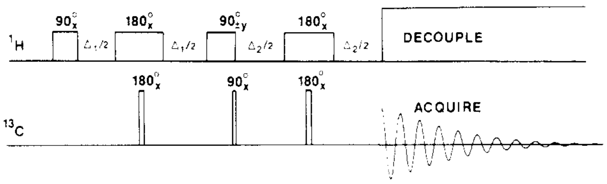


Figure 6. Pulse sequence of the INAPT experiment. The proton pulses in this scheme are soft pulses ($\gamma H_2/2\pi \sim 15$ Hz). The efficiency of polarization transfer via a long-range coupling, J, is proportional to $\sin [\pi J(\Delta_1 + 2\tau_{90})] \sin [\pi J(\Delta_2 + \tau_{90})]$, where τ_{90} is the pulse duration of the soft 90° ^1H pulse.

reference for ^{13}C (77.0 ppm) and with the small amount of residual $^1HCCl_3$ as an internal reference for the proton spectrum (7.24 ppm). Proton spectra were obtained by using the decoupling coil of the broad-band probe for observation. For **2** and **3**, simple selective decoupling experiments were sufficient to establish proton connectivity, and a proton-decoupled version of the selective population transfer experiment[29] was used for assignment of the protonated ^{13}C resonances. For compounds **1**, **4**, and **5** COSY spectra were recorded by using a 256 × 512 data matrix size, and four scans were acquired for each t_1 duration. Total measuring time for a COSY spectrum was approximately 50 min. Two COSY spectra were calculated for each acquired data set; one to show the presence of all couplings, for which a sine bell filtering function was used in both dimensions, and a second spectrum to emphasize cross peaks that are due to large homonuclear couplings only. This latter spectrum is obtained by using a Gaussian line broadening function of 10 Hz, superimposed on the sine bell filtering function. Heteronuclear chemical shift correlation spectra were recorded by using a 64 × 1024 data matrix size and 16 scans for each t_1 value; a measurement time of 1.2 h was required per spectrum. Gaussian line broadening was used in the t_2 dimension to avoid truncation and overenhanced Lorentzian to Gaussian transformation was used in the t_1 dimension to improve spectral resolution in the F_1 dimension[30] before an absolute value calculation was made. The heteronuclear shift correlation spectrum of **5** (Figure 5) was recorded in the absorption mode. This latter presentation is preferable because of higher resolution and sensitivity[31] but does require some operator interaction to phase the 2D spectrum. Both the two-dimensional and the INAPT spectra were recorded on nonspinning samples.

The INAPT sequence[6] is sketched in Figure 6 and is basically a modified version of the well-known refocused INEPT experiment.[32-34] The delays $\Delta_1/2$ and $\Delta_2/2$ were set to 20 and 25 ms, respectively, and the pulse width of the soft 90° ^1H pulse was set to 18 ms. Calibration of this 90° pulse was done by optimizing the INAPT experiment for a sample of 50% v/v 1,2-dihydronaphthalene in deuterochloroform. High-power (2 W) decoupling was used during data acquisition. Each of the INAPT spectra shown in Figures 3 and 4 results from 200 scans, which required approximately 15 min each. Occasionally a shorter value for Δ_2 has to be selected in symmetric molecules. This applies, for example, for transfer from H5 to C6a in benzo[*c*]phenanthrene. Experimentally very little transfer was observed under the conditions described above ($\Delta_2/2$ = 25 ms). This is due to the fact that H5 and H8 have identical chemical shifts and an identical coupling to C6a. In this case the system behaves like a $^{13}CH_2$ group in the regular INEPT experiment, and consequently, $\Delta_2/2$ has to be set to a shorter duration (10 ms) to optimize this transfer of magnetization.

Acknowledgment. We are indebted to Rolf Tschudin for continuous technical support.

Registry No. **1**, 196-78-1; **2**, 218-01-9; **3**, 195-19-7; **4**, 89523-51-3; **5**, 194-69-4.

---

[29] Sarkar, S. K.; Bax, A. *J. Magn. Reson.* **1985**, *62*, 109.

[30] Bax, A. In "Topics in Carbon-13 NMR Spectroscopy"; Levy, G. C., Ed.; Wiley: New York, 1984; Vol. 4, Chapter 8.

[31] Bax, A.; Sarkar, S. K. *J. Magn. Reson.* **1984**, *60*, 170.

[32] Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.

[33] Burrum, D. P.; Ernst, R. R. *J. Magn. Reson.* **1980**, *39*, 163.

[34] Bolton, P. H. *J. Magn. Reson.* **1980**, *41*, 287.

Generation and Trapping of Cyclopropene-3-carboxaldehyde and 2,3-Butadienal in Liquid Furan Photolysis

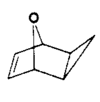
W. Alan Rendall, Manuel Torres, and Otto P. Strausz*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

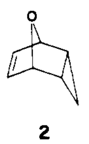
Received January 3, 1985

The photolysis of liquid furan at room temperature generated cyclopropene-3-carboxaldehyde and 2,3-butadienal, which were trapped as their Diels–Alder adducts with furan. In each case, both the exo and endo stereoisomers were obtained. The identity of these adducts, and also their stereochemistry, has been determined by MS, IR, and ^1H and ^{13}C NMR.

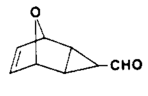
Until the pioneering work of Srinivasan in 1967, the photochemistry of furan had attracted little attention. In his first study, Srinivasan[1] reported the gas-phase triplet mercury photosensitized decarbonylation of furan. The C_3H_4 fraction formed contained cyclopropene, propyne, and allene.[1] Polymer formation also occurred.[2] A significant pressure dependence was revealed, and a maximum decarbonylation quantum yield of about 0.4 was attained at the lowest furan pressures employed (~5 torr). Under these conditions propyne was the main C_3H_4 isomer. With increasing furan pressure the CO yield decreased and the cyclopropene/propyne ratio increased.[2] At furan pressures of 0.2–1.0 atm two compounds of molecular formula C_7H_8O and a third having molecular formula $C_8H_8O_2$ were isolated. The former were assigned the structures of the exo (**1**) and endo (**2**) Diels–Alder adducts (DAa) of furan with cyclopropene, while the latter was its



1



2



3

---

[1] Srinivasan, R. *J. Am. Chem. Soc.* **1967**, *89*, 1758.

[2] Srinivasan, R. *Pure Appl. Chem.* **1968**, *16*, 65–74.

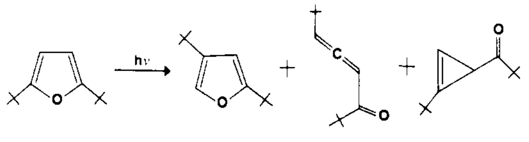
DAa with cyclopropene-3-carboxaldehyde (**3**) of unspecified stereochemistry.[2,3] In their NMR spectra neither **1** nor **2** showed coupling of its bridgehead hydrogens to the cyclopropyl methine hydrogens.

LaRochelle and Trost have prepared **1** and **2** by reacting cyclopropene with furan.[4] The adducts were separated by GC and further characterized by ^{1}H NMR. **1** was assigned the *exo*-cyclopropane ring configuration because its bridgehead hydrogens showed coupling only to the olefinic protons and not the cyclopropyl methine hydrogens. In contrast to Srinivasan's results, **2** clearly displayed coupling of its bridgehead hydrogens to both the olefinic and cyclopropyl methine hydrogens. In addition, its chemical shift data were significantly different from those reported by Srinivasan, possibly suggesting that Srinivasan's second C_7H_8O isomer was not the endo adduct **2**. These same coupling characteristics have been observed for exo and endo DAa of furan with other cyclic dienophiles.[5,6] Another species formed by furan photosensitization was 1,3-butadienone (vinylketene). In the presence of small quantities of CH_3OH or CH_3OD, methyl esters of 3-butenoic acid were formed. These compounds were derived from addition of CH_3OH and CH_3OD to the ketene.[3]

On direct irradiation, furan vapor behaved differently than in the photosensitized reaction.[7] The pressure dependence for CO formation was absent, and the C_3H_4 fraction contained mainly propyne, with a substantial amount of allene and little or no cyclopropene.

Srinivasan also irradiated furan in a solution of cyclopentane.[2] Although formation of an insoluble yellow solid indicated furan consumption, no fragmentation products or adducts similar to those found in the gas-phase experiments could be detected. Furan irradiation in the presence of cyclopentene (10%) or methanol (10%) also failed to produce adducts.[2,3] The IR spectrum of the polymer formed during furan irradiation in cyclopentane indicated a strong broad carbonyl absorption at 1715 cm^{-1} which did not appear to be incorporated in aldehyde units, and a strong OH absorption was also evident.

Subsequently van Tamelen and Whitesides studied the photolysis of *tert*-butylfuran solutions.[8,9] Direct irradiation ($\lambda > 220$ nm) of 2,5-di-*tert*-butylfuran (**4**) produced three isomeric products, **5**–**7**. Ketone **7** was isolated and its direct photolysis generated a mixture of **4**–**6**.



4 **5** **6** **7**

In addition, other substituted furans have been photolyzed and cyclopropenyl aldehyde or ketone derivatives sometimes isolated or trapped.[3,10–12] Consequently, cyclopropenyl carbonyls like **7** have become the accepted intermediates in furan photoisomerizations which produce rearrangement to different positional isomers, like **5** in the photolysis of **4**. These processes have been discussed in a number of reviews on heterocyclic compounds.[13–15]

Table I. 400-MHz ^{1}H NMR Data for 8 and 9

adduct	chem shift,[a] δH	int	J,[b] Hz	assignment[c]
8	9.40 d	1	4.1	e
	6.58 m	2		a, a′
	4.85 m	2		b, b′
	2.88 dt	1	4.1, 2.7	d
	1.96 d	2	2.7	c, c′
9	9.27 d	1	4.1	e
	6.18 m	2		a, a′
	5.05 m	2		b, b′
	2.57 m	2		c, c′
	2.01 dt	1	4.1, 2.5	d

[a] Reference 23. [b] The magnetic nonequivalence of certain protons complicates the analysis of their coupling constants. [c] The prime notation is introduced to account for the magnetic nonequivalence within sets of chemically equivalent atoms.

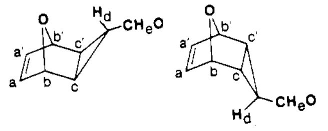
In the course of our studies on the photochemistry of thiophene[16] in the liquid phase, we found significant yields of furan dimers when using furan as a DA reagent to trap Dewar thiophene. In order to identify these compounds we have reexamined the liquid-phase photolysis of neat furan.

Results and Discussion

Photolysis of liquid furan at about 25 °C was performed with conventional steady-state photolysis and also in a cyclic photolysis reactor (cf. Experimental Section). The design of the latter improved the efficiency of the trapping process for two reasons. First, the periodic circulation of the photolysate washed the insoluble solid products out of the photolysis zone. In conventional steady-state photolysis, polymer accumulation seriously attenuates the incident radiation. Second, because trapped products were removed from the photolysis zone, long irradiation times, equivalent to high conversion in a conventional photolysis, could be used with reduced chance of secondary photolysis.

On completion of irradiation the polymer formed was separated by filtration, and excess furan was removed by distillation. A small quantity of yellow oil remained. Its GC/MS analysis indicated the presence of three principal products. Each of them was a furan dimer as indicated by their mass spectra (M$^{+\cdot}$ 136) and showed CHO loss (m/e 29) as an important fragmentation process. GC/FTIR confirmed the presence of an aldehyde group in all three products, by the characteristic C=O and C—H stretching absorptions.

The three products were separated by preparative GC and examined by ^{1}H and ^{13}C NMR. **8** and **9** were readily identified and each assigned the structure of a furan DAa with cyclopropene-3-carboxaldehyde. Exact mass measurement by MS on the separated adducts **8** and **9** gave



8 **9**

---

(3) Srinivasan, R. *J. Am. Chem. Soc.* **1967**, *89*, 4812–4813.

(4) LaRochelle, R. W.; Trost, B. M. *J. Chem. Soc., Chem. Commun.* **1970**, 1353–1354.

(5) Anet, F. A. L. *Tetrahedron Lett.* **1962**, 1219–1222.

(6) Eaton, P. E.; Lin, K. *J. Am. Chem. Soc.* **1965**, *87*, 2052–2054.

(7) Hiraoka, H.; Srinivasan, R. *J. Chem. Phys.* **1968**, *48*, 2185–2189.

(8) van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1968**, *90*, 3894–3896.

(9) van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129–6140.

(10) Hiraoka, H. *J. Chem. Soc., Chem. Commun.* **1971**, 1610–1611.

(11) Hiraoka, H. *Tetrahedron* **1973**, *29*, 2955–2961.

(12) Chambers, R. D.; Lindley, A. A.; Fielding, H. C. *J. Fluorine Chem.* **1978**, *12*, 337–340.

(13) Lablache-Combier, A. "Photochemistry of Heterocyclic Compounds"; Buchardt, O., Ed.; Wiley-Interscience: New York, 1976; Chapter 3, pp 123–206.

(14) Braslavsky, S.; Heicklen, J. *Chem. Rev.* **1977**, *77*, 473–511.

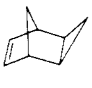
(15) Kobayashi, Y.; Kumadaki, I. "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Ed.; Academic Press: New York, 1982; Vol. 31, pp 169–206.

(16) Rendall, W. A.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 723–724.

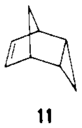
an $M^{+\cdot}$ corresponding to $C_8H_8O_2$ and showed successive loss of CHO and then CO as the major fragmentation route. A second important fragmentation pathway was a Diels–Alder retrogression to generate C_4H_4O (**8**, *m/e* 136 (2%), 107 (33%), 79 (100%), 68 (28%); **9**, *m/e* 136 (9%), 107 (52%), 79 (100%), 68 (36%)). The IR spectra of **8** and **9** showed carbonyl absorptions at 1708 and 1711 cm^{-1}, respectively, as well as aldehyde C–H stretching absorptions near 2730 and 2835 cm^{-1}. In addition, each IR revealed a very weak C=C stretching absorption near 1560 cm^{-1}. Owing to the symmetric nature of **8** and **9** (vide supra), this double bond absorption was expected to be weak. The observed position is similar to that reported for norbornene, 1575 cm^{-1}.[17] For both **8** and **9** the ^1H NMR showed three sets of two chemically equivalent protons and the ^{13}C NMR three sets of two identical carbon atoms in agreement with the C_s symmetry of the structures. The ^1H NMR data for **8** and **9** are summarized in Table I. Their ^{13}C NMR data are listed in the Experimental Section. The NMR chemical shifts are entirely consistent with the assigned structures.

Although the symmetry of **8** and **9** gives rise to three sets of magnetically nonequivalent protons and renders their ^1H NMR spectra higher than first order, selective decouplings in the ^1H NMR spectra of **8** and **9** permitted their stereochemistry to be determined. An exo configuration of the three-membered ring, as in **8**, produces a dihedral angle of nearly 90° between protons H_b and H_c. Consequently a very small J_{b-c} coupling constant would be expected. In the alternative endo configuration of the three-membered ring, as in **9**, this dihedral angle is much smaller, and therefore the coupling constant should be closer to a normal value. Selective proton decoupling experiments revealed that the adduct assigned structure **8** had no discernible coupling between its H_b and H_c protons, while in the other adduct a significant J_{b-c} coupling was observed. This is consistent with the results reported by LaRochelle and Trost[4] for the exo and endo DAa of cyclopropene with furan **1** and **2**, respectively.

In addition, it is known that the magnetically anisotropic double bond in bicyclic DAa exerts a paramagnetic effect on protons in the exo position and a diamagnetic effect on protons in the endo configuration. Consequently the endo protons are more shielded than the corresponding exo protons.[18] For instance, in the tricyclooctene isomers **10** and **11**, the endo protons are more shielded by 0.35 ppm.[19] In **8** and **9** a difference of 0.61 ppm exists for the H_c protons, with the protons in compound **8**, which have the endo configuration, being more shielded. This is consistent with the anisotropic effect of the double bond and provides further proof of the stereochemical assignment. The much larger chemical shift difference in **8** and **9** as compared with **10** and **11** may be indicative of an additional deshielding effect on the H_c protons in **9** as a result of their proximity to the O atom. A large chemical-shift difference, 0.87 ppm, was also observed for the H_d protons in **8** and **9**.



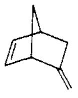
10



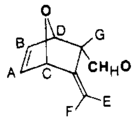
11

That the aldehyde substituent is exo to the three-membered ring in both **8** and **9** was determined from the magnitude of the J_{c-d} coupling. Selective proton decoupling experiments allowed this coupling to be measured. Values of $J_{c-d} \sim 2.7$ and 2.5 Hz were found in **8** and **9**, respectively. Typical coupling constants between such protons on a cyclopropane ring are of the order 6.6–8.0 Hz when the protons are cis and 3.6–4.6 Hz if they are trans.[20] Thus, it was concluded that in both **8** and **9** proton d was trans to the c protons. The angles imposed by the tricyclic ring structure probably account for the smaller trans coupling constant as compared with cyclopropanes. It is noteworthy that these DAa with the exo configuration of the CHO group should, for steric reasons, be preferred to those with the opposite stereochemistry, thus lending further support to the structure assigned by NMR.

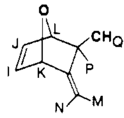
Exact mass measurement by MS showed that product **12** had molecular formula $C_8H_8O_2$ ($M^{+\cdot}$ 136). The major fragmentation process was a Diels–Alder retrogression forming C_4H_4O (**12**, *m/e* 136 (10%), 107 (33%), 79 (66%), 68 (100%)). The IR spectrum showed a carbonyl absorption at 1721 cm^{-1} and characteristic aldehyde absorptions near 2730 and 2820 cm^{-1}. A weak double bond absorption was evident at 1563 cm^{-1}, very similar in position and of somewhat greater intensity than the double bond absorptions of **8** and **9**. A much stronger double bond absorption near 1665 cm^{-1} as well as a strong absorption near 895 cm^{-1} is consistent with an exocyclic methylene moiety (vide infra). The norbornene structure, **13**, has double bond absorptions at 1575 (w) and 1667 (m) cm^{-1} as well as a strong absorption located at 876 cm^{-1}.[21] The ^1H NMR spectrum of **12** isolated by preparative GC clearly indicated the presence of two separate aldehyde compounds each having a total of eight protons. On the basis of their ^1H and ^{13}C NMR spectra the compounds were each assigned the structure of a furan DAa with 2,3-butadienal. From the ^1H NMR integrations the concentration ratio of **12a** to **12b** was 2.8/1. The ^1H and ^{13}C NMR data for **12a** and **12b** are reported in the Experimental Section.



13



12a



12b

Although many of the ^1H chemical shifts were located between about 5 and 6.5 ppm, aided by the 400-MHz NMR spectrometer the various signals were assigned by selective ^1H decoupling. The NMR integrations and self-consistency of the selective decoupling series clearly separated the proton resonances into two sets, one belonging to **12a** and the other to **12b**. The assignment of **12a** as the endo isomer and **12b** as the exo isomer was readily determined from the ^1H NMR spectra. In **12a** proton G couples to proton D, α to the O atom with a coupling constant $J_{DG} \sim 4.6$ Hz. By contrast, in **12b** proton P reveals no discernible coupling to proton L. These coupling results were obtained in selective decou-

---

[17] Dolphin, D.; Wick, A. "Tabulation of Infrared Spectral Data"; Wiley-Interscience: New York, 1977; p 56.

[18] Fraser, R. R. *Can. J. Chem.* **1962**, *40*, 78–84.

[19] Tori, K.; Ueyama, M.; Tsuji, T.; Matsumura, H.; Tanida, H.; Iwamura, H.; Kushida, K.; Nishida, T.; Satoh, S. *Tetrahedron Lett.* **1974**, 327–330.

[20] Günther, H. "NMR Spectroscopy—An Introduction"; Wiley: New York, 1980; p 384.

[21] Pouchert, C. J. "The Aldrich Library of Infrared Spectra"; Aldrich: Milwaukee, WI, 1970; p 34G.

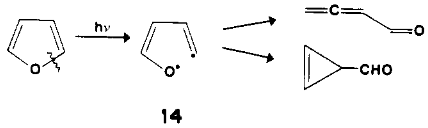
pling experiments. The differences are attributable to the differences in dihedral angle between **12a** and **12b**, analogous to the situation already described for **8** and **9**.

The effects on chemical shift of the magnetically anisotropic double bond are also manifested in the ^{1}H NMR data of DAa **12a** and **12b**. Proton P in **12b** has an endo configuration and is more shielded than proton G in **12a** by 0.66 ppm. Once again the observed chemical shift difference is larger than in the tricyclooctenes, **10** and **11**. In addition the aldehyde proton in **12b** is 0.41 ppm downfield with respect to its counterpart in **12a**. The exact interpretation of these chemical shift data is complicated by the presence in each of these adducts of so many magnetically anisotropic groups in the vicinity of the protons concerned.

As seen in the NMR data presented in the Experimental Section, only one carbonyl carbon resonance was detected (δ 199.7) for the mixture of trapped butadienal adducts with furan. To prove that the carbonyl absorptions in **12a** and **12b** were fortuitously identical, the ^{13}C spectrum was remeasured with selective irradiation of proton Q (δ 9.49). In this way the carbonyl signal for **12a** was split into a doublet by its coupling with H, and the weaker carbonyl resonance for **12b** at δ 199.7 was clearly uncovered and confirmed. Subsequently, GC of the adduct mixture on Carbowax 20M successfully resolved **12a** and **12b** and a concentration ratio of 2.7/1, respectively, was determined by GC.

The furan DAa with 2,3-butadienal described here represent the first reported trapping of this parent aldehyde as a photolysis product from furan. van Tamelen and Whitesides[8,9] previously found the *tert*-butyl ketone **6** as a stable product of 2,5-di-*tert*-butylfuran photolysis. It was not definitely established that **6** was a primary photolysis product, although the authors preferred a mechanism in which secondary photolysis of the cyclopropenyl ketone **7** produced **6**. Direct irradiation of **7** did indeed generate a mixture of **4**–**6**. Photolysis of 2,3,5-tri-*tert*-butylfuran also produced a cyclopropenyl ketone but as a minor product.

In the present study photolysis wavelengths of 214 and 229 nm were employed. The π systems of the C=O and C=C chromophores in **7** are not conjugated, and so it is unlikely that the π–π^* absorptions in this molecule have any significant extinction between λ = 215–230 nm. The n–π^* carbonyl absorption is located at much longer wavelength than we have used for photolysis. For instance, with **7**, van Tamelen and Whitesides reported the following UV data in pentane solution: $\lambda_{\max}$ ~293 nm, ϵ ~50 M^{-1} cm^{-1}.[9] In addition, the present investigation included both conventional steady-state and cyclic photolyses. The chemical yields of **8**, **9**, and **12** were estimated to be approximately 6%, 12%, and 8%, respectively, in steady-state photolysis experiments where the furan conversion was ~1%. Regardless of the different experimental conditions, the adducts **8**, **9**, and **12** were always formed in the same ratio. This would indicate that in the current experiments the 2,3-butadienal was not formed by secondary photolysis of the cyclopropenyl aldehyde. Whether it might arise by a 1,2-H migration in a 1,5-diradical such as **14** or by the dark reaction of a vibrationally excited cyclopropenyl aldehyde cannot be decided at present. the initial step in furan photolysis is widely accepted to be C–O bond cleavage to produce a diradical such as **14**.



14

We have employed the direct photolysis of furan (214, 229 nm) in generating the cyclopropenyl aldehyde–furan DAa **3**. Srinivasan[2,3] has isolated **3** from the gas-phase triplet mercury photosensitized reaction of furan, implicating the intermediacy of a triplet state. In the present solution phase study, two DAa between furan and the cyclopropenyl aldehyde were formed and isolated; however, no evidence was found for the formation of the cyclopropene adducts **1** or **2**. Hiraoka and Srinivasan[7] consider "the formation of cyclopropene" and therefore presumably its DAa with furan in the neat solution phase "a significant test for the presence of triplet state furan". Consequently the absence of **1** and **2** in our products would seem to suggest that the triplet state of furan is not implicated in the liquid-phase direct photolysis.

In addition to the principal furan photolysis products characterized in this work, GC/MS indicated the presence of two additional furan dimers, M$^{+\cdot}$ 136. GC/FTIR analysis of these two compounds revealed intense C=O absorptions at 1809 and 1818 cm^{-1}. The low yield of these minor products has hampered their isolation and characterization by NMR. The IR data are suggestive of a cyclic ketone possibly derived from trapping of the 1,3-butadienone. As mentioned previously this species was trapped by Srinivasan following furan photosensitization. Further studies are in progress.

Experimental Section

Photolyses were typically continued for about 60 h using either a Zn (214 nm) or Cd (229 nm) resonance lamp as the radiation source. Furan degassing under high vacuum with repeated freeze–pump–thaw cycles or deoxygenation by bubbling N_2 for 0.5 h was employed for small-scale runs. However, the presence of O_2 did not prevent adduct formation. Photolyses were performed by using both a "static" steady-state photolysis design and a modified system providing periodic cycling of the furan. Rapid stirring of the liquid furan was maintained during all photolyses.

In a high-conversion conventional photolysis experiment complications due to secondary photolysis can arise, and polymer formation on the inner cell walls severely attenuates the incident light intensity as the photolysis progresses. The heart of the cyclic photolysis apparatus was an all-quartz reactor very similar in appearance to a Soxhlet apparatus, but modified to permit irradiation and stirring of the liquid furan, and fitted with a sidearm which siphons a portion of the solution. In this device, furan was distilled from a reservoir maintained at about 35 °C and condensed filling the photolysis zone. When this region was filled the lamp was started. As fresh furan continued to distill the reactor was filled above the photolysis zone. After approximately 0.25 h the sidearm connected to the reactor siphoned roughly 50% of the furan solution back to the reservoir. At all times the liquid furan level filled the entire photolysis zone, thereby maximizing the "contact time" between the liquid and the incident light yet providing a means of removing some of the generated photolysis products from the irradiation region. From the reservoir unreacted furan redistilled back to the photolysis zone, while the adducts were retained. This design helped reduce the risk of secondary photolysis during long irradiations and considerably reduced the incident light attenuation effect of the polymer by washing it out of the reactor. Commercial furan (Aldrich) was shaken with aqueous 5% KOH, dried with $CaSO_4$, and distilled under N_2 from Na, immediately prior to use.[22] As a result of the larger quantities of furan, about 75 mL per run, required for the cyclic photolysis reactor it was sometimes used in these experiments as commercially received. This did not affect relative adduct formation nor were any new products obtained.

GC/MS results were obtained by using a 10% SE-52 column (~3.2 mm × 3 m, 150 °C) coupled to an AEI MS12. High-res-

---

[22] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. "Purification of Laboratory Chemicals", 2nd ed.; Pergamon Press: Oxford, 1980; p 270.

olution MS of adduct fractions separated by preparative GC, on a 15% SE-30 column (~6.4 mm × 2 m, 112 °C), were performed on an AEI MS50. GC/FTIR experiments were performed with the same SE-52 column (145 °C) interfaced to a Nicolet 7199 FTIR. All 400-MHz ^{1}H and 100-MHz ^{13}C spectra were recorded on a Bruker WH-400 NMR spectrometer. To detect the ^{13}C resonance of the quaternary carbon atoms in **12a** and **12b**, a total of 88000 scans were performed on a Bruker WH-200 NMR spectrometer. This comparatively large number of scans was required since these carbon atoms having no attached hydrogens possess longer relaxation times.

NMR Data.[23] 100-MHz ^{13}C (δ): **8**, 197.5 (C=O), 138.4 (=CH), 77.4 (—HC—O—), 40.8 (—H*C*—CHO), 30.1 (—H*C*—C); **9**, 195.6 (C=O), 131.5 (=CH), 78.8 (—HC—O—), 46.5 (—H*C*—CHO), 24.8 (—H*C*—C); **12a**, 199.7 (C=O), 141.4 (=CH$_2$), 135.2 (=CH$_A$*), 133.0 (=CH$_B$*), 107.5 (C=), 82.6, 79.8 (—HC—O—), 57.1 (—H*C*—CHO); **12b**, 199.7 (C=O), 144.7 (=CH$_2$), 136.2 (=CH$_J$*), 134.5 (=CH$_I$*), 109.0 (C=), 81.9, 80.2 (—HC—O—), 56.0 (—H*C*—CHO) [*tentative assignments based on the well-known γ-gauche steric interaction[24,25]]. 400-MHz ^{1}H (δ): **12a**, 9.08 (H), 3.47 (G), 5.02 (F), 5.24 (E), 5.21 (D), 5.17 (C), 6.51 (A, B); **12b**, 9.49 (Q), 2.81 (P), 5.06 (N), 5.33 (M), 5.15 (L), 5.29 (K), 6.41 (J), 6.52 (I).

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for continuing financial support and the Alberta Heritage Scholarship Fund (W.A.R.). We also thank Dr. T. Nakashima and the NMR laboratory, Dr. A. Hogg and the MS laboratory, and J. Hoyle (GC/FTIR) for technical assistance. The assistance of Prof. G. Toth in the interpretation of some of the NMR data is gratefully acknowledged.

Registry No. 8, 97334-54-8; 9, 97334-55-9; 12a, 97277-62-8; 12b, 97277-63-9; CH$_2$=C=CHCHO, 53268-92-1; furan, 110-00-9; cyclopropene-3-carboxaldehyde, 36998-21-7.

---

(23) Chemical shifts in CDCl$_3$ relative to Me$_4$Si.

(24) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden and Son: London, 1978; pp 27–29, 37–38.

(25) Marchand, A. P., Ed. "Methods in Stereochemical Analysis"; Verlag Chemie: Deerfield Beach, IA, 1982; Vol. 1, pp 22–27.

Weak Base Promoted β-Elimination Reactions in 1-Phenyl-1-propyl Derivatives. Evidence for an Intermediate in the E2C Reaction

Harold Kwart† and Kazimiera A. Wilk*‡

Department of Chemistry, The University of Delaware, Newark, Delaware 19711

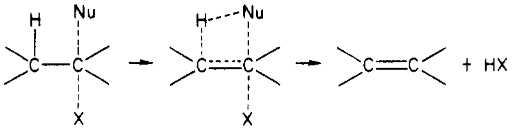
Received August 12, 1983

We describe the observation of a nucleophile trigger mechanism in the case of the weak base promoted β-elimination (E2C process) and suggest permutational isomerism of TBP intermediates. Weak bases, namely, bromide and fluoride ions, bring about elimination in a bent transition state to which only a small fraction of a covalent bond to the nucleophile–base and some leaving group departure must be achieved in an orienting intermediate. These studies provide evidence for a TBP structure surrounding C-α in the 1-phenyl-1-propyl system and attribute the equal availability of abstractable H and D of both diastereoisomers to the action of the promoter bases.

The E2C mechanism has been the subject of vigorous controversy for many years, and several proposals for the transition state (TS) have been advanced.[1-3] Several contributors to the field of elimination mechanisms concluded that E2C-like transition states were utilized by strong carbon but weak hydrogen bases (e.g., Br$^-$, Cl$^-$, RS$^-$) in their reaction with very weakly acidic compounds containing good leaving groups.[1,4,5] It has been postulated that these eliminations occurred in a trans-periplanar fashion,[1d,e,6] with the base anti to the leaving group (Scheme I). Such transition states were "loose", with the double bond well developed and the base bound to both β-hydrogen and α-carbon.

Recently, we defined the E2C mechanism in fluoride ion promoted elimination of β-phenylethyl substrates in an aprotic medium.[7] Other evidence for an E2C mechanism was found in the course of bromide[8] and amine base[9] promoted eliminations in α-bromo ester substrates. From the latter, the E2C mechanism is not S$_N$2-like but may be regarded as a well-precedented nucleophilic trigger[10] mechanism involving a trigonal bipyramid carbon intermediate (TBP).

Scheme I. The E2C Process



The principal purpose of the present work was to adduce further evidence for TBP carbon intermediate invoked by triggering the E2C mechanism with weak bases and focused at C-α of the substrate.

[†] Deceased, March 31, 1983.

[‡] Address correspondence to Institute of Organic and Polymer Technology, Technical University of Wroclaw, 50370 Wroclaw, Poland.

(1) (a) Winstein, S.; Darwish, D.; Holness, N. J. *J. Am. Chem. Soc.* **1956**, *78*, 2915. (b) Winstein, S. *Chim. Teor.* **1965**, 327. (c) Biale, G.; Parker, A. J.; Smith, S. G.; Stevens, I. D. R.; Winstein, S. *J. Am. Chem. Soc.* **1970**, *92*, 115. (d) Biale, G.; Cook, D.; Lloyd, D. J.; Parker, A. J.; Stevens, I. D. R.; Takahashi, J.; Winstein, S. *J. Am. Chem. Soc.* **1971**, *93*, 4735. (e) Beltrame, P.; Biale, G.; Lloyd, D. J.; Parker, A. J.; Ruane, M.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2240.

(2) (a) Bunnett, J. F.; Eck, D. L. *J. Am. Chem. Soc.* **1973**, *95*, 1897, 1900. (b) Bunnett, J. F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 225.

(3) (a) McLennan, D. J. *Tetrahedron* **1975**, *31*, 2999. (b) Ford, W. T. *Acc. Chem. Res.* **1973**, *6*, 410.

(4) Parker, A. J.; Ruane, M.; Biale, G.; Winstein, S. *Tetrahedron Lett.* **1968**, 2113, 5183, 5715.

(5) Ko, E. C. F.; Parker, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 6447.

(6) Bartsch, R. A. *J. Am. Chem. Soc.* **1971**, *93*, 3683.

(7) Kwart, H.; Wilk, K. A.; Chatellier, D. *J. Org. Chem.* **1983**, *48*, 756.

(8) Kwart, H.; Gaffney, A. H. *J. Org. Chem.* **1983**, *48*, 4502.

(9) Kwart, H.; Gaffney, A. H.; Wilk, K. A. *J. Org. Chem.* **1983**, *48*, 4509.

(10) Kwart, H.; Schwartz, J. L. *J. Org. Chem.* **1974**, *39*, 1575.

0022-3263/85/1950-3038$01.50/0