# REACTION OF DICHLOROCARBENE WITH 2,2,4-TRIMETHYL-1,2-DIHYDROQUINOLINE AND ITS DERIVATIVES

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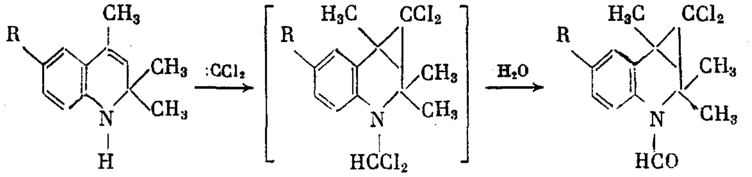
UDC 542.91:547.512'131:547.831.3

The double bond in 2,2,4-trimethyl-1,2-dihydroquinoline (Ia) and its acylic derivatives has a weak tendency to undergo electrophilic addition reactions. In particular, this bond is not oxidized by organic peracids [1], is not brominated [2], and is only slowly protonated by strong inorganic acids or Lewis acids to form a carbocation capable of participating in Friedel—Crafts alkylation reactions [3]. Such a diminution of olefinic nature of a double bond is related to a possible direct interaction of the double bond π-electrons with the nitrogen p-electrons, leading to a special type of "aromatization" of the double bond [4].

We studied the cycloaddition of dichlorocarbene (DCC), which acts as an electrophile in this reaction [5], at the double bond of 2,2,4-trimethyl-1,2-dihydroquinoline and its derivatives (I) and (IV). DCC was generated from chloroform under phase transfer conditions [5]. Greibrokk [6] has described the reaction of DCC with 1-methyl-1,2-dihydroquinoline, leading under these conditions, to the insertion of this carbene at the C—H bond followed by [1 + 2] cycloaddition at the double bond with the formation of a mixture of 30% 1-methyl-2-dichloromethyl-4,4-dichlorocyclopropane[c]quinoline and 20% 1-methyl-4-dichloromethyl-2,2-dichlorocyclopropane[b]quinoline.

Under these conditions, we find initial insertion of DCC at the N—H bond with the formation of dichloromethyl derivatives (IIa)-(IIc) for 6-R-2,2,4-trimethyl-1,2-dihydroquinolines (Ia)-(Ic), which have a free N—H bond, in addition to the smooth [1 + 2]cycloaddition of DCC at the double bond. Dichloro derivatives (IIa)-(IIc), upon hydrolysis, give 7-R-1-formyl-2,2,5-trimethyl-4,4-dichlorocyclopropane[c]quinolines (IIIa)-(IIIc). However, it proved impossible to isolate the products of selective formylation at the N—H bond, even when the substrate/chloroform mole ratio was 1:1.



(Ia—c) (IIa—c) (IIIa—c)

R = H (a), $CH_3$ (b), $OC_2H_5$ (c).

The reaction product yield drops in the series (Ia) > (Ib) > (Ic). This behavior is apparently related to the circumstance that electron-donor substituents at $C^6$ increase the nucleophilicity of the nitrogen atom to a greater extent than the nucleophilicity of the double bond. For this reason, we were apparently unable to isolate the product of the addition of DCC to the N-methyl derivative (IVa). On the other hand, N-acyl derivatives (IVb) and (IVc) readily add DCC. Using 50% aq. NaOH in the phase transfer catalysis, the hydrolysis of the acyl groups did not proceed and 1-acyl-2,2,5-trimethyl-4,4-dichlorocyclopropane-[c]quinolines (Vb) and (Vc) were isolated.

Under the indicated conditions, thin-layer chromatography indicated that 100% conversion of the starting compounds, except (IVa), could be achieved at 40°C over 5 h for (Ia)-(Ic) and 3 h for (IVb) and (IVc). However, the tarry side-products formed in addition to (IIIa)-(IIIc), (Vb), and (Vc) could not be identified.

The structures of all the compounds were demonstrated by IR and PMR spectroscopy (Table 1). Products (IIIa)-(IIIc), (Vb), and (Vc) are colorless, crystalline compounds with good solubility in many organic solvents.

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0568-5230/88/3706-1248$12.50

TABLE 1. Spectral Parameters of 7-R-1-Acyl-2,2,5-trimethyl-4,4-dichlorocyclopropane[c]quinolines

| Compound | PMR spectrum, δ, ppm | | | | PMR spectrum, δ, ppm | | IR spectrum, ν, cm$^{-1}$ | |
|---|---|---|---|---|---|---|---|---|
| | 7-R | 1-R' | 5-CH$_3$ | 3-CH | C(CH$_3$)$_2$ | aromatic protons | quinoline ring | NCO |
| (IIIa) | — | 8,50 s (1H) | 1,34 s (3H) | 1,80 s (1H) | 1,83; 2,00, 2 s (2×3H) | 7,10–7,45m (4H) | 1600 | 1664 |
| (IIIb) | 2,36 s (3H) | 8,51 s (1H) | 1,27 s (3H) | 1,74 s (1H) | 1,84; 1,94, 2 s (2×3H) | 7,05–7,42 m(3H) | 1598 | 1652 |
| (IIIc) | 1,45 t (3H)<br>4,14 q (2H) | 8,57 s (1H) | 1,30 s (3H) | 1,78 s (1H) | 1,84; 1,90, 2s (2×3H) | 6,80–7,75m (3H) | 1602 | 1655 |
| (Vb) | — | 2,06 s (3H) | 1,33 s (3H) | 1,74 s (1H) | 1,84; 1,92, 2 s (2×3H) | 6,68–7,45 m(4H) | 1590 | 1660 |
| (Vc) * | — | — | 1,51 s (3H) | 1,77 s (1H) | 1,84; 1,93, 2 s (2×3H) | 6,41–7,75m (9H) | 1598 | 1645 |

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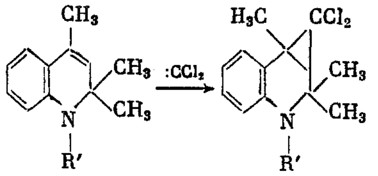
*The benzoyl group protons overlap the aromatic protons.

TABLE 2. Yields and Properties of the Products

| Compound | Mp, °C | Yield, % | Found/Calculated, % |  |  |  | Chemical formula |
|---|---|---|---|---|---|---|---|
|  |  |  | C | H | Cl | N |  |
| (IIIa) | 154–155 | 41 | 59,41/59,15 | 5,37/5,28 | 24,48/24,96 | 5.03/4,92 | $C_{14}H_{15}Cl_2NO$ |
| (IIIb) | 130–131 | 26 | 60.84/60,40 | 5,92/5,70 | 23.65/23,80 | 4.91/4,70 | $C_{15}H_{17}Cl_2NO$ |
| (IIIc) | 119–120 | 16 | 58,71/58,53 | 5,94/5,79 | 21,45/21,62 | 4.18/4,27 | $C_{16}H_{19}Cl_2NO_2$ |
| (Vb) | 123–124 | 37 | 60,49/60,40 | 5,47/5,70 | 23,99/23,80 | 4,82/4,70 | $C_{15}H_{17}Cl_2NO$ |
| (Vc) | 137–138 | 49 | 68,57/68,97 | 6,21/6,03 | 20.62/20,37 | 4.18/4,02 | $C_{20}H_{21}Cl_2NO$ |



(IV a–c) (V b, c)

R' = $CH_3$ (a), $COCH_3$ (b), COPh (c)

## EXPERIMENTAL

The course of the reaction and purity of the products were monitored by thin-layer chromatography on Silufol UV-254 plates with elution by 5:1 $CCl_4$–ether using iodine vapor as the developer. The IR spectra were taken for vaseline mulls on a UR-20 spectrometer. The PMR spectra were taken on a Tesla BS-467 spectrometer at 60 MHz in $CCl_4$ with TMS as the internal standard.

7-R-Acyl-2,2,5-trimethyl-4,4-dichlorocyclopropane[c]quinolines (IIIa)-(IIIc), (Vb), and (Vc). A mixture of 0.1 mole of the corresponding 6-R-2,2,4-trimethyl-1,2-dihydroquinoline (Ia)-(Ic) or (IVa)-(IVc), 15 ml $CHCl_3$, 50 ml 50% aq. NaOH, and 0.2 g tetrabutylammonium iodide was stirred at 40°C for 3-5 h. The reaction mixture was poured into 100 ml water, extracted with $CHCl_3$, and evaported at reduced pressure. The residue was crystallized from ethanol. The yields and physical indices of the products are given in Table 2.

## CONCLUSIONS

1. The reaction of dichlorocarbene with 6-R-2,2,4-trimethyl-1,2-dihydroquinolines gives formylation at the N–H bond followed by [1 + 2] cycloaddition at the double bond with formation of the corresponding 7-R-1-formyl-2,2,5-trimethyl-4,4-dichlorocyclopropane[c]-quinolines.

2. The yields of the [1 + 2] cycloaddition products decreases with increasing nucleophilicity of the nitrogen atom in the dihydroquinoline ring.

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