(max.) 258-259 mμ (min.)] and from the filtrate there was obtained 193 mg. (67%) of 1,2,3,4-tetraphenylcyclobutene (VI) (calcd. for $C_{28}H_{22}$: C, 93.8; H, 6.2. Found: C, 93.6; H, 6.3), identified by its spectral properties (λ_{max}^{EtOH} 303 mμ (19,500) n.m.r. [CCl_4]: 2 proton singlet at δ = 4.62, 10 Ph protons at δ = 6.78, 10 Ph protons at δ = 7.0–7.5; ν_{Raman} 1635 cm.$^{-1}$) and by its conversion to II on bromination.[14]

The solid dication V is stable to light and dry air but reacts instantly when its solution is exposed to water or other weak nucleophiles. Paralleling the known chemistry of tropylium, aqueous solvolysis of V yields a mixture of products including tetraphenylfuran, *cis*-dibenzoylstilbene and didesyl.[15] Solution of V in glacial acetic acid causes rapid deposition of colorless crystals, containing active halogen, tentatively identified as 3,4-dichlorotetraphenylcyclobutene (75%) (m.p. 193–195°; calcd. for $C_{28}H_{20}Cl_2$: C, 78.7; H, 4.7; Cl, 16.6. Found: C, 79.0; H, 4.5; Cl, 16.7), presumably by chloride attack on the unstable 3,4-diacetoxytetraphenylcyclobutene. V is stable to approximately 150°, at which temperature it decomposes to yield tin tetrachloride and 1,4-dichlorotetraphenylbutadiene, m.p. 181–183°, identical with the product obtained from the thermal decomposition of tetraphenylcyclobutadiene-palladium chloride complex.[20] Further studies on the fundamental nature of the dication are in progress.

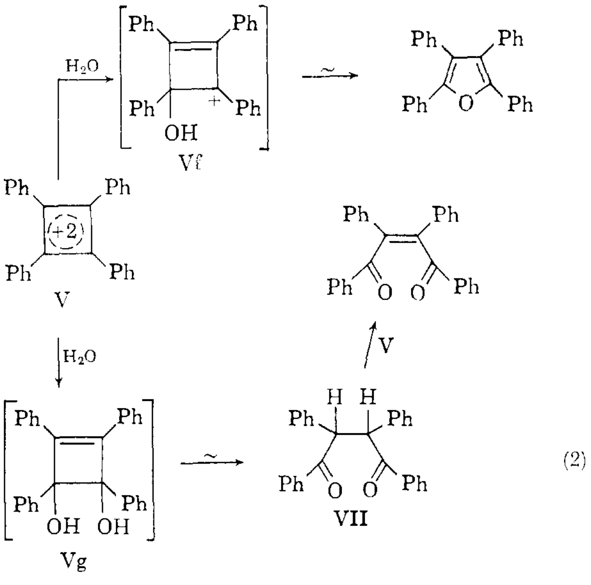
Acknowledgments.—The authors are grateful to Dr. P. M. Maitlis for a stimulating discussion and for the sample of 1,4-dichlorotetraphenylbutadiene.

[13] D. Bryce-Smith and N. A. Perkins, *Chem. and Ind.*, 1022 (1959).

[14] The unambiguous proof of structure of VI reopens the question of the identity of the hydrocarbon $C_{28}H_{22}$, m.p. 122–123°, obtained from the hydrogenation of the tetraphenylcyclobutadiene-nickel bromide complex.[2] The similarity of the δ values for the nonphenyl protons of VI and the 122° hydrocarbon (two singlets at δ = 4.10 and 5.97)[2] suggests certain environmental similarities for these protons, but the non-identity of the proton singlet of VI (δ = 4.62) to either of these latter bands makes untenable our previous conclusion that the 122° hydrocarbon is a mixture of the *cis* and *trans* isomers of VI. (However, the importance of the proof of structure of the 122° hydrocarbon as evidence for the presence of a four-membered ring in the tetraphenylcyclobutadiene-nickel bromide complex, became an academic one in the light of the preparation of II).

[15] The fact that tropylium[16] and cyclopropenium[17] salts can be recovered from their acidified, aqueous solutions, whereas the dication V cannot be so recovered, reflects the reversibility of the solvolysis of the former two species (eq. [1]) and the nonreversibility of the latter (eq. [2]). The formation of tetraphenylfuran is the expected intramolecular solvolysis product of the mono-hydroxy carbonium ion Vf, analogous to the formation of ditropyl ether by the intermolecular attack of tropylium on the initially formed tropyl alcohol.[18] It is also conceivable that the unstable glycol Vg is also formed which gives rise by tautomeric rearrangement to didesyl (VII). The latter may account for the presence of *cis*-dibenzoylstilbene, which by analogy with the disproportionation of tropylium to cycloheptatriene and tropone,[19] probably arises by hydride abstraction from VII by excess V. This also accounts for the variation in production composition, which would be markedly dependent on the availability of excess dication V. A detailed study of this reaction is in progress.

$$R^+ + 2H_2O \rightleftharpoons ROH + H_3O^+ \qquad (1)$$



[16] W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1959).

[17] R. Breslow, J. Lockhart and Hai Won Chang, *ibid.*, **83**, 2375 (1961), and refs. cited therein.

[18] W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

[19] K. Ikemi, T. Nozoe and H. Sugiyama, *Chem. and Ind.*, 932 (1960); K. M. Harmon, *et al.*, *J. Am. Chem. Soc.*, **84**, 120 (1962).

[20] A. T. Blomquist and P. M. Maitlis, *ibid.*, **84**, 2329 (1962).

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RECEIVED JULY 18, 1962

FORMATION OF IMINES BY ELECTROPHILIC SUBSTITUTION AT SATURATED CARBON IN THE BECKMANN AND SCHMIDT REACTIONS[1]

Sir:

Although the insertion of neutral, electron-deficient nitrene intermediates into unactivated C-H bonds is well known,[2] the replacement of paraffinic hydrogen by a *cationic* nitrogen species has not been noted.[3] We now wish to report such an electrophilic substitution involving intramolecular attack by an iminium ion,[4] generated under Beckmann or Schmidt reaction conditions, on a non-adjacent saturated carbon atom.

The key model compound, 4-bromo-7-*t*-butyl-1-indanone,[5] was chosen because normal Beckmann rearrangement of its oxime (I) would be expected to proceed with great difficulty[6] and also because

[1] This research was supported by Grant No. 550-A of the Petroleum Research Fund, American Chemical Society. Grateful acknowledgment is made to the donors of this fund for their generous support.

[2] (a) D. H R. Barton and L. R. Morgan, *J. Chem. Soc*, 622 (1962); (b) G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4717 (1960); (c) J. W. ApSimon and O. E. Edwards, *Can. J. Chem.*, **40**, 896 (1962).

[3] In two cases, acid-catalyzed reactions of ketoxime sulfonates have yielded as minor products pyrazines, which are allegedly derivable from azacyclopropenes (P. A. S. Smith, *J. Am. Chem. Soc.*, **70**, 323 (1948)). Such possible intermediates could result from an insertion of the type discussed here or by cyclization of a vinyl nitrene (*cf.* G. Smolinsky, *ibid.*, **83**, 4483 (1961)).

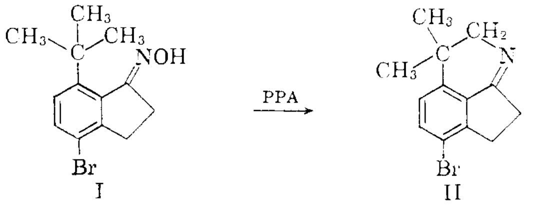
[4] The term "iminium ion" is used here essentially for brevity and is not meant to infer that polyphosphate ion is first lost from the esterified oxime, yielding a discrete cationic intermediate which inserts in a subsequent step. It has been pointed out, however (D. E. Pearson and R. M. Stone, *ibid.*, **83**, 1715 (1961)), that bond-breaking is well advanced in the rearrangement of oxime polyphosphates; moreover, aryl participation is not of importance in the indanone system (ref. 6). Thus, usage of the term iminium ion appears justified.

[5] L. F. Fieser and D. K. Snow, *ibid.*, **60**, 176 (1938).

[6] L. G. Donaruma and W. Z. Heldt, "Organic Reactions," R. Adams, Ed., Volume 11, John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 11-12.

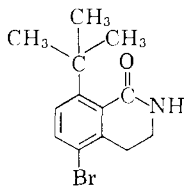
no features conducive to oxime fragmentation[7] were present. Moreover, since iminium ions have been shown to react intramolecularly with such nucleophiles as aromatic rings[8] and alkenes,[9] there was reason to expect C–C or C–H insertion into the proximal *t*-butyl group of oxime I in the Beckmann rearrangement or in the related Schmidt reaction.

Reaction of I with polyphosphoric acid resulted in 75–80% conversion to a 2:1 mixture of imine II and lactam III. In a typical experiment, 0.65 g. of oxime I[10] and 10 g. of polyphosphoric acid were heated (130°) for one minute until the oxime had melted and dissolved. After standing for 16 hours at room temperature, water was added and the aqueous solution extracted with ether. Work-up of the extract gave 0.2 g. of crude III (see below). The aqueous solution then was made alkaline and again extracted with ether. Careful processing gave the imine II (ν_{max} 1655 cm.$^{-1}$; no vinyl proton signal in n.m.r. spectrum) as an extremely unstable material which darkened rapidly. Isolation was possible, however, by conversion to the perchlorate (0.40 g.), m.p. 204–205° (ν_{max} 1680 cm^{-1}). Sodium borohydride reduction of II-perchlorate afforded the saturated amine IV as an oil (no $>$C=N—absorption at 1655 cm.$^{-1}$); IV yielded a crystalline *p*-nitrobenzamide, m.p. 186–187°. Hydrogenolysis of IV over palladium-on-carbon in ethanol containing triethylamine gave the debrominated amine V, again isolated and analyzed as the *p*-nitrobenzamide, m.p. 174–175°. Structures II, IV and V were unambiguously confirmed by an independent synthesis of the latter from 1-indanone and methallylamine. Crude mine VI (ν_{max} 1655 cm.$^{-1}$) was reduced with borohydride and the unsaturated amine (ν_{max} 3300 cm.$^{-1}$; no absorption at 1655 cm.$^{-1}$) cyclized to V with polyphosphoric acid at room temperature. The *p*-nitrobenzamide of V prepared in this manner was identical in all respects with the material obtained from II. The imine, rather than enamine, structure for II was confirmed by the n.m.r. spectrum, and the similarity in magnitude of the shift (25 cm.$^{-1}$) in the $>$C=N-stretching absorption in going from the base to the perchlorate salt when comparing II and 1-methyl-3,4-dihydroisoquinoline.[11] The evidence for the structure of the lactam III, m.p. 134–135°, (ν_{max} 3300 cm.$^{-1}$, 1660 cm.$^{-1}$) rests mainly on its conversion by hydrogenolysis to 8-*t*-butyl-3,4-dihydroisocarbostyril, m.p. 124–126°, whose n.m.r. spectrum was clearly different in the –CH$_2$– region from that of 3,4-dihydrocarbostyril, the former showing a multiplet centered at 3.4 ppm. downfield from TMS due to methylene protons adjacent to amide nitrogen,[12] as in the spectrum of 3,4-dihydroisocarbostyril.

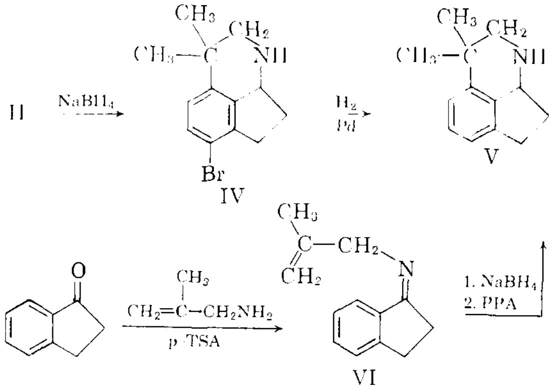


I

II



III



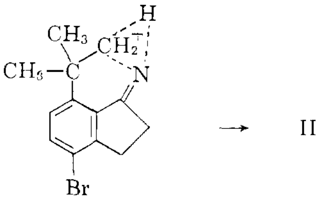
IV

V

VI

The Schmidt reaction of the parent indanone was carried out at *ca.* 55° in polyphosphoric acid. Under conditions selected to prevent decomposition, over 25% of ketone was recovered and a 50–55% yield of II and III was isolated as above, with III now the major product (*ca.* 2:1). Interestingly, III results from net methylene migration whereas 1-indanone gives only aryl migration when subjected to the Schmidt reaction.[13]

The mechanism of the electrophilic bond insertion leading to II may be similar to that postulated by Corey for a similar reaction involving positive oxygen,[14] wherein a three-center process was invoked, *e.g.*



Such a transition state, in which little neophyl carbonium ion character is developed, would be compatible with the absence of alkyl or aryl migration.[15] We are presently investigating the mechanism, scope and limitations of this interesting insertion reaction, which may be of appreciable

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[7] (a) R. K. Hill, *J. Org. Chem.*, **27**, 29 (1962); (b) R. K. Hill and O. T. Chortyk, *J. Am. Chem. Soc.*, **84**, 1064 (1962).

[8] Y. Arata and S. Sugasawa, *Chem. Pharm. Bull.*, **9**, 104 (1961).

[9] (a) J. Meinwald, *Proc. Chem. Soc.*, 286 (1958); (b) R. Griot and T. Wagner-Jauregg, *Helv. Chim. Acta*, **42**, 121, 605 (1959).

[10] All new compounds gave satisfactory C,H analyses.

[11] On the other hand, the pyrrolidine enamine of 1-indanone shows a 60 cm.$^{-1}$ shift to higher frequency when converted to the salt.

[12] L. M. Jackmann, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 56. Also, for several exemplary spectra, see Varian Spectra Catalog, Varian Associates, 1962, spectra 68 and 116.

[13] L. H. Briggs and G. C. De Ath, *J. Chem. Soc.*, 456 (1937).

[14] E. J. Corey and R. W. White, *J. Am. Chem. Soc.*, **80**, 6686 (1958).

[15] An alternative but less likely mechanism would involve the formation of a vinyl nitrene (see footnote 3) and then insertion.

value in the synthesis of heterocyclic rings. It should be pointed out that insertion products such as II may have been formed in other Beckmann or Schmidt reactions and were inadvertently missed since they would remain in the oft-discarded diluted acidic solution from which the usual neutral products are removed by filtration or extraction.

[16] National Aniline Research Fellow, 1961–1962.

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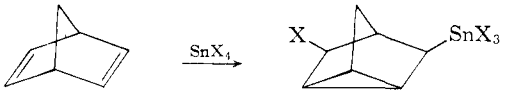
TIN TETRAHALIDE ADDUCTS OF BICYCLOHEPTADIENE AND THEIR FRAGMENTATION[1]

Sir:

Although olefins generally are known to be attacked by electrophilic reagents, few studies have been published on the interaction of olefins with strong Lewis acids other than boron hydrides.[2] Recently it has shown that BCl_3 and $C_6H_5BCl_2$ will add to several reactive olefins, including bicycloheptadiene.[3]

We now wish to report the addition of $SnCl_4$ and $SnBr_4$ to bicycloheptadiene (I) to yield crystalline 1:1 adducts, which like the boron halide adducts[3] are formulated as substituted nortricyclenes (II).

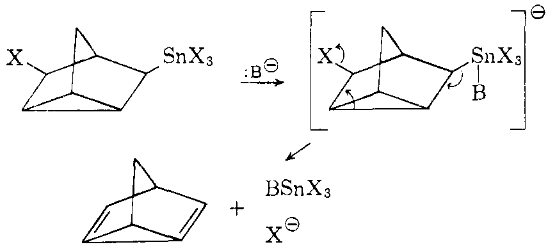


I II

These products presumably arise through homoconjugative addition of the type described by Winstein and Shatavsky.[4] The compounds are prepared simply by mixing the reactants in approximately equimolar proportion in dry isopentane at 0° and allowing the solution to stand. The colorless crystals which form may be recrystallized from fresh isopentane; m.p. for $C_7H_{10}SnCl_4$, 60.5–61.5°; for $C_7H_{10}SnBr_4$, 58–59°.

The infrared spectra of the two compounds provide strong support for the nortricyclene structure. Both compounds have strong bands at 3070 and 1020 cm.$^{-1}$, which are diagnostic for the cyclopropane ring in nortricyclenes.[5] A band also appears in the 800–818 cm.$^{-1}$ region in both compounds, consistent with the fact that the cyclopropyl ring is not substituted.[5] The complex proton magnetic spectra of the two compounds are very similar, differing only in slight shifts of peak positions and in relative intensities. These n.m.r. spectra have not yielded to analysis, perhaps because several stereoisomers are present. However, protons in at least eight different environments are found, consistent with the nortricyclene structure and inconsistent with alternative pi-complex formulations.

Upon treatment with water or bases the compounds undergo a remarkable fragmentation reaction,[6] with the reformation of bicycloheptadiene and a tin-containing fragment. This reaction may be explained as a delta-elimination brought about by attack of the base at tin



The fragmentation is quantitative and was used for approximate analysis of the compounds, sufficient to show that they are 1:1 adducts. In a typical hydrolysis, the $SnCl_4$ adduct gave bicycloheptadiene, 25.9; Sn, 35.8; Cl, 38.0 (calcd. for $C_7H_{10}SnCl_4$; bicycloheptadiene, 26.5; Sn, 33.4; Cl, 40.0). The $SnBr_4$ adduct gave bicycloheptadiene, 16.3; Sn, 19.6; Br, 60 (calcd. for $C_7H_{10}SnBr_4$, bicycloheptadiene, 17.6; Sn, 22.3; Br, 60.1). Conventional combustion analyses were impractical because of the instability of the compounds.

The adducts are stable pure or under hydrocarbons at 0° or below, but at room temperature or in contact with polar solvents they decompose with the formation of tarry masses apparently containing polymerized material It seems not unlikely that similar adducts may be formed during the polymerization of diolefins by $SnCl_4$. Experiments are under way with other Lewis acids and olefins to determine the generality of the addition reaction. Preliminary results indicate that $GeBr_4$ and $C_6H_5SnCl_3$ form adducts with bicycloheptadiene, but that SnI_4, $SiCl_4$ and $(C_6H_5)_2SnCl_2$ do not.

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RECEIVED SEPTEMBER 7, 1962

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[1] This research was supported by the directorate of Chemical Sciences, Air Force Office of Scientific Research, under grant No. AF-AFOSR-62-244.

[2] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[3] F. Joy and F. M. Lappert, *Proc. Chem. Soc. (London)*, 353 (1960).

[4] S. Winstein and M. Shatavsky, *Chem. and Ind.*, 56 (1956).

[5] G. E. Pollard, *Spectrochim. Acta*, **18**, 837 (1962). *Cf.* J. D. Roberts, E. R. Trumbull, W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3116 (1950); E. R. Lippincott, *ibid.*, **73**, 2001 (1951).

[6] C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955); C. A. Grob, "Fragmentation in Solvolysis Reactions," in "Theoretical Organic Chemistry" (papers presented at the Kekule Symposium), Butterworths, London, 1959, pp. 114–126.