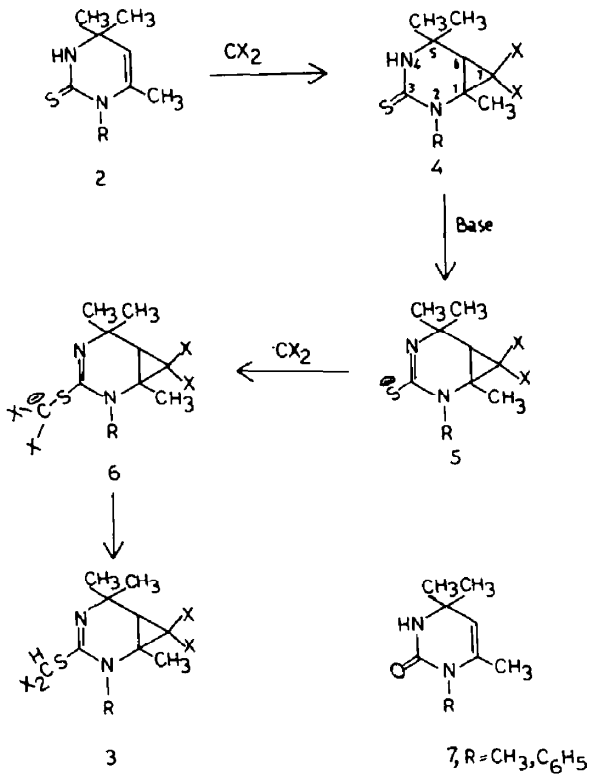
On heating, **3**, (i) in quinoline solution at 200° (ii) as such at 210–220°, (iii) in a sealed tube in methanol solution containing sodium methoxide and (iv) in dioxane solution in the presence of potassium t-butoxide, sodium hydride or sodium amide, only **4** was formed which did not undergo any further change.

We argued that the adducts of dibromo- or diiodocarbenes with **2**, due to the bulkiness of the halogen atoms and low dissociation energy of C–Br and C–I bonds compared to C–Cl bond, might undergo ring expansion reaction. Hence, we studied reactions of dibromo- and diiodocarbenes with derivatives of **2**.

Dibromocarbene generated from bromoform and potassium t-butoxide in t-butanol/dioxane with **2** (R = Me) gave two products, R_f 0.45 and 0.25, in 20% yield each. The component, R_f 0.45, in its mass spectrum showed the parent ion peak at M^+, *m/e* 327. In its ^1H NMR spectrum, it showed four 3H singlets at 1.37, 1.46, 1.8 and 3.5 due to four Me groups, like its dichlorocarbene adduct analog and was assigned the structure: 7,7-dibromo-1,2,5,5-tetramethyl-2,4-diazabicyclo-[4.1.0] heptan-3-thione **4** (R = Me, X = Br). The second component, R_f 0.25, was found to



Scheme 1.



X = Cl, Br

R = CH_3, C_2H_5, C_6H_5, p tolyl.

Scheme 2.

be devoid of sulphur and in its IR spectrum, exhibited a strong absorption band at 1685 cm^{-1}. In its mass spectrum it exhibited the parent ion peak at $M^{+\cdot}$ *m/e* 154. All the above three observations, i.e. absence of sulphur, absorption due to $>C=O$ in the IR spectrum and difference of 16 mass units in the molecular weights of the precursor and the product, indicate that in this reaction $>C=S$ has been converted to $>C=O$, and it was assigned the structure 1,4,4,6-tetramethyl-1,4-dihydropyrimidine-2(3H) one **7** (R = Me). It was further corroborated by its ^1H NMR spectrum which showed the presence of $\begin{smallmatrix} CH_3 & H \\ \diagdown & / \\ N-C=C \\ \diagup \end{smallmatrix}$ -(*cis*) Under catalytic-two-phase conditions dibromocarbene with **2** (R = Me) again formed **4** (R = Me, X = Br) and **7** (R = Me). On reaction with **2** (R = Ph) dibromocarbene formed only **7** (R = Ph) and the analogous **4** (R = Ph, X = Br) was not detected.

Diiodocarbene generated from iodoform and potassium t-butoxide with **2** (R = Me) gave only **7** (R = Me) and the analogous diiodocyclopropane adduct **4** was not formed in this case. Under catalytic-two-phase conditions also only **7** (R = Me) was formed. Similarly, under both these conditions, **2** (R = Ph) gave the corresponding **7** (R = Ph). In these reactions iodine was isolated in large amounts, pointing to the possibility that iodine in the presence of potassium t-butoxide as well as under catalytic-two-phase conditions in aqueous sodium hydroxide in the presence of TEBACl might be responsible for the conversion of $>C=S$ to $>C=O$. The reluctance of diiodo- and dibromocarbenes to form adducts with **2** might be attributed to the bulkiness of the halogen atoms.

Subsequently, it has been demonstrated that iodine or bromine in the presence of potassium t-butoxide, as well as under catalytic-two-phase conditions in the presence of TEBACl was capable of converting $>C=S$ of **2** to the corresponding $>C=O$ derivatives.[10]

EXPERIMENTAL

Mp's were determined in capillaries and are uncorrected. IR and UV spectra were recorded with C.Z. specord-71 and VSU-2P spectrophotometers. ^1H NMR and ^{13}C NMR spectra were determined with Tesla BS 487C 80 MHz and Varian XL-100 instruments respectively. The multiplicities of the various signals in off resonance proton decoupled spectra are indicated by the appropriate symbols in parentheses. Mass spectra were recorded on Hitachi Perkin Elmer RMU 60 and varian Mat CH-7 mass spectrometers. For tlc, plates coated with silica gel G were used, and spots were developed with iodine. Elemental analysis were performed at microanalytical laboratory Calcutta University, Calcutta, India.

Reactions of **2**, (R = Me) *with dichlorocarbene*

(a) *Under catalytic-two-phase conditions.* A cooled soln of 50% NaOH aq. (20 ml) was added dropwise to a stirred soln of **2** (0.01 mole) in $CHCl_3$ (25 ml) containing triethylbenzylammonium chloride (TEBACl, 0.2 g) as catalyst. The mixture was stirred for 3 hr, and was diluted with water. The organic layer was separated and the residue was chromatographed over neutral alumina. The composition of the product mixtures and the data of the products are given below:

Compound **3** (R = Me, X = Cl). 30%, m.p. 140–2° (benzene:petroleum ether, 3:2). Mass: M^+ *m/e* 334. The other prominent peaks were present at *m/e* 299 (334-Cl), 251 (334-$CHCl_2$), 219 (334-S-$CHCl_2$), 217 (299-$CHCl_2$), 185 (299-S-$CHCl_2$), 159 (185-Cl). ^1H NMR ($CDCl_3$): δ1.75 (s, 3H), 1.81 (s, 3H) (gemdimethyl H), 1.87 (s, 3H, C_1-CH_3), 2.00 (s, 1H, C_6H), 3.5 (s, 3H, N-CH_3) and 7.42 (s, 1H, -$SCHCl_2$). (Found: C, 35.59; H, 4.58; N, 8.25. Calc. for $C_{10}H_{14}N_2SCl_4$: C, 35.93; H, 4.19; N, 8.38%).

Compound **4** (R = Me, X = Cl): 60%, m.p. 186–7° (chloroform: petroleum ether, 2:1). Mass: M^+ *m/e* 252. The other prominent peaks were present at *m/e* 217 (252-Cl), 216 (252-HCl), 201 (216-CH_3). ^1H NMR ($CDCl_3$): δ1.42 (s, 3H), 1.5 (s, 3H) (gemdimethyl H), 1.75 (s, 1H, C_6H), 1.77 (s, 3H, C_1-CH_3), 3.53 (s, 3H, N-CH_3) and 6.56 (1H, a broad signal exchanged with D_2O, NH). ^{13}C NMR ($CDCl_3$): δ 176.3 (s), 65.17 (s), 49.76 (s), 43.68 (d), 37.9 (q), 32.94 (q), 25.8 (q) and 20.5 (q). IR: 3350, 2900, 1480, 1455, 1390 cm^{-1}.

Compound **3** (R = Et, X = Cl): 30%, m.p. 86–7° (benzene: petroleum ether, 3:2). Mass: $M^{+\cdot}$ *m/e* 348. The other prominent peaks were present at *m/e* 313 (348-Cl), 265 (348-$CHCl_2$), 250 (265-CH_3), 233 (348-$SCHCl_2$), 231 (313-$CHCl_2$), 198 (313-$SCHCl_2$). ^1H NMR ($CDCl_3$): δ1.25 (s, 6H), 1.42 (s, 3H) one gemdimethyl group), 1.62 (s, 1H, C_6 H), 1.65 (s, 3H, C_1-CH_3), 3.38 (q, J = 7 Hz, 2H, N-CH_2 CH_3) and 7.30 (s, 1H, -$SCHCl_2$).

Compound **4** (R = Et, X = Cl): 60%, m.p. 163–4° (chloroform:petroleum ether, 3:2). Mass: $M^{+\cdot}$ *m/e* 266. The other prominent peaks were present at *m/e* 231 (266-Cl), 195 (231-HCl), 166 (195-CH_2CH_3). ^1H NMR ($CDCl_3$). δ1.33 (t, 3H, N-$CH_2-C\underline{H}_3$), 1.4 (s, 3H), 1.49 (s, 3H) (gemdimethyl H), 1.79 (s, 3H, C_1-CH_3), 4.13 (q, J = 7 Hz, 2H, N $\underline{CH}_2CH_3$) and 7.00 (1H, a broad signal exchanged with D_2O due to NH).

Compound **3** (R = C_6H_5, X = Cl): 60%, m.p. 90–91° (petroleum ether:n-pentane, 4:1). Mass: $M^{+\cdot}$ *m/e* 396. The other prominent peaks were present at *m/e* 361 (396-$CHCl_2$), 281 (396-$SCHCl_2$), 277 (361-:CCl_2), 246 (361-$SHCCl_2$). ^{13}C NMR ($CDCl_3$): δ127.77 (d), 127.63 (d), 124.34 (d), 71.76 (s), 53.15 (d), 29.50 (q), 27.73 (q), 24.99 (q) and 18.56 (q). ^1H NMR ($CDCl_3$) δ1.37 (s, 6H, gemdimethyl H), 1.52 (s, 3H, C_1-CH_3), 1.88 (s, 1H, C_6 H), 7.18 (s, 1H, $SCHCl_2$) and 7.37 (m, 5H, aromatic H) (Found: C, 44.98; H, 4.91; N, 6.54 Calc. for $C_{15}H_{16}N_2SCl_4$: C, 45.55, H, 5.05; N, 7.0%).

Compound **4** (R = C_6H_5, X = Cl): 30%, m.p. 260–2° (ethylacetate:benzene, 3:1). Mass: $M^{+\cdot}$ *m/e* 314 corresponded with molecular formula $C_{14}H_{16}N_2Cl_2S$. The other prominent peaks were present at *m/e* 279 (314-Cl), 143 (279-HCl), 228 (243-CH_3). ^1H NMR (TFA): δ1.6 (s, 3H), 1.7 (s, 3H) (gemdimethyl H), 1.8 (s, 3H, C_1 CH_3), 2.3 (s, 1H, C_6-H), 7.62 (m, 5H, aromatic H) and 8.5 (1H, a broad signal exchanged with D_2O, N-H).

Compound **3** (R = *p*-tolyl, X = Cl): 60%, m.p. 62–63° (petroleum ether). Mass: $M^{+\cdot}$ *m/e* 410 corresponded with molecular formula $C_{16}H_{18}N_2SCl_4$ ^{13}C NMR ($CDCl_3$): δ128.45, 126.76, 126.56 (d), 71.84 (s), 50.88 (s), 46.33 (s), 42.94 (d), 29.33 (q), 24.31 (q), 19.33 (q) and 18.39 (q). ^1H NMR ($CDCl_3$): δ1.40 (s, 9H, gemdimethyl H and p-tolyl-CH_3), 1.58 (s, 3H, C_1 CH_3), 2.0 (s, 1H, C_6 H), 7.28 (s, 1H, $SCHCl_2$) and 7.5 (s, 4H, aromatic H). (Found: C, 46.18; H, 4.28; N, 7.17 Calc. for $C_{16}H_{18}N_2SCl_4$: C, 46.8; H, 4.4; N, 6.83%).

Compound **4** (R = *p*-tolyl, X = Cl): 30%, m.p. 120–2° (chloroform:petroleum ether, 3:1). Mass: M^+ *m/e* 328. ^1H NMR ($CDCl_3$): δ1.46 (s, 3H), 1.53 (s, 3H) (gemdimethyl H), 1.60 (s, 3H, C_1-CH_3), 1.93 (s, 1H, C_6 H), 2.42 (s, 3H, p-tolyl-CH_3), 6.5 (1H, a broad signal exchanged with D_2O, NH) and 7.3 (s, 4H, aromatic H).

(b) *Dichlorocarbene generated from potassium t-butoxide and chloroform.* BuOK (10 g) was added to a soln of **2** (0.01 mole) in THF or dioxane (60 ml). $CHCl_3$ (20 ml) mixed with the solvent was added dropwise over a period of 2 hr to the stirred mixture. It was stirred for additional 10 hr. The salt which separated was filtered off and the filtrate concentrated under reduced pressure. The mixture was chromatographed

over neutral alumina and the yields of the corresponding **3** and **4** are tabulated below:

Sr. No.	R =	Amount of (2) taken	% age (a) of (4) formed	% age of (3) formed	% age of unreacted (2)
1.	CH_3	1.70	70	5	20
2.	C_2H_5	1.84	70	5	22
3.	C_6H_6	2.32	10	8	75
4.	p-tolyl	2.46	12	4	75

(a) The yields tabulated are as obtained after chromatography.

(c) *Dichlorocarbene generated from sodium trichloracetate.* A soln of sodium trichloroacetate (1.84 g, 0.01 mole) in DME (25 ml) was added dropwise to a refluxing soln of **2** (0.01 mole) in DME (25 ml) over a period of 45 min. The mixture was refluxed for additional 3 hr. It was cooled, filtered and the solvent was removed under reduced pressure. The mixture thus obtained was chromatographed over alumina to give the corresponding **3** and **4** in yields tabulated below:

S. No.	R =	Amount of (2) taken	% of (4)	% of (3)	% of Unreacted (2)
1.	CH_3	1.70	40	—	35
2.	C_2H_5	1.84	40	—	40
3.	C_6H_6	2.32	8	−10	75
4.	p-tolyl	2.42	5	7	80

Transformations of **3** *to* **4** (X = Cl). The data about these transformations is tabulated below:

S. No	Reaction conditions	Heating bath temp (C°)	Time	% of (4)
1.	solid, as such	130–140	30 min.	90[a]
2.	methanol/sodium methoxide, sealed tube	90–95	1 hr	90[b]
3.	conc. HCl or 10% H_2SO_4	90–95	6 hr	90[b,c]
4.	quinoline	200–210	2 hr	90[b,c]
5.	dioxane/t-BuOK	100–110	10 hr	90[b]

[a] After crystallization; [b] after chromatography; [c] worked up by neutralization and extraction with chloroform.

Single pot synthesis of **4** (X = Cl). The mixtures obtained in the reactions of **2** with dichlorocarbene were heated on a water bath in conc HCl for 6 hr. The mixture was cooled, neutralized with $NaHCO_3$ aq and extracted with $CHCl_3$ to give only **4**.

Attempted transformation of **4** (X = Cl). Under all the reaction conditions described for transformation of **3** by giving prolonged reaction time, **4** did not undergo any change and the starting material was recovered unchanged.

Reaction of **2** *with dibromocarbene*

(a) *Under catalytic-two-phase conditions.* A cooled soln of 50% NaOH aq. (20 ml) was added dropwise to a stirred soln of **2** (R = Me) (0.01 mole) in benzene (50 ml) containing bromoform (12 ml) and (TEBACl, 0.15 g) as catalyst. The mixture was stirred for 10 hr and was diluted with water. The organic layer which separated was washed with water three times. The mixture consisted of three components *viz* **2** (R = Me), **4** (R = Me) and **7** (R = Me). **4** (R = Me, X = Br) 20%, m.p. 186–87°. ^{1}H NMR ($CDCl_3$): δ1.37 (s, 3H), 1.46 (s, 3H) (gemdimethyl H), 1.8 (s, 3H, C_1–CH_3), 3.5 (s, 3H, N–CH_3) and 1.6 (s, 1H, C_6–H). **7** (R = Me): 20%, m.p. 122–25°. Mass: $M^{+\cdot}$ *m/e* 154. The other prominent peaks were present at *m/e* 139 (154-CH_3), 111 (139-CO), 96 (139-HNCO). ^{1}H NMR ($CDCl_3$): δ1.25 (s, 6H, gemdimethyl H), 1.87 (d, J = 1.5 Hz, 3H, $\begin{matrix}CH_3 & H\\ | & /\\ C=C\end{matrix}$, *cis*), 3.12 (s, 3H, N–CH_3), 4.5 (m, 1H, $\begin{matrix}CH_3 & H\\ | & /\\ C=C\end{matrix}$- *cis*) and 5.85 (1H, broad signal exchanged with D_2O, –NH). ^{13}C NMR ($CDCl_3$): δ154.91 (s), 142.33 (s), 106.64 (d), 31.75 (q), 29.33 (q), 19.03 (q), 18.45 (q). IR: 3300 (NH), 2980 (CH), 1660 (C = O), 1430, 1400 cm^{-1}.

Under these conditions, **2** (R = Ph) gave only **7** (R = Ph) 50%, m.p. 144–6° (benzene). Mass: $M^{+\cdot}$ *m/e* 216. The other prominent peaks were present at *m/e* 201 (216-CH_3), 173 (201-CO), 119 (201-HNCO). ^{13}C NMR ($CDCl_3$): δ154.20 (s), 143.28 (s), 132.98, 129.90, 107.44 (d), 93.437, 29.94 (q), 28.71 (q), 20.26 (q). ^{1}H NMR ($CDCl_3$): δ1.25 (s, 6H, gemdimethyl H), 1.5 (d, J = 1.5 Hz, 3H, $\begin{matrix}CH_3 & H\\ | & /\\ C=C\end{matrix}$ *cis*), 4.6 (m, J = 1.5 Hz, 1H, $\begin{matrix}CH_3 & H\\ | & /\\ C=C\end{matrix}$ *cis*), 4.96 (1H, exchanged with D_2O, NH) and 7.44 (m, 5H, aromatic H). IR: 3336 (NH), 2920 (CH), 1690 (C = O) cm^{-1}.

(b) Similarly, **2** (R = Me) on reaction with dibromocarbene generated from BuOK and bromoform formed **4** (R = Me, X = Br) as well as **7** (R = Me) whereas **2** (R = Ph) under these conditions formed only **7** (R = Ph) in good yields.

Reaction of **3** *with diiodocarbene* A cooled 50% NaOH aq (25 ml) was added dropwise at room temp to a stirred soln of iodoform (8.0 g, 0.02 mole) and **2** (0.01 mole) in benzene CH_2Cl_2 (100 ml) containing TEBACl (0.2 g) as catalyst, over a period of 0.5 hr. It was stirred at room temp for 3 days. The reaction was diluted with water, the organic layer separated, washed with water and dried (Na_2SO_4). The solvent was distilled off and the mixture was chromatographed to give the corresponding **7** in yields tabulated below:

S. No.	R =	Amount of (2) taken	% of (7) formed[a,b]	% of unreacted (2)
1.	CH_3	1.70	30	60
2	C_6H_5	2.32	60	35

[a]In these reactions analogous (4) were not formed; [b]when diiodocarbene was generated from iodoform and t-BuOK, again the same product was formed in the same yield but the time taken was considerably less (48 hr).

Reaction of **2** *with bromine and* t-BuOK*in* t-BuOH. A soln of **2** (0.01 mole) in t-BuOH (50 ml) containing an excess of t-BuOK and Br_2 (0.2 ml) was refluxed. The progress of the reaction was monitored through tlc of aliquot portions of the mixture drawn at regular intervals. The reaction was worked up after 12 hr. The solvent was distilled off and the residue treated with water. It was extracted with EtOAc (100 ml), dried and solvent removed to give a mixture which on chromatography over neutral alumina gave the corresponding **7** in almost quantitative yield.

Similarly, when instead of Br_2, I_2 was used in catalytic amount again the corresponding **7** was formed in good yields.

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