

chemistry. This structure extends the list of structurally characterized boron hydrides to include B_2H_6 , B_4H_{10} , B_5H_9 , B_6H_{11} , B_6H_{10} , B_9H_{15} , $B_{10}H_{14}$, $B_{10}H_{16}$, $B_{18}H_{22}$ and i - $B_{18}H_{22}$.

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Tricyclo[2.1.1.0^{5,6}]hexane-5-*t*-butylcarboxamide: Synthesis and Carbanion Formation¹

Sir:

Several years ago we described the n.m.r. spectrum of *exo*-5-chlorobicyclo[2.1.1]hexane-*exo*-6-*t*-butylcarboxamide (Ia), which exhibited a dramatic long range spin-spin coupling ($J = 7$ c.p.s.) between the distant *endo* C-5 and C-6 protons.² We now wish to report a

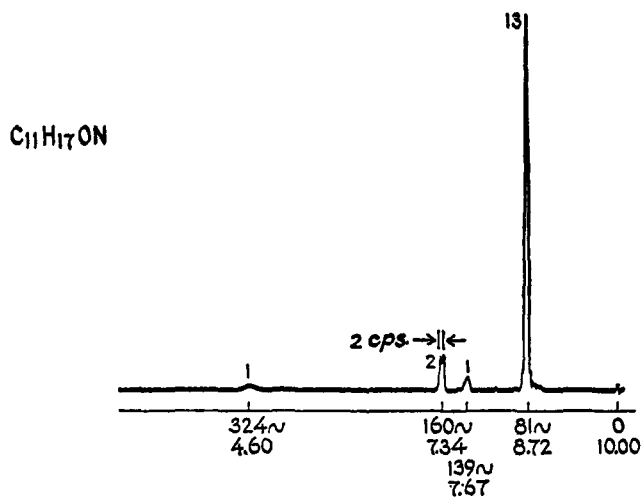
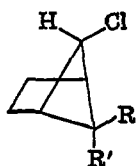


Fig. 1.—N.m.r. spectrum, 60 Mc., ($CDCl_3$ solution) of $C_{11}H_{17}ON$ (numbers over peaks give relative areas; peak positions are given relative to tetramethylsilane in c.p.s. and τ).

novel dehydrohalogenation of Ia to a system forming a new type of carbanion. Treatment of Ia with excess *n*-butyllithium followed by quenching with water yielded a saturated crystalline product, $C_{11}H_{17}ON$,³ m.p. 159.5–160.0°, whose infrared and n.m.r. (see Fig. 1) spectra showed the *t*-butylcarboxamide function to be still intact [infrared max. (CCl_4), N—H, 2.95 μ ; C=O, 6.00 μ].



- Ia. R = CONHC(CH₃)₃; R' = H
Ib. R = H; R' = CONHC(CH₃)₃
Ic. R = CONHC(CH₃)₃; R' = D

(Analogous treatment of the epimeric *exo*-5-chlorobicyclo[2.1.1]hexane-*endo*-6-*t*-butylcarboxamide (Ib)

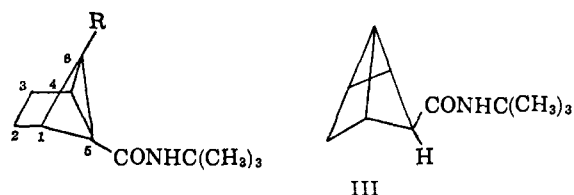
(1) The support of this work by research grants from the National Science Foundation and the National Institutes of Health is acknowledged with pleasure.

(2) J. Meinwald and A. Lewis, *J. Am. Chem. Soc.*, **83**, 2769 (1961); W. D. Kumler, A. Lewis and J. Meinwald, *ibid.*, **83**, 4591 (1961).

(3) Satisfactory analytical data have been obtained for these new compounds.

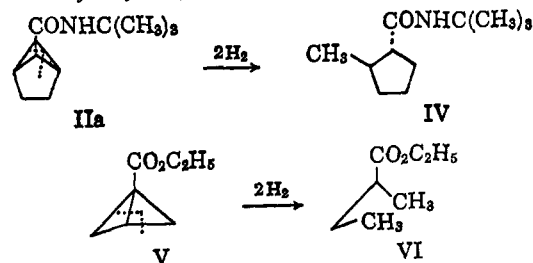
with *n*-butyllithium or even *t*-butyllithium yielded only starting material.)

These data require a tricyclic structure, the two most likely possibilities being IIa and III. The relatively simple n.m.r. spectrum (Fig. 1) favors the more symmetrical structure IIa, since III has no two of its skeletal protons equivalent.



- IIa. R = H IIc. R = CH₃
IIb. R = D IIe. R = CO₂H
 IIe. R = CO₂CH₃

Chemical evidence supporting structure IIa was provided by hydrogenolysis which yielded, after the uptake of two moles of hydrogen, *trans*-2-methylcyclopentane-*t*-butylcarboxamide (IV)³ identified by direct comparison with an authentic sample.⁴ That both moles of hydrogen were absorbed simultaneously, or in rapid succession, was shown by the absence of the possible dihydro compounds (which have been synthesized) in partially hydrogenated samples. The course of hydrogenolysis is closely analogous to that of 1-carboethoxybicyclo[1.1.0]butane⁵ (V → VI).



Structure III does not appear compatible with the formation of this hydrogenolysis product, since the required reductive cleavage of a carbon-carbon bond which is not part of a three-membered ring lacks analogy. Further chemical evidence in favor of structure IIa is not available, as attempts to hydrolyze the *t*-butylamide function without destroying the ring system have been unsuccessful.

In studying the mechanism of the novel cyclization of Ia, it became desirable to investigate the behavior of the analogous deuterated compound Ic.² Following the procedure previously described, the product IIa was found to have lost its deuterium. However, when either Ia or Ic was cyclized with *n*-butyllithium and quenched with D₂O, the 6-deuterio product IIb was obtained. The same product was obtained by treatment of IIa itself with *n*-butyllithium, followed by D₂O. The n.m.r. spectrum of IIb shows exactly the expected relationship to that of IIa, and provides excellent support for the proposed structures. Thus, the unresolved multiplet assigned to the C-6 proton (7.67 τ) vanishes, and the doublet assigned to the C-1 and C-4 protons (7.34 τ) (previously split by the C-6 proton) becomes a singlet.

These results lead to the surprising conclusion that the proton on C-6 is sufficiently acidic to be removed by *n*-butyllithium. Further diagnostic reactions of the anion were obtained by quenching the reaction mixture with methyl iodide to give the methylated product IIc,

(4) An authentic sample of *trans*-2-methylcyclopentane carboxylic acid was made available to us by Prof. J. R. Johnson and Mr. E. Raleigh of these laboratories.

(5) K. B. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959).

and with carbon dioxide to give the acid II_d.³ The n.m.r. spectra of II_c and of the methyl ester of the acid II_e³ are again consistent with the proposed structures. It is interesting that in the latter case (II_e), the four protons on C-2 and C-3 are observed as a separate peak no longer lying under the *t*-butyl peak.

The formation of a carbanion at C-6 seems unprecedented, since there is no simple way to delocalize the negative charge. This property must be due to a change in hybridization resulting in increasing *s*-character for the C-6 H bond, brought about by the unusually small bond angles required in structure II_a. The correlation of acidity with *s*-character is well known,⁶ examples of such acidic protons being those on acetylenic carbons and the olefinic protons of cyclopropene.⁷ Since the carboxamide group is certainly converted into an anion in *n*-butyllithium solution and is therefore unlikely to aid in stabilization of the carbanion, and since the two-carbon bridge should not make a large difference in the C-C bond angles, the acidity of II_a would seem to be a property intrinsic in the bicyclo[1.1.0]butane portion of its skeleton. The validity of this conclusion is at present being investigated.

(6) A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947).

(7) K. B. Wiberg, R. K. Barnes and J. Albin, *J. Am. Chem. Soc.*, **79**, 4994 (1957); G. L. Closs and L. E. Closs, *ibid.*, **85**, 99 (1963).

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Photo-Conversion of Diphenylamines to Carbazoles, and Accompanying Transient Species

Sir:

In the course of flash-excitation studies on *N*-substituted diphenylamines in solution, we have observed new transient species which are neither the triplet states nor the positive ions. The hypothesis that the transients are cyclized structures suggested that under oxidative conditions carbazoles should be formed, and this is indeed found to be the case. Our results are related to recent proposals of mechanisms and kinetic intermediates in analogous oxidative photocyclization reactions.^{1,2}

When triphenylamine is flashed³ in deoxygenated hexane, EPA or tetrahydrofuran solution, two main transients are observed, with absorption peaks at 530 $m\mu$ and 610 $m\mu$, respectively. At room temperature, the major product is the 610 $m\mu$ compound, but low temperature favors formation of the 530 $m\mu$ substance. In EPA solution, at -150° , phosphorescence, which decays at precisely the same rate as the 530 $m\mu$ absorption, is observed. This peak is therefore assigned to the lowest triplet state of triphenylamine.

The 610 $m\mu$ compound has a lifetime of 0.5 msec. at room temperature in hexane and a slightly longer lifetime in polar solvents. It undergoes strictly first-order decay to the ground state, with an activation energy of about 10 kcal./mole in the temperature range 25° to -70° . On flashing *N*-methyl-diphenylamine, two main transients are again formed, with absorption spectra similar to those obtained from triphenylamine. However, the lifetime of the 610 $m\mu$ transient of *N*-methyl-diphenylamine (16 msec. at room temperature,

(1) F. B. Mallory, J. T. Gordon and C. S. Wood, *J. Am. Chem. Soc.*, **85**, 828 (1963).

(2) W. M. Moore, D. D. Morgan and F. R. Stermitz, *ibid.*, **85**, 829 (1963).

(3) Discharge energies of about 100 w.-sec. were used, with flash durations of about 5 μ sec. Temperatures could be varied from 30° to -150° . The apparatus had the general configuration of that described earlier by H. Linschitz and K. Sarkanen, *ibid.*, **80**, 4826 (1958).

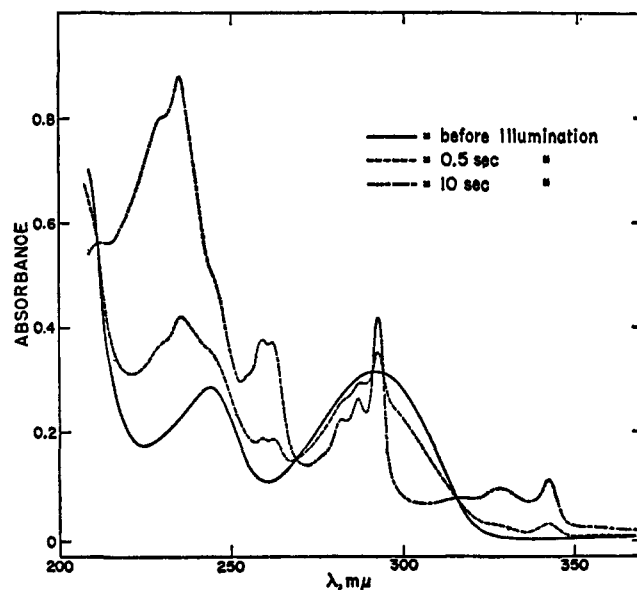
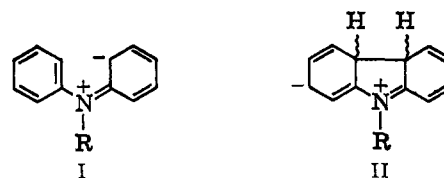


Fig. 1.—Photo-conversion of *N*-methyl-diphenylamine to *N*-methylcarbazole. Absorption spectrum of *N*-methyl-diphenylamine in aerated hexane: solid line, before illumination; dotted line, after half-second illumination; dashed-dotted line after 10-second illumination; concn. $2.6 \times 10^{-5} M$; sample in 1 cm. quartz cell, placed 5 cm. from Hanovia Type SH mercury lamp; room temperature.

in hexane) is much longer than that of the corresponding triphenylamine compound (0.5 msec.).

The positive ion of triphenylamine absorbs at 650 $m\mu$,⁴ with a spectrum easily distinguished from that of the 610 $m\mu$ product. Moreover, if the ion were formed by photo-ionization of the amine in fluid non-polar solvents, it would be expected to decay by extremely fast, second-order kinetics, with a low activation energy for recombination⁵ and with little lifetime dependence on *N*-methyl or *N*-phenyl substitution. Thus, the 610 $m\mu$ transient cannot be the positive ion. Two possibilities may be suggested for this transient, an excited ionic species I, stabilized by Franck-Condon effects, and the cyclized intermediate II.



Other resonance forms of I and II can evidently be written.

The assignment of structure II for the 610 $m\mu$ compound is supported by the high activation energy for decay and by the formation of carbazoles in high yield when the amines are illuminated in organic solvents, exposed to air. Figure 1 shows the changes in absorption spectrum of a hexane solution of *N*-methyl-diphenylamine, caused by brief illumination by a 150 w. mercury lamp. The final spectrum is identical with that of *N*-methylcarbazole and corresponds to about 70% conversion. In other experiments, *N*-methylcarbazole was isolated and identified by its m.p. ($85.5-86.5^\circ$), mixture melting point (no depression) and infrared spectrum. The illumination of triphenylamine gave the ultraviolet spectrum of *N*-phenylcarbazole (about 65% yield) which was similarly isolated and further identified by its m.p. (88.5°), mixture melting point (no depression) and infrared spectrum. The photo-

(4) G. N. Lewis and D. Lipkin, *ibid.*, **64**, 2801 (1942).

(5) H. Linschitz and J. Eloranta, *Z. Elektrochem.*, **64**, 169 (1960).