

PREPARATION AND HYDROLYSIS OF PHENYLBISDIALKYLAMINOCYCLOPROPENIUM CATIONS

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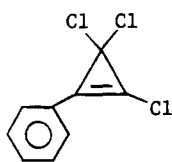
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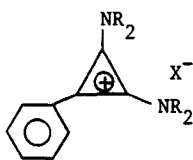
The availability and chemical versatility of tetrachlorocyclopropene¹ have made it a useful starting material for preparative cyclopropene chemistry. It undergoes *inter alia* Friedel-Crafts condensation with aromatic hydrocarbons to give arylchlorocyclopropenes² and nucleophilic substitution with amines³ or thiols⁴ to give stable trisamino or tris thiocyclopropenium cations. These products may be converted to cyclopropenones or cyclopropenethiones, with ring opening to acrylate or allenic species as observed side reactions.^{2b,5,6}

We have applied this chemistry to the preparation of aryldialkylaminocyclopropenones 3,⁷ but in the case of the dimethylamino analog obtained exclusively a novel ring-opened product.

Reaction of phenyltrichlorocyclopropene² with excess diisopropylamine ($\text{CH}_2\text{Cl}_2/25^\circ \rightarrow 40^\circ$) followed by addition of 70% HClO_4 ³ gave (>90%) phenylbisdiisopropylaminocyclopropenium perchlorate 2a⁸ m.p. 223-225°; $\lambda_{\text{max}}^{\text{MeOH}}$ 242nm (ϵ_m 6940); ir (njl) 5.21, 6.45 μ ; nmr δ 1.27 (12H, d, J=7), 1.42 (12H, d, J=7), 4.00 (4H, overlapping septets), 7.43 (5H, broad s); ms 313 ($\text{M}^+ - \text{ClO}_4$)⁹. The strong 5.21 and 6.45 μ ir bands and the isopropyl nmr bands check closely the corresponding bands reported for the chlorodiisopropylaminocyclopropenium cation, including the non-equivalence of the isopropyl groups.¹⁰



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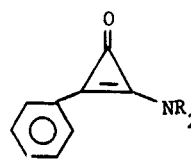


2a, R = $-\text{CH}(\text{CH}_3)_2$, X = ClO_4

2b, R = CH_3 , X = ClO_4

2c, R = CH_3 , X = Cl

2d, R = CH_2CH_3 , X = Cl



3a, R = $\text{CH}(\text{CH}_3)_2$

3b, R = CH_3

3c, R = CH_2CH_3

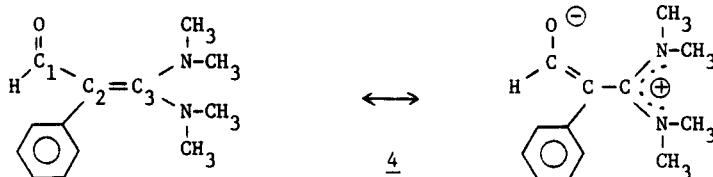
3d, R = $\text{CH}(\text{CH}_3)_2$, O=S

Hydrolysis of 2a (5% KOH in 1:1 $\text{H}_2\text{O}-\text{CH}_3\text{OH}/25^\circ/20$ hr.) yielded phenyldiisopropylaminocyclopropenone 3a (65%) m.p. 121-123°; $\lambda_{\text{max}}^{\text{MeOH}}$ 278nm (ϵ_m 17,840); ir (njl) 5.40, 6.20 μ ; nmr δ 1.35 (12H, d, J=7), 3.57, 4.13 (2H, two centers of overlapping multiplets), 7.42 (5H, m); ms 229 (M^+), 201 ($\text{M}^+ - \text{CO}$). The cyclopropenone 3a was also obtained by treatment of 2a with dilute aqueous Na_2S , an unexpected result in view of the use of these conditions to form thiones in analogous

cases.⁵ However, thione 3d was obtained in good yield by reaction of 3a with $\text{H}_2\text{S}/\text{Et}_3\text{N}$ in THF $25^\circ/16$ hr. Thione 3d had m.p. $128-130^\circ$ dec; $\lambda_{\text{max}}^{\text{MeOH}}$ 240nm (ϵ_m 4260); ir (njl) 5.52, 6.71 μ ; nmr δ 1.45 (6H, d, $J=7$), 1.55 (6H, d, $J=7$), 4.15 (2H, overlapping multiplets), 7.65 (5H, m); ms 245 (M^+).

Reaction of 1 with excess dimethylamine ($\text{CH}_2\text{Cl}_2/0^\circ-40^\circ$) followed by isolation as the perchlorate gave a homogeneous (tlc) gum that was not the anticipated 2b; it lacked the expected 5.2 μ ir band, absorbed in the uv at 223nm ($E_{\text{cm}}^{1\%}$ 253), 272 (457) and 340 (393), and possessed ca three dimethylamino groups (nmr). Alkaline hydrolysis (5% KOH in 1:1 $\text{H}_2\text{O}-\text{CH}_3\text{OH}/25^\circ/65$ hr.) yielded a crystalline solid (90%), m.p. $110-112^\circ$ - clearly not formulable as 3b. The substance ($\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}$) was neutral and soluble in water as well as in benzene: $\lambda_{\text{max}}^{\text{H}_2\text{O}}$ 221nm (ϵ_m 8700), 272 (13800), 320 (9960); ir 3.70, 6.30, 6.35, 6.54, 6.64, 6.78, 6.90 μ ; ^1H nmr δ 2.80 (12H, s, N- CH_3), 7.13 (5H, broad s, Ar-H), 9.00 (1H, s - no change on addition of D_2O - $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}=0$); ^{13}C nmr δ 41.64 (s, N- CH_3), 101.66 (C_2), 124.04 (phenyl C_p), 128.34 (broad, phenyl C_o , $\text{C}_m + \text{C}_3$), 183.06 (C_1); ms 218 (M^+), 201 ($\text{M}^+ -17$), 174 ($\text{M}^+ -44$), 146 ($\text{M}^+ -72$).

The physical data, especially the ^1H and ^{13}C nmr spectra which show the presence of two equivalent $-\text{N}(\text{CH}_3)_2$ groups and a non-exchangeable downfield H, favor structure 4 - 2-phenyl-3,3-bisdimethylaminoacrolein. This structure is supported by the physical data reported for 3,3-bisdimethylaminoacrolein;¹¹ pertinent bands in the ^1H nmr, ir and ms spectra of the latter are in close conformity with analogous bands in the corresponding spectra of 4. In particular the respective mass spectra have prominent peaks for M^+ , $\text{M}^+ -17$, $\text{M}^+ -44$, and $\text{M}^+ -72$ and the respective ^1H nmr spectra have bands near δ 2.80 (12H, s, two $\text{N}(\text{CH}_3)_2$) and 9.00 (1H, aldehydic H)

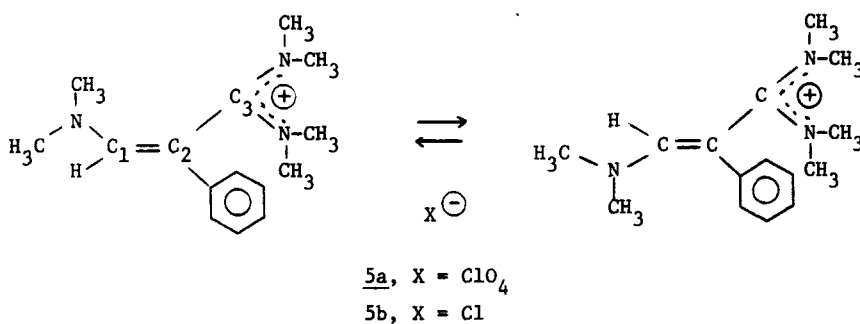


The nature of the precursor to 4 was ascertained following the successful preparation of the phenylbisdimethylaminocyclopropenium system as the chloride 2c by reacting 1 with dimethylaminotrimethylsilane ($\text{CH}_2\text{Cl}_2/0^\circ$)¹² followed by addition of ether. This procedure gave 2c (90%), m.p. $\sim 270^\circ$; $\lambda_{\text{max}}^{\text{MeOH}}$ 285nm (ϵ_m 16,300), 292 inf1. (15,580); ir 5.12, 6.22 μ ; nmr δ 3.57 (12H, s), 7.57 (5H, s); ms 201 ($\text{M}^+ -\text{Cl}$). Salt 2c in 0.7M aqueous KOH was rapidly (<15 min) converted to authentic cyclopropenone 3b (65%) m.p. $86-88^\circ$; $\lambda_{\text{max}}^{\text{MeOH}}$ 282nm (20,470), 276 (20,350); ir 5.35, 6.18 μ ; nmr δ 3.30 (6H, s), 7.47 (5H, m); ms 173 (M^+), 145 ($\text{M}^+ -28$). This sequence was also carried out in good yield with $\text{Et}_2\text{NSiMe}_3$ yielding 2d m.p. $142-145^\circ$ and 3c oil (m.p. $<0^\circ$).⁷

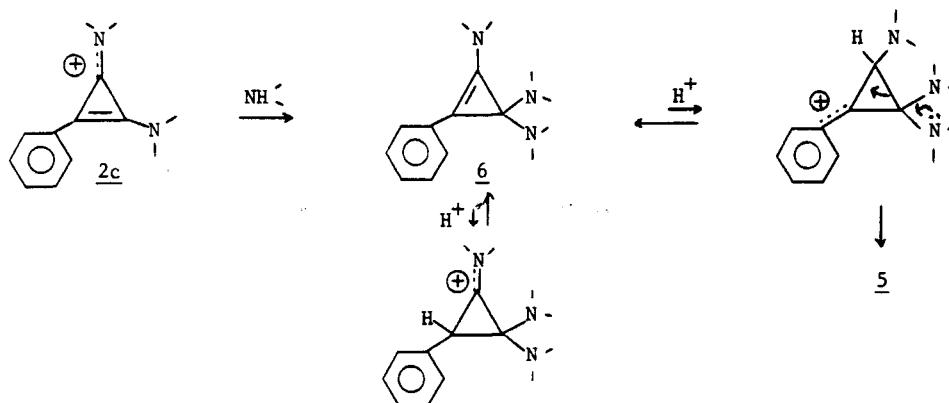
Successive treatment of 2c with dimethylamine ($\text{CH}_2\text{Cl}_2/0^\circ/2$ hr.) and HClO_4 gave a gummy perchlorate identical with the precursor to 4. However, product isolation with 6N HCl gave a crystalline chloride, $\text{C}_{15}\text{H}_{24}\text{N}_3\text{Cl}$, ($\sim 60\%$) m.p. $210-212^\circ$; $\lambda_{\text{max}}^{\text{H}_2\text{O}}$ 223nm (ϵ_m 8490), 275 (17,310), 345 (12,580); ir 6.15, 6.38, 6.60, 6.70 μ ; ms 246 ($\text{M}^+ -\text{Cl}$).

The uv spectra indicate close structural conformity with 4 and the salts are formulated respectively as enamine derivatives 5a and 5b of 4. The salts 5 are stable thermally to 200° in vacuum and are not affected by (at least brief) treatment with aqueous mineral acid at 25°. Aqueous base (10% aq-KOH/25°/48 hr.), however, leads smoothly (75-80%) to 4 as the sole product.

Both the ^1H and ^{13}C nmr spectra of 5b showed peak doubling indicating the presence of two species in the ratio of ~3:2: ^1H nmr δ 3.02 (s), 3.10(s) (~12H), 3.18(s), 3.45(s) (~6H) [N-CH₃], 7.00(m), 7.35(m) (~5.4H) [phenyl H + partial C₁ H], 8.05 (s, 0.6H) [partial C₁H]. ^{13}C nmr δ 42.56, 42.85, 43.95, 44.56 [N-CH₃], 94.90, 95.70 [C₂], 126.16, 126.42 [phenyl C_p], 126.59, 130.48 [phenyl C_o], 128.54, 129.28 [phenyl C_m], 135.73, 138.25 [phenyl subst C], 153.02, 156.86 [C₃], 169.79, 173.58 [C₁]. Presumably sufficient C₁-C₂ double bond character is present to permit detection of discrete cis-trans isomeric forms.



Routes for conversion of bisdimethylaminocyclopropenium cation 2c to acyclic cationic species 5 require addition of $\text{N}(\text{CH}_3)_2$ to C₃, H to C₁ and opening of the 3-membered ring.¹³ Presumably the process is impeded sterically in the bisdiisopropylamino series. The reaction may be considered formally to proceed via Michael addition of the nucleophile followed by H^+ addition to C₁ via equilibration with 6 and electron shift to give the resonance stabilized acyclic unsaturated cationic system 5.



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