were: $[\alpha]^{22}\text{D}$ −53.1, −33.8, and −20.5° (c 1, dimethylformamide), respectively. The deuterated active ester contents of these samples were 0, 0, and 4% as determined by mass spectrometric analysis using m/e 282–283 peaks. The ratios of k_e/k_α of the one-point pseudo-first-order rate constants for two experiments of 24 and 49 hr were found to be 0.00 and 0.03, respectively, indicating isoracemization.[11]

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM 06579 and 08795). We are grateful to Dr. R. L. Foltz for the mass spectrometric analysis which was done at the Battelle HRMS Center facilities, and to Dr. I. Lengyel for the helpful discussion of the mass spectra.

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[11] In these calculations the transesterification reaction was not taken into account; however, consideration of this side reaction would decrease the k_e/k_α value.

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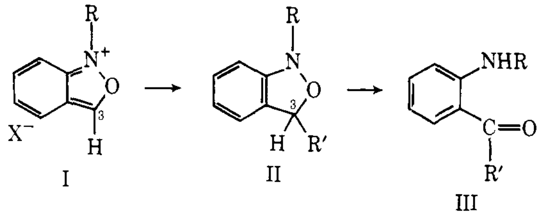
Received April 29, 1970

Reactions of Anthranilium Salts with Bases. Isolation of *N-tert*-Butylbenzoazetinone

Sir:

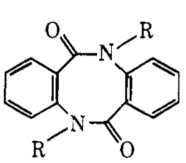
A recent report[1] that *N-tert*-butylanthranilium BF_4^- (Id) is reduced by $NaBH_4$ to the isoxazoline (IId, R′ = H) which can be thermally rearranged to 2-*tert*-butylaminobenzaldehyde (IIId, R′ = H) prompts us to communicate some of our own results on the reactions of 3-unsubstituted anthranilium cations I with nucleophiles.



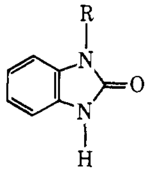
a, R = CH_3
b, R = CH_2Me
c, R = $CHMe_2$
d, R = CMe_3

The salts[2] I are all easily prepared by alkylation of anthranil with oxonium or carboxonium ions[3] or $HClO_4$–*tert*-BuOH mixtures[4] (nmr Ia–d, $C_3H \sim \delta$ 9.95, CD_3NO_2) and they react cleanly with many anions besides hydride to give the simple C_3 addition products II.[5] For example, the ethyl salt Ib yielded the acetal IIb (R′ = OMe, bp 75–76° (0.3 mm), C_3H at δ 6.42) on treatment with MeOH containing Et_3N and similarly on reaction with aqueous solutions of NaCN or NaN_3 the respective unstable adducts IIb (R′ = CN, ir 4.50 μ (w), C_3H at δ 6.23; R′ = N_3, ir 4.77 μ, C_3H at δ 6.33) rapidly oiled out.[6] Note that the experiments in water show that, as expected, attack of I by anions is much more facile than reaction with uncharged nucleophiles, a selectivity which as will be seen in later papers has valuable consequences in some new synthetic methods based on this work.

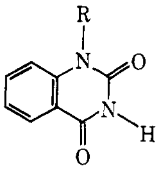
The thermal conversion of II to III also occurred in these more complex systems though often additional complications were observed. For example, IIb (R′ = OMe) rearranged to the known amino ester[7] IIIb (R′ = OMe) when refluxed in xylene, but the dimeric IVb (mp 192°) was also formed[8] (IVb was the only isolable product from the thermolysis of IIb, R′ = CN). When boiled in CCl_4 the azide IIb (R′ = N_3) was cleanly converted to the benzimidazolone Vb (compared with authentic sample[9]). This product would be anticipated



IV



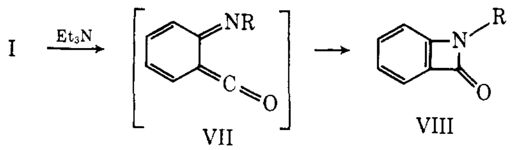
V



VI

from a Curtius rearrangement of an initially generated acyl azide IIIb (R′ = N_3). Direct spectroscopic evidence for the intermediacy of the related IIId (R′ = N_3, ir 4.67, 6.04 μ) was secured in the analogous transformation of IId (R′ = N_3) to Vd (mp 145–146°). The entire process, I → V, could be performed as one step, and in another example the known quinazoline[10] VIb was made (60%) just by heating Ib with NaOCN in CH_3CN [Ib → IIb (R′ = NCO) → IIIb (R′ = NCO) → VIb].

The isolable but thermally unstable acyl azide IIId (R′ = N_3) and other compounds of structure III could be synthesized directly from I at room temperature by titration of I in CH_2Cl_2 with 1 equiv of Et_3N or i-Pr_2NEt[11] followed by addition of R′H, the conjugate acid of the nucleophile. Based on spectroscopic evidence (strong ir peak 5.5–5.6 μ) the species obtained in the first step in this latter procedure is the benzoazetinone (VIII). At 25° in solution VIIIa and VIIIb decomposed within 1 hr while VIIIc had a lifetime of a day. The more hindered *N-tert*-butylbenzoazetinone (VIIId), however, was stable (though very reactive toward nucleophiles to give IIId) and could be obtained pure in 84% yield by precipitation



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[1] R. V. Coombs and G. E. Hardtmann, *J. Org. Chem.*, **35**, 2440 (1970).

[2] Satisfactory elemental analyses and corroborative spectroscopic data have been obtained for all stable new compounds.

[3] H. Meerwein, *Org. Syn.*, **46**, 113, 120 (1966); R. B. Silverman and R. A. Olofson, *Chem. Commun.*, 1313 (1968); S. Kabuss, *Angew. Chem., Int. Ed. Engl.*, **5**, 675 (1966); K. Dimroth and P. Heinrich, *ibid.*, **5**, 676 (1966); R. F. Borch, *J. Org. Chem.*, **34**, 627 (1969): Ia, mp 64–65°; Ib, 79.5–80.5°; Ic, 78–79° (all X = BF_4).

[4] R. B. Woodward and D. J. Woodman, *J. Org. Chem.*, **31**, 2039 (1966); D. J. Woodman, *ibid.*, **33**, 2397 (1968): Id (X = ClO_4) mp 146° dec.

[5] This also seems to be the preferred site of nucleophilic attack on the parent anthranils though simple adducts are not isolated: E. C. Taylor and J. Bartulin, *Tetrahedron Lett.*, 2337 (1967), and references therein.

[6] The upfield C_3H nmr shift excludes alternative salt structures (I, X = R′). Minor equilibrium amounts of such species could still, however, be present in solution.

[7] D. Vörlander, *Chem. Ber.*, **34**, 1645 (1901).

[8] The known IVa [G. Schroeter and O. Eisleb, *Ann.*, **367**, 101 (1909)] was similarly made by heating IIa, R′ = OMe.

[9] J. Davoll and D. H. Laney, *J. Chem. Soc.*, 314 (1960).

[10] N. A. Lange and F. E. Sheibley, *J. Amer. Chem. Soc.*, **55**, 2113 (1933).

[11] For logic of base choice see: R. A. Olofson, S. W. Walinsky, J. P. Marino, and J. L. Jernow, *ibid.*, **90**, 6554 (1968).

of the by-product, $Et_3NH^+ ClO_4^-$, with ether followed by vacuum distillation: yellow liquid; bp 84° (0.2 mm); ir 5.52 μ; nmr δ 1.40 (s, 9), 6.38–7.15 (m, 4); mass spectrum, P 175.0999 (calcd 175.0997) (*Anal.* Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.59; H, 7.38). To our knowledge VIIId is the first isolated benzoazetinone, though definitive spectroscopic and chemical evidence for the intermediacy of the *N*-phenyl derivative in the photolysis of benzotriazinones has been published[12] and a similar photochemical experiment has produced *N*-phenylnaphtho[2,3-*b*]azetinone.[13]

We believe that the reaction of Et_3N with I begins not with the usual nucleophilic addition but instead with proton abstraction at C_3 and concerted ring scission to the iminoketene (VII) which subsequently cyclizes to VIII. The ring opening has precedent in the reactions of 3-unsubstituted isoxazolium[14] and benzisoxazolium salts[15] with nucleophiles, but the ketoketenimines generated from the former do not close to the cyclic iminoethers, even when constrained in an s-cis conformation,[14] whereas the intermediates generated from the latter system are too reactive for structural characterization.[15,16]

It is not yet known whether the formation of III from VIII involves attack of the nucleophile at the carbonyl of VIII or at the electrophilic carbon of VII, possibly present as a minor equilibrium component in solution. Also, although the adduct II can be excluded (reaction rate, temperature data) as an intermediate on the pathway from VIII to III, it is not yet clear whether the rearrangement, II → III, always proceeds by a direct route or sometimes involves a reversion to I (X = R′), followed by generation of VIII (*i.e.*, II $\rightleftharpoons$ I (X = R′) → VII and VIII + R′H → III), but experiments designed to solve these problems are under way. The intriguing question of the relationship between VIII and benzocyclobutadiene (is VIII an amide with significant amide resonance stabilization or is it an amino ketone?) has not yet been answered, but further chemical studies are in progress as are attempts to prepare a crystalline analog of VIIId which would allow the resolution of this issue by X-ray crystallography.[17]

Acknowledgment. We are grateful to the U. S. Public Health Service for a grant (GM-13980) to support this research.

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(12) E. M. Burgess and G. Milne, *Tetrahedron Lett.*, 93 (1966); G. Ege, *Chem. Ber.*, **101**, 3079 (1968); G. Ege and F. Pasedach, *ibid.*, **101**, 3089 (1968).

(13) G. Ege and E. Beisiegel, *Angew. Chem., Int. Ed. Engl.*, 7, 303 (1968).

(14) R. B. Woodward and R. A. Olofson, *Tetrahedron Suppl.*, No. 7, 415 (1966); R. A. Olofson and Y. L. Marino, *Tetrahedron*, **26**, 1779 (1970), and references therein

(15) D. S. Kemp and R. B. Woodward, *ibid.*, **21**, 3019 (1965); D. S. Kemp, *ibid.*, **23**, 2001 (1967).

(16) This statement is also true for *N-tert*-butylbenzisoxazolium ClO_4^-, mp 165–166°.

(17) Here just the angle of the N–R bond with the plane of the ring system (is stereochemistry at N trigonal or pyramidal?) should provide a first level answer.

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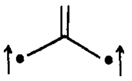
Received January 9, 1971

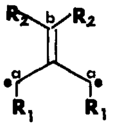
2-Isopropylidenecyclopentane-1,3-diyl. Preparation, Properties, and Reactions of a Distorted Trimethylenemethane. Direct Evidence for a Triplet Reaction[1]

Sir:

Dowd's work[2] has shown that the unsubstituted trimethylenemethane molecule (**1**) has a triplet ground state. It is a plausible and widely held[3a] but so far unproven assumption that this species is an intermediate in the formation of the dimeric product, 1,4-dimethylenecyclohexane. An unsymmetrically substituted trimethylenemethane (**2**) provides the means to test the effect of symmetry on the ordering of the singlet and triplet energy levels. Moreover, because dimerization is expected to lead to mixtures resulting from four modes of combination (aa + aa, ab + ab, ab + ba, aa + ab), the product composition can be used to test the postulate that various methods of generation of the species lead to a common intermediate. The present study of 2-isopropylidenecyclopentane-1,3-diyl (**3**) bears on these two problems. It also provides direct evidence that at least part of the dimeric products from **3** arise from reactions of a triplet species.



1



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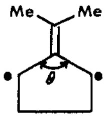
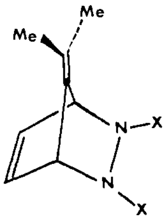
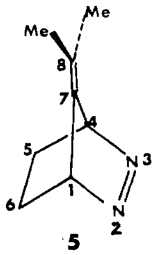


3

Dimethyl azodicarboxylate and 6,6-dimethylfulvene in 1:1 ether–pentane at 0° react to give 96% of adduct **4**,[4] mp 100–101°, which by successive selective hydrogenation[4] of the endocyclic double bond (10% Pd/C, EtOAc), saponification (KOH, aqueous EtOH), oxidation (HgO), and sublimation (40° (<0.1 mm)) is converted in 65% yield to the azo compound **5**, an unstable white solid: nmr ($CDCl_3$) τ 4.63 (2 H, broad q, J = 1.5 Hz, H_1, H_4), 8.3–9.0 (4 H, m, H_5, H_6), 8.37 (6 H, s, Me).



4: X = CO_2Me



5

Pyrolyses of azo compound **5** in sealed tubes in the gas phase (80°, 2 hr, naphthalene internal standard) give four hydrocarbon products (dimers of **3**) in total yields that increase from 68 ± 4% at an initial pressure

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We are also grateful to the National Science Foundation (GP-11017X) and the National Institute of General Medical Sciences (GM 15166) for partial support.

(2) (a) P. Dowd, *J. Amer. Chem. Soc.*, **88**, 2587 (1966); (b) P. Dowd and K. Sachdev, *ibid.*, **89**, 715 (1967); (c) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

(3) (a) For a review, see F. Weiss, *Quart. Rev., Chem. Soc.*, **24**, 278 (1970). (b) See the additional pertinent observations of G. Köbrich and H. Heinemann, *Chem. Commun.*, 493 (1969). We thank Professor H. R. Ward for this reference.

(4) J. J. Tufariello and J. J. Spadaro, Jr., *Tetrahedron Lett.*, 3935 (1969).