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PREPARATION OF 1- AND 2-ADAMANTYLDIAZOMETHANES AND THEIR APPLICATION FOR SYNTHESIS OF SOME ADAMANTANE DERIVATIVES[1]

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Adamantyldiazomethanes have not been described in the extensive literatures on adamantane chemistry[2] in spite of their expected utility for the synthesis of adamantane derivatives.[3] We now report on the preparation of 1- and 2-adamantyldiazomethanes and their application for the synthesis of some adamantane derivatives.

1-Adamantanecarboxaldehyde (Ia)[4] prepared by oxidation of the corresponding alcohol with a Sarett reagent was converted to p-toluenesulfonylhydrazone Ib, mp 145-148°,[5] by the usual procedure (64% overall yield). Treatment of Ib with an equimolar amount of n-butyl lithium (15% w/w n-hexane solution) in tetrahydrofuran at -15° for 0.5 hr and at 20° for 0.5 hr, followed by removal of the solvent under reduced pressure (0.1 mm) gave lithium salt Ic as a colorless solid. Pyrolysis of Ic at 70-120° under reduced pressure (0.07-1.0 mm) for 1 hr afforded 1-adamantyldiazomethane II which was trapped at dry ice-acetone temperature in 85% yield as a deep yellow oil: ν_{max}^{neat} 2040 cm^{-1}; $\delta(CCl_4)$ 3.25 (s, CHN_2). II was very unstable at room temperature and had a half-life of ca. 10 min in CCl_4 at 25°. The decomposition product was isolated as colorless crystals after repeated recrystallizations from n-hexane (34%) and was characterized as azine III: ν_{max}^{KBr} 1640 cm^{-1}; $\delta(CDCl_3)$ 7.50 (s, 2H), and 2.22-1.6 (m, 30H).[6]

Treatment of II with a slight excess amount of benzoic acid in ether at

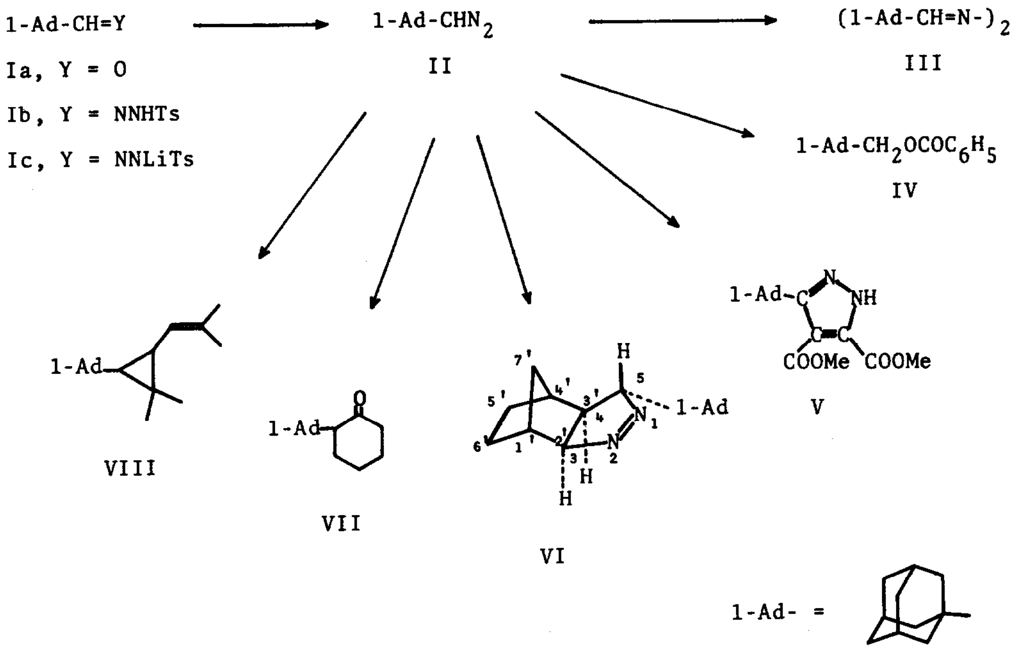
-80° for 24 hr, followed by a general purification procedure afforded the corresponding 1-adamantylmethyl ester IV in 48% yield, mp 64-65° (aqueous acetone): ν_{max}^{KBr} 1720, 1280, 1120 and 715 cm^{-1}; $\delta(CDCl_3)$ 7.3-8.2 (m, 5H), 3.89 (s, 2H), and 2.16-1.5 (m, 15H).

On treatment with an equimolar amount of dimethyl acetylenedicarboxylate in ether under ice-cooling for a few minutes, II afforded pyrazole derivative V in 83% yield as colorless crystals, mp 216-219°(aqueous methanol): ν_{max}^{KBr} 3400 and 1722 cm^{-1}; $\delta(CDCl_3)$ 11.0 (s, 1H, NH), 3.80 (s, 3H), 3.68 (s, 3H), and 2.1-1.4 (m, 15H). Similar treatment of II with norbornene (4 molar excess) in ether at -5° for 2 days afforded pyrazoline derivative VI, mp 135-141° in 60% yield: ν_{max}^{KBr} 1560 (N=N) cm^{-1}; $\delta(CDCl_3)$ 4.32 (d,d, *J*=8.5 and 3.5 Hz, 1H, H^3=$H^{2'}$), 3.50 (unsymmetrical t, *J*=*ca*.3.5 Hz, 1H, H^5), 2.77 (s, 2H, $H^{1'}$ and $H^{4'}$), 2.2-1.1 (m, 20H, other protons), and 0.71 (AB-q, *J*=11 Hz, *J*/$\Delta\delta$=0.458, 2H, $H^{7'}$x 2). The appearance of $C_{7'}$protons of VI at 0.5 ppm higher field compared with those of unsubstituted norbornane (δ 1.21), and the coupling constants of *ca*. 3.5 Hz for J_{H^5,H^4} and J_{H^5,H^3} supported the assigned stereochemistry.[7,8]

Treatment of II with a large excess amount of cyclopentanone in ether at room temperature for 1 day, followed by purification on a silica gel column (CH_2Cl_2) afforded 2-(1-adamantyl)cyclohexanone VII, a ring-expansion product, as an oil (10%): ν_{max}^{neat} 1718 cm^{-1}; $\delta(CDCl_3)$ 2.2-1.2 (m, 24H); *m/e* 232 (M^+).

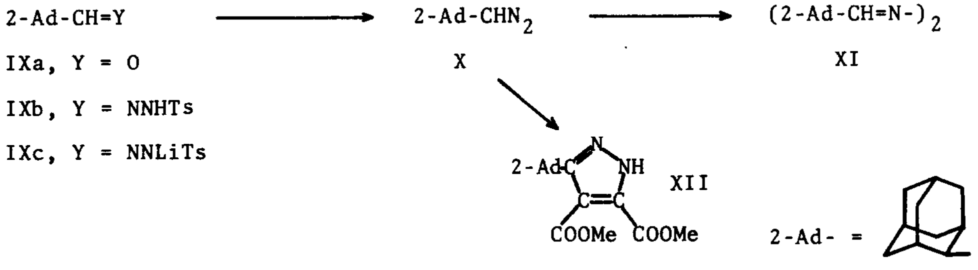
The decomposition of Ib in refluxing 2,5-dimethyl-2,4-hexadiene for 3 hr and the usual work-up on a silica gel column (*n*-hexane) gave a 1-adamantylcarbene adduct VIII (*ca*.1:1 mixture of *cis*- and *trans*-isomers) as an oil (43%): ν_{max}^{neat} 3020, 1610 and 845 cm^{-1}; $\delta(CDCl_3)$ 5.15 and 4.82 (a pair of d, *J*=8.5 Hz, 1H), 2.07-0.8 (m, 28H), and 0.5-0.07 (m, 1H); *m/e* 258 (M^+), indicating the normal carbene addition to double bond (Scheme 1).

Similarly, 2-adamantyldiazomethane X was prepared from IXa[9] *via* IXb, mp 103-105°, and lithium salt IXc in 60% yield as a faintly yellow oil: ν_{max}^{neat} 2030 cm^{-1}; $\delta(CDCl_3)$ 3.30 (d, *J*=10 Hz, $CHC\underline{H}N_2$). X was also unstable at room temperature and had a half-life of *ca*. 30 min (neat). The main decomposition product was the corresponding azine XI which was isolated in 30% yield as colorless crystals by recrystallization from *n*-hexane, mp 205-209°; ν_{max}^{KBr} 1635 cm^{-1};



Scheme 1

δ(CDCl$_3$) 8.02 (d, J=5.5 Hz, 2H), and 2.3-1.5 (m, 30H); m/e 324 (M$^+$). Treatment of X with a slight excess amount of dimethyl acetylenedicarboxylate in ether for 24 hr at room temperature afforded pyrazole derivative XII as colorless crystals in 12% yield, mp 153-155^0 (methanol): ν_{max}^{KBr} 3420 and 1740 cm^{-1}; δ(CDCl$_3$) 11.0 (s, 1H, NH), 3.95 (s, 3H), 3.84 (s, 3H), and 2.3-1.3 (m, 15H) (Scheme 2).



Scheme 2

All of these results indicate that adamantyldiazomethanes II and X are useful intermediates for synthesis of 1- and 2-adamantane derivatives.

REFERENCES

1. Synthesis of Adamantane Derivatives. XXVII. Part XXVI: T. Sasaki, S. Eguchi and F. Hibi, Chem. Commun., in press.
2. R. C. Bingham and P. v. R. Schleyer, "Chemistry of Adamantane," Splinger-Verlag, New York, N. Y., 1971.
3. G. W. Cowell and A. Ledwith, Quart. Rev. (London), **24**, 119 (1970).
4. For preparation of Ia by other methods, see K. Bott, Angew. Chem., **80**, 970 (1968); F. N. Stepanov and D. L. Dovgan, Zh. Org. Khim., **4**, 277 (1968); Chem. Abstr., **68**, 104612 (1968); E. R. Squib, Neth. Appl., 6,613,232; Chem. Abstr., **68**, 68538 (1968); I. Tabushi, Z. Yoshida and N. Takahashi, J. Amer. Chem. Soc., **92**, 6670 (1970).
5. Satisfactory elemental analyses and spectral data consistent with the structural assignments have been obtained for all new compounds.
6. The pyrolysis of Ib at 240-260° (2 mm) has been reported very recently to afford azine III as well as a mixture of hydrocarbons such as 3-homo-adamantene dimers: M. Farcasiu, D. Farcasiu, R. T. Conlin, M. Jones, Jr., and P. v. R. Schleyer, J. Amer. Chem. Soc., **95**, 8207 (1973).
7. Cf. E. L. Allred and J. C. Hinshaw, ibid., **90**, 6885 (1968).
8. R. J. Crawford, A. Mishra and R. J. Dummel, ibid., **88**, 3959 (1966).
9. J. Scharp, H. Wynberg and J. Strating, Rec. Trav. Chim. Pays-Bas, **89**, 18 (1970); D. Farcasiu, Synthesis, 615 (1972).