

A NOVEL, CYCLOBUTANONE-FORMING CARBENE INSERTION REACTION.
TETRACYCLO[7.3.1.0^{2,5}.0^{5,10}]TRIDECAN-4-ONE FROM 1-(TRICYCLO-
[5.3.1.0^{3,8}]UNDEC-3-YL)-2-DIAZOETHAN-1-ONE

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Decomposition of 1-(tricyclo[5.3.1.0^{3,8}]undec-3-yl)-2-diazoethan-1-one (IV) in toluene gave predominantly tetracyclo[7.3.1.0^{2,5}.0^{5,10}]tridecan-4-one (V) under silver oxide catalysis, while tetracyclo[5.4.1.1^{1,9}.0^{5,13}]tridecan-11-one (VI) was the major reaction product in the presence of cupric sulfate.

While a variety of 3-substituted derivatives have been prepared in our studies^{1,2} on the functionalization reaction of 4-homoisotwistane (tricyclo[5.3.1.0^{3,8}]undecane) (I), Bott acetic acid synthesis^{3,4} applied to 3-bromo-4-homoisotwistane (II) was found unsuccessful. Arndt-Eistert synthesis⁵ of the hoped-for acid (III) was then attempted.

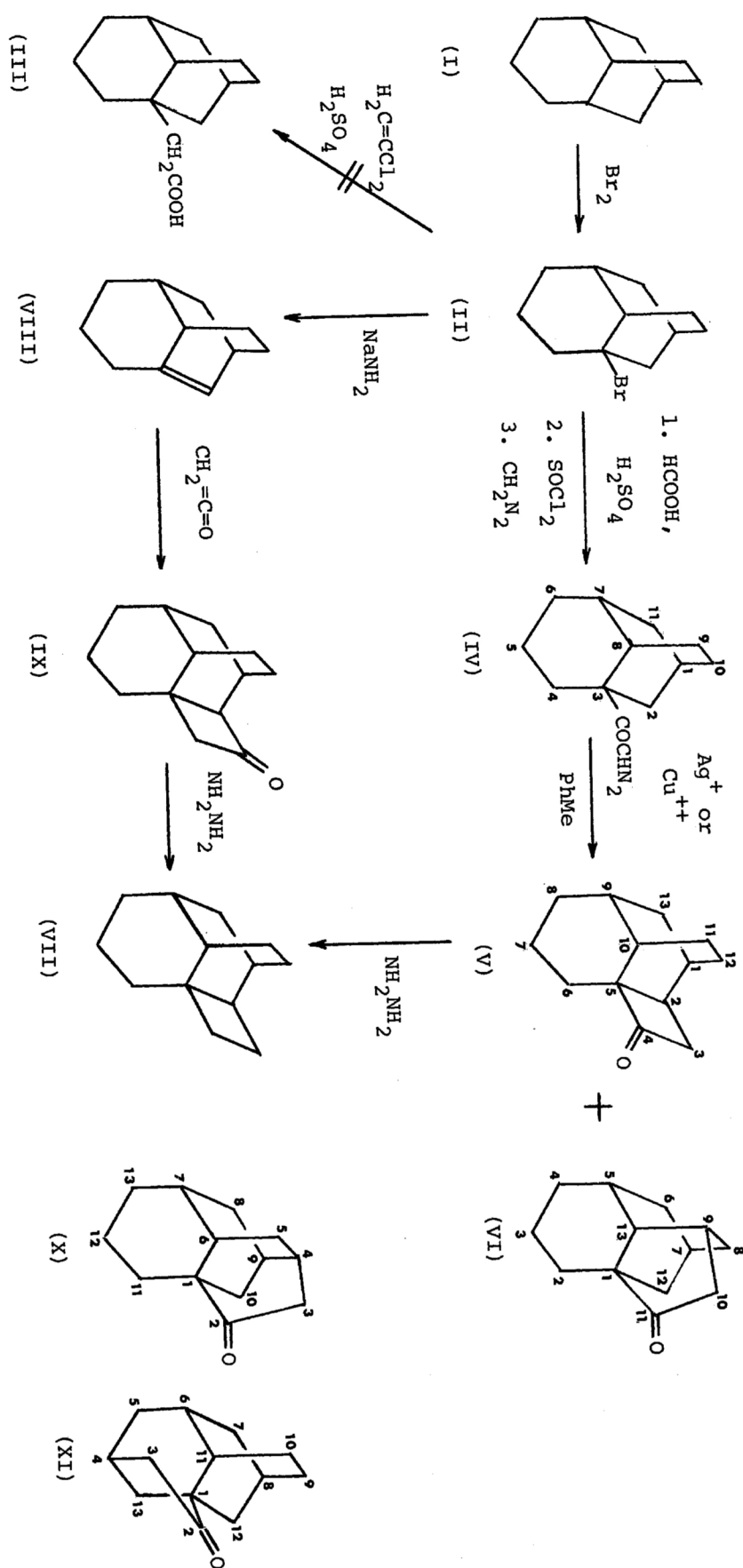
Reaction of 4-homoisotwist-3-ylcarbonyl chloride,⁶ bp 96 - 97°C (0.9 mmHg), n_D^{22} 1.5238, ir (neat) 1790 cm⁻¹, prepared from the corresponding acid¹ and thionyl chloride, with excess diazomethane in ether⁵ gave crude 1-(4-homoisotwist-3-yl)-2-diazoethan-1-one (IV), ir⁷ (neat) 2100, 1630 cm⁻¹. Wolff rearrangement of IV in methanol in the presence of silver benzoate and triethylamine⁸ yielded two ketones (V and VI) in 6.5/1 ratio (23% combined yield) besides expected acetates, as separated and characterized by GC-MS. Decomposition of IV in toluene at reflux under silver oxide catalysis gave the same two ketones in 44% combined yield, the ratio of V to VI being reduced to 1.8/1. Use of cupric sulfate in place of silver oxide led to a predominant formation of VI (V/VI = 1/7.8).

The ketone V isolated on preparative VPC, mp 79°, ir (neat) 1770 cm⁻¹,

ms m/e 190 (15, M^+), 148 (70), 18 (100) was found to be a new compound,⁶ and its structure was determined as tetracyclo[7.3.1.0^{2,5}.0^{5,10}]tridecan-4-one (V) on the following basis. The ir spectrum of V suggested a cyclobutanone structure. Wolff-Kishner reduction of V gave a tetracyclotridecane, ms m/e 176 (20, M^+), 148 (100). The mass spectrum and VPC retention times of this hydrocarbon completely agreed with those of an authentic tetracyclo[7.3.1.0^{2,5}.0^{5,10}]tridecane (VII) prepared by Wolff-Kishner reduction of tetracyclo[7.3.1.0^{2,5}.0^{5,10}]tridecan-3-one (IX),⁶ mp 104 - 105°C, ir (neat) 1770 cm^{-1} , ms m/e 190 (4, M^+), 148 (98), 94 (100), which in turn was obtained by the addition of ketene to 4-homoisotwist-2(3)-ene (VIII).² Formation of V is one of a few examples⁹ of ring closure to cyclobutanes by intramolecular carbene insertion to C-H bond, whereas cyclization to cyclopropanes and cyclopentanes has been well documented in bi- and polycyclic systems.^{7,10}

The other ketone (VI),⁶ mp 89°C, ir (neat) 1740 cm^{-1} , ^{13}C nmr 16.3 ppm (t), ms m/e 190 (58, M^+), 148 (46), 119 (49), 18 (100), was tentatively assigned the structure of tetracyclo[5.4.1.1^{1,9}.0^{5,13}]tridecan-11-one (VI) on the basis of its ir spectrum, with reference to that of isotwistan-4-one (1740 cm^{-1}).¹¹ The keton VI may be regarded as 3,8-trimethyleneisotwistan-4-one. Since the attachment of trimethylene (the C-2 through C-4 in VI) does not substantially distort the isotwistane framework, the ir carbonyl absorption in VI should be similar as in the unsubstituted isotwistane. An abnormally high field methylene carbon resonance (16.3 ppm) of VI seems to be consistent with the structure. This signal may be assigned to the C-3, considering a large upfield shift (~ 11 ppm) caused by two β -axial methylene substituents (the C-6 and C-12) in chair-form cyclohexane.¹²

Two possible alternatives to VI, tetracyclo[5.3.3.0^{1,6}.0^{4,9}]tridecan-2-one (X) and tetracyclo[6.3.1.1^{1,4}.0^{6,11}]tridecan-2-one (XI), could be excluded on the basis of ir and ^{13}C nmr spectra. The structure X should exhibit a similar ir carbonyl absorption as twistan-4-one (1718 cm^{-1}),¹³ because substitution by the trimethylene (the C-11 through C-13 in X) could affect little the skeleton of the twistan-4-one moiety of the molecule. XI does not have any structural feature corresponding to a di- β -axially substituted chair-form cyclohexane, thus offering no good explanation for the 16.3 ppm ^{13}C nmr signal of VI. Moreover, the diazoketone IV should assume, on carbene insertion to form XI, an unfavorable



transition state involving the boat conformation of the cyclohexane ring (the C-3 through C-8) in IV.

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