Tetrahedron Letters Vol. 21, pp 3241 - 3242 0040-4039/80/0815-3241$02.00/0
©Pergamon Press Ltd. 1980. Printed in Great Britain

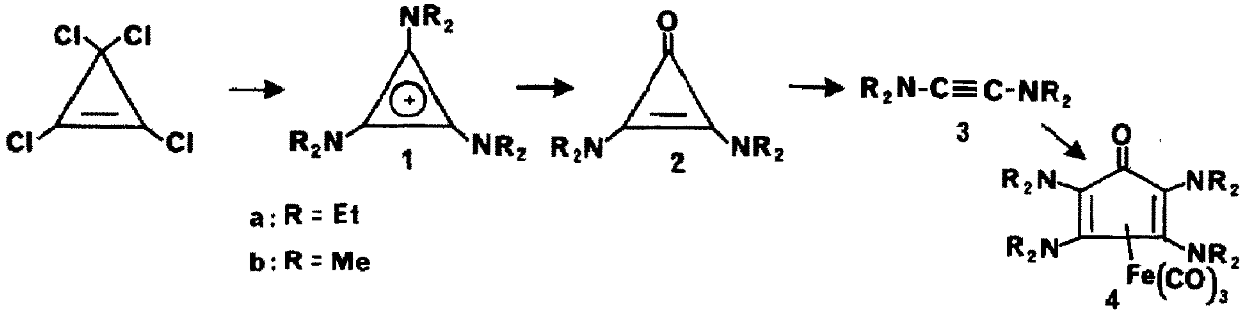
A CONVENIENT SYNTHESIS OF BIS-DIALKYLAMINOACETYLENES

Craig Wilcox and Ronald Breslow*

Department of Chemistry, Columbia University
New York, New York 10027

SUMMARY: The novel compounds tris-diethylaminocyclopropenyl perchlorate, bis-diethylaminocyclopropenone, and bis-dimethylaminocyclopropenone have been made. Pyrolysis of the cyclopropenones affords bis-dimethylamino- and bis-diethylaminoacetylene, and with iron carbonyl these have been converted to iron complexes of tetrakis-dialkylaminocyclopentadienones.

As part of a program directed to the synthesis of stabilized cyclopentadienyl cations we were attracted to the iron carbonyl complex 4a reported by King.[1] This complex is formed in good yield when bis-diethylaminoacetylene (3a) is allowed to react with iron pentacarbonyl under thermal or photolytic conditions, assembling the entire desired cyclopentadienyl carbon skeleton in one step. The major problem with this approach is the general unavailability of diaminoacetylene derivatives. Although 3a can be prepared from diethylamine and dichloroacetylene (generated in situ),[2] the corresponding bis-dimethylaminoacetylene 3b is reported[2] to be formed only from isolated dichloroacetylene. The capricious nature of this process, together with the considerable hazards involved in the preparation and handling of toxic unstable dichloroacetylene, prompted us to search for some efficient alternative. Acetylenes can be prepared by the pyrolysis of cyclopropenones.[3] We now wish to report that this decarbonylation process furnishes a particularly convenient method for the synthesis of 3a and 3b which seems likely to be of general applicability.



Tetrachlorocyclopropene[4] was treated in dichloromethane with excess diethy amine for 36 hours at room temperature. Addition of 70% perchloric acid and workup as described[5] for the tris-dimethylaminocyclopropenyl perchlorate 1b afforded tris-diethylaminocyclopropenyl perchlorate[6] 1a, m.p. 37.5-38.5° [IR ($CHCl_3$, cm^{-1}) 1525, 1205. HMR($CDCl_3$) δ 1.30 (t, 3H, J = 6.5 Hz), 3.36 (q, 2H, J = 6.5 Hz)]. Hydrolysis of this salt in 15% aqueous KOH at 60-65°C for 2 hour provided, after evaporative distillation (130°C, 0.3 mm), the bis-diethylaminocyclopropenone[6] 2a in 81% yield [IR (CCl_4, cm^{-1}) 1900, 1600. HMR ($CDCl_3$) δ 1.2 (t, 3H, J = 7 Hz), 3.25 (q, 2H, J = 7 Hz). UV (CH_3CN) λ_{max} = 234 nm, log ε = 3.99]. Ir similar fashion bis-dimethylaminocyclopropenone[6] 2b was prepared in 91% yield from 1b and had m.p. 55-57° [IR(CCl_4, cm^{-1}) 1885, 1615. HMR ($CDCl_3$) δ 2.97 (s). UV(CH_3CN) λ_{max} = 230 nm, log ε = 4.00].

The cyclopropenones 2a and 2b were pyrolyzed as follows. The ketone (2.0 mmol) was placed in a 10 mL flask fitted with a side-arm for the admission of argon and connected to a dry ice-acetone cooled trap through a heated (525°C) 2 cm. tube packed with glass helices. The apparatus was connected to a vacuum pum the argon flow was adjusted to maintain a pressure of 5 mm, and the cyclopropenone was distilled through the hot zone. With 2a this led to the collection of an 85% yield of 3a as a light yellow liquid identical with an authentic sample prepared by published[2] procedures. The product was > 95% pure by NMR. With 2b the pyrolysis produced an 80% yield of 3b [HMR ($CDCl_3$) δ 2.68], again as a slightly yellow liquid of > 95% purity.

The bis-dimethylaminoacetylene 3b reacted with $Fe(CO)_5$ in similar fashion to that of 3a. Thus 160 mg of crude 3b was heated with 2.35 mmol of freshly distilled iron pentacarbonyl in 4.5 mL of n-octane at reflux under argon for 17 hours. Solvent was removed by distillation, and the dark residue extracted wit CH_2Cl_2. Chromatography on basic alumina afforded 152 mg (55% based on crude alkyne, 39% overall from 2a) of the iron complex 4b as a crystalline orange solid[6], m.p. 97-98°C [IR (CH_2Cl_2, cm^{-1}) 2010, 1970, 1620, 1485. HMR ($CDCl_3$) δ 2.71 (s, 6H), 2.67 (s, 6H)]. Further transformation of 4a and 4b will be described elsewhere.

Acknowledgements: We thank the National Science Foundation for support of this work, and the National Institutes of Health for a postdoctoral fellowship to Craig Wilcox.

References

1. King, R.B.; Harman, C.A. Inorg. Chem., 1976, 15, 879-885.
2. Viehe, H.G.; Delavarenne, S.Y. Ber. Dtsch. Chem. Ges., 1970, 103, 1209-1215
3. Breslow, R.; Eicher, T.; Krebs, A.; Peterson, R.A.; Posner, J. J. Amer. Che Soc., 1965, 87, 1320-1325.
4. West, R.; Tobey, S.W. J. Amer. Chem. Soc., 1966, 88, 2481-2488.
5. Yoshida, Z.; Tawara, Y. J. Amer. Chem. Soc., 1971, 93, 2573-2574.
6. A satisfactory elemental analysis was obtained; 2b $\cdot H_2O$, 2a $\cdot \frac{1}{2}H_2O$.

(Received in USA 14 April 1980)