form acronycine (**4b**) is brought about by a procedure described in the literature.[2] The product obtained is identical with acronycine.

Microanalytical data and nmr, ultraviolet, and infrared spectra are all in agreement with the structural assignments.

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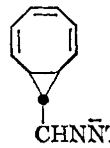
*Received May 19, 1967*

## Three Bicyclic Nonatrienes from Bicyclo[5.1.0]octa-2,4-dien-8-yl Carbene[1,2]

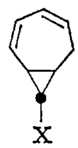
*Sir:*

A preliminary report on the synthetic utility of rearrangements of highly unsaturated bicyclic carbenes has been made.[3] Bicyclo[4.2.2]deca-2,4,7,9-tetraene and the 9,10-dihydronaphthalenes were shown to be the products of thermal decomposition of I. We describe here a further example of such a rearrangement, the synthesis of three bicyclic nonatrienes, and comment upon the mechanism of these remarkable changes.

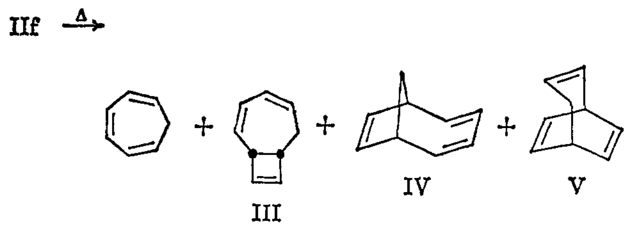
Following the procedure of Korte,[4] ethyl or methyl diazoacetate was catalytically decomposed in tropilidene to give IIa. This compound could be converted *via* IIb–e in conventional steps to the salt IIf. Decomposition of IIf under vacuum at 90–120° led to a complex mixture of isomers from which the four major products could be isolated by preparative gas–liquid partition chromatography. These are, in order of elution from a 3.5-m, 10% Carbowax 20M on 45–60 Chromosorb P column operated at 100° with a helium flow of 100 cc/min, tropilidene (19%; relative retention time 1.00), bicyclo[5.2.0]nona-2,4,8-triene (III, 27%; relative retention time 3.38; infrared: 3010, 2920, 2900, 2850, 1640, 1445, 1375, 1284, 1222, 998, 922, 715, and 675 cm$^{-1}$), bicyclo[4.2.1]nona-2,4,7-triene (IV, 37%; relative retention time 4.66), and bicyclo[3.2.2]nona-2,6,8-triene (V, 12%; relative retention time 5.25; infrared 3030, 3005, 2945, 2910, 2860, 2800, 1630, 1610, 1422, 1378, 1366, 1325, 1276, 1249, 1195, 1040, 980, 959, 886, 870, 715, and 688 cm$^{-1}$). The over-all yield of hydrocarbons was *ca.* 35%. Compound IV was identified by comparison of infrared and nuclear magnetic resonance spectra with those of authentic material[5,6] and by hydrogenation to bicyclo[4.2.1]nonane identical with that prepared from bicyclo[4.2.1]nonan-9-one[7] by Wolff–Kishner reduction. Compound V absorbed 3 moles of hydrogen to give a hydrocarbon identical with that prepared from bicyclo[3.2.2]non-6-en-2-one[8] by hydrogenation and Wolff–Kishner reduction. The structure of III was determined in a similar fashion. *cis*-Bicyclo[5.2.0]non-8-ene (VI) was synthesized from cycloheptene by the method of Kirmse.[9] This material had an infrared spectrum identical with that of the compound prepared by Fonken by photolysis of the cyclononadienes[10] or by thermal cyclization of *cis*,-*trans*-1,3-cyclononadiene.[11] Hydrogenation of VI gave *cis*-bicyclo[5.2.0]nonane (VII), again identical with material made by Fonken.[11] Allinger[12] originally synthesized both *cis*- and *trans*-bicyclo[5.2.0]nonanes from the known and characterized[13] *cis*- and *trans*-1,2-dicarboxycyclobutanes. Fonken identified his materials by comparison of spectra with those of Allinger. Accordingly, the assignment of stereochemistry in VI and VII is secure. Hydrogenation of III led to the uptake of 3 moles of hydrogen and the formation of VII as the sole product. The skeleton and stereochemistry of III can therefore be assigned with confidence. In all cases infrared and nmr spectra were consistent, if not uniquely so, with the assigned structures.

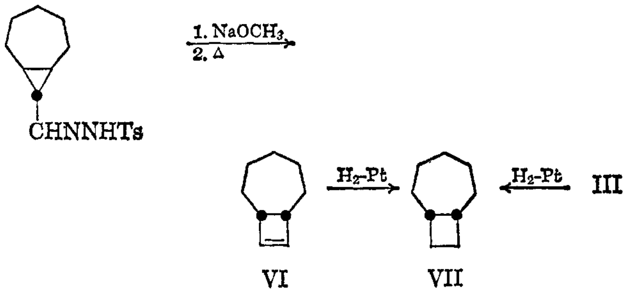


I



IIa, X = COOCH$_3$
b, X = COOH
c, X = COCl
d, X = CHO
e, X = CHNNHTs
f, X = CHNN̄TsNa$^+$





Isolation of III allows some comments to be made on the mechanism of the changes observed in this and previous[3] work. The possible paths for the formation of IV and V include the sigmatropic rearrangement of the cyclobutene III. A thermally allowed shift of the order [1,5] would lead to IV, while V is the product of a hypothetical shift of the order [1,3], an event expected

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[1] We are pleased to thank the Lilly Research Laboratories for most generous support of this work.

[2] Taken in part from the A.B. Thesis of S. D. Reich, Princeton University, 1967.

[3] M. Jones, Jr., and L. T. Scott, *J. Am. Chem. Soc.*, **89**, 150 (1967).

[4] F. Korte, K.-H. Büchel, and F. F. Wiese, *Ann.*, **664**, 114 (1963).

[5] W. Grimme, *Chem. Ber.*, **100**, 113 (1967). We are particularly grateful to Dr. Grimme for informing us of his work prior to publication and for supplying us with many excellent spectra.

[6] L. G. Cannell, *Tetrahedron Letters*, 5967 (1966).

[7] C. D. Gutsche and T. D. Smith, *J. Am. Chem. Soc.*, **82**, 4067 (1960).

[8] J. A. Berson and M. Jones, Jr., *ibid.*, **86**, 5017, 5019 (1964). We thank Professor Berson for a sample of this compound.

[9] W. Kirmse and K.-H. Pook, *Chem. Ber.*, **98**, 4022 (1965).

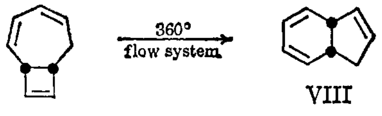
[10] K. M. Shumate and G. J. Fonken, *J. Am. Chem. Soc.*, **88**, 1073 (1966).

[11] K. M. Shumate, P. N. Neuman, and G. J. Fonken, *ibid.*, **87**, 3996 (1965). We thank Professor Fonken for copies of these spectra.

[12] N. L. Allinger, M. Nakazaki, and V. Zalkow, *ibid.*, **81**, 4074 (1959).

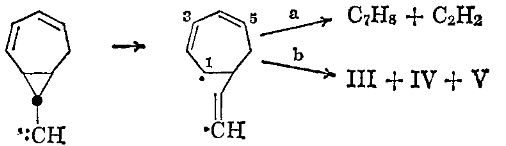
[13] W. H. Perkin, Jr., *J. Chem. Soc.*, 572 (1894).

to take place thermally only with difficulty.[14] This path was tested and ruled out as a source of IV and V. Thermal rearrangement of III in a flow system at 360° gave only *cis*-8,9-dihydroindene (VIII) and a minor product of as yet unknown structure. Under these conditions IV is stable and thus does not arise from III. Authentic VIII was synthesized by the method of Vogel,[15] and an infrared spectrum of *trans*-8,9-dihydroindene[16] was kindly provided by Dr. Wolfram Grimme.[5]



III VIII

As III is now eliminated as a source of IV and V, it seems likely that the carbene formed in the decomposition of IIf is involved. The intermediate IX, related to the carbene by the breaking of a carbon–carbon bond, appears capable of yielding the observed products. Path a proceeds by further carbon–carbon bond cleavage to give acetylene and the observed tropilidene. Abundant analogy for this path exists.[17] Path b consists of closure at the 1, 5, and 3 positions to give the three observed products III, IV, and V.



IX

A similar scheme would suffice to explain our earlier[3] observations. In this system the product of closure at the 1 position, bicyclo[6.2.0]deca-2,4,6,9-tetraene (X), is not stable at *ca.* 120° but rearranges to the observed mixture of *cis*- and *trans*-9,10-dihydronaphthalenes in which the *trans* isomer predominates. This rearrangement now has analogy in the conversion of III to VIII. The product of closure at the 5 and/or 3 positions, bicyclo[4.2.2]deca-2,4,7,9-tetraene, is stable and isolable. The preference for the formation of *trans*-9,10-dihydronaphthalene over the *cis* form permits the tentative identification of the cyclodecapentaene intermediate in the transformation from X. The formulations of Woodward and Hoffmann[18] require that *trans*-9,10-dihydronaphthalene be *thermally* related to the cyclodecapentaene with one *trans* double bond and not to the all-*cis* or di-*trans* isomer (XI and XII). In consonance with this is the finding of van Tamelen and Burkoth[19] that *trans*-9,10-dihydronaphthalene is *photochemically* converted to a cyclodecapentaene (XI and/or XII) which closes *thermally* to *cis*-9,10-dihydronaphthalene.

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(14) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(15) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Letters*, 673 (1963).

(16) E. Vogel, W. Grimme, and E. Dinné, *ibid.*, 391 (1965).

(17) P. B. Shevlin and A. P. Wolf, *J. Am. Chem. Soc.*, **88**, 4735 (1966), and references therein.

(18) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(19) E. E. van Tamelen and T. L. Burkoth, *ibid.*, **89**, 151 (1967).

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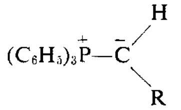
## Temperature Dependence of the P–C–H Nuclear Magnetic Resonance Spectra of Methylenetriphenylphosphoranes

*Sir:*

The hindered internal rotation of alkoxycarbonylalkylidenetriphenylphosphoranes can be investigated by variable-temperature nmr spectroscopy.[1] During the course of such a study it was discovered that phosphorane **1** exhibits a second temperature-dependent feature apparently unrelated to the rotation process.



$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(H)R$

**1a**, R = H  **c**, R = $CO(CH_2)_2C_6H_5$  **e**, R = $CO_2CH_3$
**b**, R = CN  **d**, R = $COCH_3$  **f**, R = CHO

In the absence of further spin–spin interaction the hydrogen $\alpha$ to phosphorus is observed at low temperatures as a well-separated doublet reflecting the expected P–C–H spin–spin coupling. Upon warming the phosphorane solution, however, this doublet gradually coalesces to an unshifted sharp singlet.[2] Three compound classes are to be differentiated.

The simplest case is represented by ylide **1a**,[3] R = H, the temperature-dependent nmr of which is depicted in Figure 1a ($J_{\mathrm{PCH}}^{-28^\circ} = 7.0$ cps[4]). The cyano derivative[5] **1b** exhibits identical proton nmr behavior at $\tau$ 8.38 ($J_{\mathrm{PCH}}^{-60^\circ} = 7.5$ cps).

The second variation is displayed by phosphorane **1c**,[6] R = $CO(CH_2)_2C_6H_5$. In this case rotation about the C–R bond is in principle possible, but is not observed. The invariant multiplicity and resonance position of the $\alpha$-keto ethyl group at $\tau$ 7.15 throughout the relevant temperature range establish this point. Figure 1b is illustrative. Nonetheless, the methine hydrogen low-temperature doublet ($\tau$ 6.29, $J_{\mathrm{PCH}}^{-19^\circ} = 25.0$ cps) coalesces to a clean unshifted singlet at raised temperatures. Phosphorane **1d**,[6] R = $COCH_3$, behaves likewise ($\delta_H = \tau$ 6.32, $J_{\mathrm{PCH}}^{-28^\circ} = 24.5$ cps).

The final and most complex substitution type is represented by ylide **1e**,[7] R = $CO_2CH_3$. Hindered internal rotation about the C–R bond is realized, and the *cis–trans* conformational isomers **2** and **3** can be distinguished at low temperatures.[1,8] Accordingly, the

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(1) H. J. Bestmann, G. Joachim, I. Lengyel, S. F. M. Oth, J. Mereny, and J. Weitkamp, *Tetrahedron Letters*, 3335 (1966). The complete results and structural implications of hindered rotation for stable alkylidenephosphoranes will be reported elsewhere.

(2) All spectra were obtained in deuteriochloroform with TMS as an internal standard on a Japan Electron Optics Laboratory C-60 nmr spectrometer.

(3) G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954). We are grateful to H. Liberda, Institut für Organische Chemie, Universitat Erlangen-Nurnberg, for providing a sample of this salt-free ylide in the solid state.

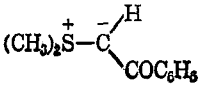
(4) Relative to TMS in chlorobenzene.

(5) Mp 192–193°; S. Trippet and D. M. Walker, *J. Chem. Soc.*, 3874 (1959), report mp 195–196°.

(6) (a) R = $COCH_3$, mp 200–202° (lit.[6b] 200–202°); R = $CO(CH_2)_2C_6H_5$, mp 148–150° (lit.[6b] 148–150°; (b) H. J. Bestmann and B. Arnason, *Chem. Ber.*, **95**, 1513 (1962).

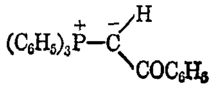
(7) Mp 169.0–169.5°; O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957), report mp 163°.

(8) Ratts and Yao[9] observed a broadened methine proton at room temperature for the sulfonium ylide 7 and the phosphorane **8**. Since



$(CH_3)_2\overset{+}{S}-\overset{-}{C}(H)COC_6H_5$

**7**



$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}(H)COC_6H_5$

**8**