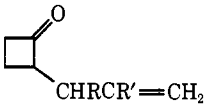
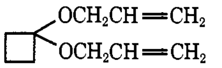
A Synthesis of α-Substituted Cyclobutanones and Its Application to the Confirmation of the Rearrangement of a Bicyclo[2.2.1]heptane to a Bicyclo[3.1.1]heptane Derivative

Sir:

Recently there has been considerable interest in methods for the synthesis of α-substituted cyclobutanones.[1] None of these methods involves substitution of cyclobutanone itself.[2] We have found that 2-allylcyclobutanone (**1**) can be conveniently prepared from cyclobutanone diallyl ketal (**2**).[3] The ketal **2**, bp 81–82° (15.5 mm), $n^{26}\text{D}$ 1.4445,[6] was prepared in 93% yield from cyclobutanone and allyl alcohol in the presence of 2,2-dimethoxypropane and *p*-toluenesulfonic acid (TSA). Heating of **2** at 185° in the presence of TSA gave **1**, bp 89–90° (72 mm), $n^{26}\text{D}$ 1.4476, in quantitative yield. The hitherto unknown, functionally substituted cyclobutanone **1** provides a potential source of a variety of α-substituted cyclobutanones, as illustrated below. The potential generality of the reaction of **2** to give **1** has been demonstrated by the successful preparation of the cyclobutanones **3** and **4** from the corresponding analogs of **2**.



1, R = R′ = H
3, R = H; R′ = Me
4, R = Me; R′ = H



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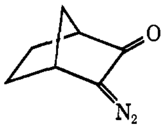
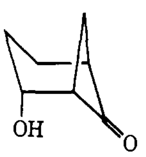
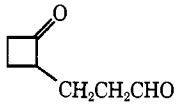
It has previously been reported from these laboratories[7] that one of the products formed on acid-catalyzed decomposition of 3-diazo-2-norbornanone (**5**) is the ketol **6**; this represented the first demonstration of the rearrangement of a bicyclo[2.2.1]heptane derivative to a bicyclo[3.1.1]heptane derivative.[8] However, Friedman[9] has cast doubt on the structural assignment **6**, stating erroneously that it was based solely on nmr data. We have now confirmed the assignment by the independent synthesis from **1** of 2-oxocyclobutanepropionaldehyde (**7**), the retroaldol cleavage product previously obtained from **6**.[7]



5



6



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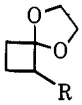

8, R = $CH_2CH{=}CH_2$
9, R = $CH_2CH_2CH_2OH$
10, R = CH_2CH_2CHO

Treatment of **1** with ethylene glycol in the presence of TSA gave the ketal **8**, bp 67–68° (7.5 mm), in 93% yield. This was subjected to hydroboration with disiamylborane followed by treatment with aqueous sodium hydroxide and hydrogen peroxide to give the alcohol **9**, which was oxidized with chromium trioxide in pyridine to the aldehyde **10**, which in turn was converted by acidic hydrolysis to **7**, bp 77–78° (1.3 mm); the overall yield of **7** from **8** was 49%. The remote possibility that **7** had undergone acid-catalyzed rearrangement to 3-oxocyclobutanepropionaldehyde is excluded by the ^{13}C nmr spectrum of the product, which shows seven distinct signals. Its ir and pmr spectra are identical with those of the product obtained from **6**.

Acknowledgment. We thank the National Research Council of Canada for support of this work.

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[1] M. Hanack, J. Häffner, and I. Herterich, *Tetrahedron Lett.*, 875 (1965); M. Hanack and I. Herterich, *ibid.*, 3847 (1966); M. Hanack, I. Herterich, and V. Vött, *ibid.*, 3871 (1967); B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **93**, 3773 (1971); H. H. Wasserman, H. W. Adickes, and O. Espejo de Ochoa, *ibid.*, **93**, 5586 (1971); J. R. Salaün and J.-M. Conia, *Tetrahedron Lett.*, 2849 (1972).

[2] *Cf.* J.-M. Conia and J.-P. Sandré, *Bull. Soc. Chim. Fr.*, 752 (1963).

[3] This method has previously been applied to cyclopentanones and cyclohexanones,[4] but not to cyclobutanones. The only related method in the cyclobutanone series is restricted to the formation of polyhalogenated compounds.[5]

[4] N. B. Lorette and W. L. Howard, *J. Org. Chem.*, **26**, 3112 (1961).

[5] C. G. Krespan, *Tetrahedron*, **23**, 4243 (1967).

[6] Satisfactory elemental analyses have been obtained for all compounds whose boiling points are given; the ir, pmr, and mass spectra of all compounds were in accord with expectation.

[7] P. Yates and R. J. Crawford, *J. Amer. Chem. Soc.*, **88**, 1561 (1966).

[8] Other examples of such rearrangements have been reported subsequently: C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *ibid.*, **89**, 3940 (1967); Y. Lin and A. Nickon, *ibid.*, **92**, 3496 (1970); W. Kirmse, G. Arend, and R. Siegfried, *Angew. Chem., Int. Ed. Engl.*, **9**, 165 (1970).

[9] L. Friedman in "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., Vol. II, Interscience, New York, N. Y., 1969, Chapter 16.

Radical Intermediates in Photosubstitution Reactions of Anthraquinones

Sir:

We wish to propose a mechanism for photosubstitution reactions of aromatic compounds possessing low-lying n,π^* states and to present preliminary findings which suggest occurrence of the process with substituted anthraquinones.[1]

Letsinger and coworkers[2] and Havinga and coworkers[3] have studied photosubstitution reactions of nitrophenyl ethers and acetophenones[4] with nucleophiles. These reactions appear to occur by direct nucleophilic attack on the rings of π,π^* excited molecules.[3,5] Aromatic carbonyl or nitro compounds with lowest energy n,π^* states are typically inert toward direct nucleophilic photosubstitution but readily undergo photoreduction initiated by hydrogen abstraction or electron transfer.[6,7] We were struck by the possibility

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[1] This work was presented at the 8th Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., Nov 9, 1972.

[2] R. L. Letsinger and J. H. McCain, *J. Amer. Chem. Soc.*, **91**, 6425 (1969), and references therein.

[3] E. Havinga and M. E. Kronenberg, *Pure Appl. Chem.*, **16**, 137 (1968).

[4] R. L. Letsinger and A. L. Colb, *J. Amer. Chem. Soc.*, **94**, 3665 (1972).

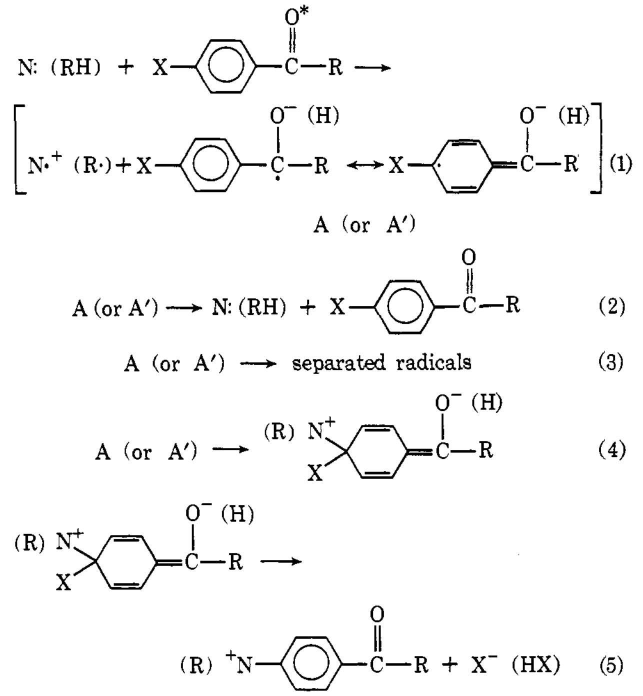
[5] W. C. Peterson and R. L. Letsinger, *Tetrahedron Lett.*, 2197 (1971).

[6] P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 87 (1968).

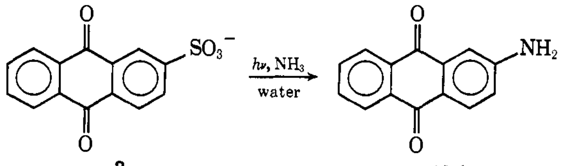
[7] (a) H. A. Morrison in "The Chemistry of the Nitro and Nitroso Groups," Part I, H. Feuer, Ed., Interscience, New York, N. Y., 1969, Chapter 4. (b) G. G. Wubbels, J. W. Jordan, and N. S. Mills, *J. Amer. Chem. Soc.*, **95**, 1281 (1973).

that a geminate radical pair formed by photoinduced electron or hydrogen atom transfer might consummate a substitution process in the presence of a suitable leaving group (Scheme I).[8]

Scheme I



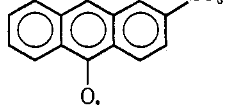
Anthraquinones known to undergo efficient conversion ($\Phi = 1$) to $^3n,\pi^*$ states on photoexcitation[9] appeared attractive possibilities for demonstration of the process. Irradiation of sodium anthraquinone-2-sulfonate (**1**) (10^{-2} *M*) under N_2 in aqueous ammonia (0.1 *M*) using Pyrex-filtered light from a 450-W Hanovia immersion lamp gave 1-aminoanthraquinone in 45% yield.[10,11] Similar irradiation of sodium anthraquinone-2-sulfonate (**2**) gave 2-aminoanthraquinone in yields up to 60%. In contrast, irradiation of **2** (2×10^{-3} *M*) in aqueous diethylamine (0.1 *M*) under N_2 on a preparative scale gave an intensely reddish brown solution which became nearly colorless on exposure to air. After extended irradiation, the uv spectrum of a diluted air-saturated aliquot showed no loss of **2**.



2

60%

Further investigation was carried out on dilute solutions using cuvettes. Irradiation of **2** (1.0×10^{-4} *M*) in N_2-flushed aqueous diethylamine (0.1 *M*) for 10 min caused λ_{max} at 325 nm ($A = 0.51$) to disappear completely and new maxima to appear at 400 ($A = 0.64$), 429 ($A = 0.57$), and 497 nm ($A = 0.53$). Absorptions of the irradiated solution were diminished only slightly by several days standing at 25°. Mixing air with the solution caused immediate loss of the visible absorptions and reappearance of the original spectrum. When the aerated solution was degassed and irradiated again, the spectral changes were reproduced. Similar results were obtained using triethylamine or 2-propanol–NaOH (0.1 *M*) in place of diethylamine. When the irradiation of **2** in aqueous diethylamine was conducted in the probe of an esr spectrometer, a well-resolved spectrum identical with that reported[12] for **3** was observed.[13] The photochemical behavior of **1** in aqueous diethylamine was analogous to that of **2** (original λ_{max} at 322 nm ($A = 0.45$) disappeared and new maxima appeared at 380 ($A = 0.58$, sh), 396 ($A = 0.98$), and 485 nm ($A = 0.43$, br)). These observations provide strong evidence for clean semiquinone radical formation in photolyses of **1** and **2** with alkylamines.



3

Irradiation of **1** or **2** in aqueous ammonia (0.1 *M*) caused appearance of very low intensity absorptions of the semiquinone radicals. With **2** the major reaction formed an air-stable product showing the absorptions of 2-aminoanthraquinone[14] (λ_{max} at 300 ($A = 0.88$) and 457 nm ($A = 0.16$)). When **2** was irradiated in aqueous NaOH (0.1 or 0.01 *M*), about 70% of **2** which disappeared could be accounted for as semiquinone radical. Blyumenfel'd, *et al.*,[15] have found that 6- and 7-hydroxyanthraquinone-2-sulfonates are products of this photoreaction.

Since n,π* excitation of anthraquinone would not increase the electron deficiency of the aromatic rings, direct nucleophilic attack by ammonia on $^3n,\pi^*$ anthraquinonesulfonates would not be facile.[16] This conclusion accords with observations on other systems.[4,5] A displacement process initiated by photolytic loss of sulfonate appears unlikely since starting material was regenerated completely (by exposure to air) after extended irradiation of **1** or **2** with diethylamine. Cohen has reported convincing evidence for electron transfer interactions between $^3n,\pi^*$ benzophenones and amines which occur at rates near the diffusion limit.[17] Since

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(8) Reaction of an aromatic ketone is shown, but the reaction of an aromatic aldehyde or nitro compound could be represented similarly. The geminate radical pairs probably tend to remain proximate through the influence of a solvent cage or of charge-transfer complexing.

(9) (a) F. Wilkinson, *J. Phys. Chem.*, **66**, 2569 (1962); (b) D. Schulte-Frohlinde and C. V. Sonntag, *Z. Phys. Chem. (Frankfurt am Main)*, **44**, 314 (1965); (c) H. H. Dearman and A. Chan, *J. Chem. Phys.*, **44**, 416 (1966); (d) A. Kuboyama and S. Yabe, *Bull. Chem. Soc. Jap.*, 40, 2475 (1967).

(10) After completing this work we discovered a literature report of this reaction of **1**: A. V. El'tsov, O. P. Studzinskii, O. V. Kul'bitskaya, N. V. Ogal'tsova, and L. S. Efros, *Zh. Org. Khim.*, **6**, 638 (1970).

(11) Structures were established by comparison (mixture melting point, ir spectra, and chromatographic movement) with authentic samples.

(12) P. J. Baugh, G. O. Phillips and J. C. Arthur, *J. Phys. Chem.*, 70, 3061 (1966).

(13) We are grateful to Professor Wayne C. Danen of Kansas State University for performing this experiment.

(14) R. H. Peters and H. H. Sumner, *J. Chem. Soc.*, 2101 (1953).

(15) G. V. Fomin, L. M. Gurdzhiyan, and L. A. Blyumenfel'd, *Dokl. Akad. Nauk SSSR*, **191**, 151 (1970). These authors proposed a mechanism analogous to Scheme I for the dark reaction at elevated temperature of **2** with OH^- giving 2-hydroxyanthraquinone.

(16) Nucleophilic substitution by NH_3 on ground-state 2-chloroanthraquinone occurs at 220°: M. Phillips, *Ind. Eng. Chem.*, **17**, 721 (1925).

(17) S. G. Cohen and N. M. Stein, *J. Amer. Chem. Soc.*, **93**, 6542 (1971), and references therein.

anthraquinone is more electrophilic than benzophenone,[18] electron transfer to $^3n,\pi^*$ anthraquinones should be more facile than to $^3n,\pi^*$ benzophenones. Thus, a primary process involving electron transfer from alkylamines to photoexcited **1** or **2** appears reasonable. Since amines bearing no α hydrogen, *e.g.*, *tert*-butylamine, participate in electron-transfer interactions with $^3n,\pi^*$ benzophenones,[17] we would expect ammonia to interact similarly with $^3n,\pi^*$ anthraquinones.

Geminate radical pairs formed by electron transfer (A in Scheme I) could react by several routes.[19] Reversal of electron transfer would result in quenching (eq 2). Adduct formation and elimination of a leaving group would give a substitution product (eq 4 and 5). Separation of geminate radicals by diffusion (eq 3) and subsequent reactions would result in carbonyl reduction and amine oxidation products.[20]

For the reactions of **1** and **2** with ammonia, the major route is adduct formation and elimination leading to the substitution product. Since little absorption due to the anion radical was observed, only a small fraction of geminate radicals undergoes separation. With diethylamine the major route involves separation of geminate radicals with no detectable substitution. A rationale for the different behaviors of ammonia and alkylamines lies in the possibility of α-proton loss from alkylamines (eq 6). Following electron transfer, **3**

$$\mathrm{RCH_2{-}\overset{+}{N}HR'} \longrightarrow \mathrm{H^+ + R\dot{C}HNHR'} \qquad (6)$$

could accept an α proton from the alkylaminium radical. The conjugate acid of **3** and the neutral carbon radical (eq 6) would be expected to associate only weakly allowing the radicals to diffuse apart. Stronger association leading to adduct formation would be expected for geminate radicals **3** and $H_3N\cdot^+$.

Photosubstitution giving 1- or 2-aminoanthraquinone occurs, but in very low yield, when 1- or 2-chloroanthraquinone is irradiated in *tert*-butyl alcohol containing ammonia. In both cases the major reaction forms adducts containing ammonia and *tert*-butyl alcohol derived fragments.

Research is in progress to elucidate further the mechanistic details and generality of these photosubstitution processes.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work and to the Alfred P. Sloan Foundation (grant to Grinnell College).

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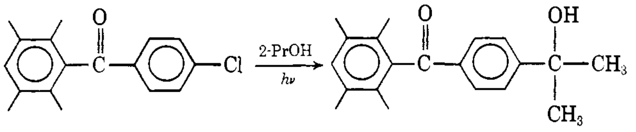
(18) Half-wave reduction potentials of anthraquinone and benzophenone in DMF are −0.33 and −1.22 V: P. H. Given, M. E. Peover, and J. Schoen, *J. Chem. Soc.*, 2674 (1958).

(19) A well-defined instance in which the mechanism of Scheme I appears to operate with a hydrogen atom donor was recently reported by F. A. Lamb and B. M. Vittimberga at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 28, 1972, Abstract No. ORGN-019.



(20) The fate of cation radicals derived from diethyl- or triethylamine has not been determined in our system. Imines or their hydrolysates have been found as end products in similar systems.[17]

(21) National Science Foundation–Undergraduate Research Participant, summer 1970.

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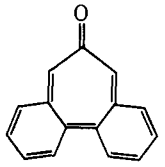
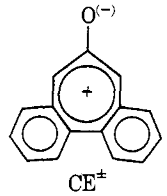
Dibenzo[*c*,*e*]tropone. A New, Potent Six π-Electron Component for Cycloadditions

Sir:

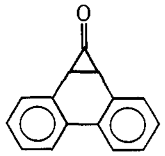
The *o*,*o*′-diphenoquinone moiety of dibenzo[*c*,*e*]tropone (CE) might be expected to make this molecule an exceptionally potent six electron component in cycloadditions, particularly those of the [6 + 4] variety. CE is also potentially capable of existing in a cyclopropanone valence tautomeric form (CE′). The relationship between CE and CE′ is thus essentially that of a Favorskii zwitterion and its corresponding cyclopropanone, a comparison which seems the more relevant in view of the expected high polarity of CE (see CE±). Finally there exists the interesting possibility that the high reactivity of the trienic termini of CE may be partially satisfied by a 1,3 covalent (homoaromatic) interaction. The normal dibenzotropones (*b*,*d* and *b*,*f*) are already well known and the abnormal dibenzotropone BE has recently been trapped by maleic anhydride and its stable conjugate acid prepared.[1] The present communication concerns the generation of CE and its trapping by dienes, the preparation of its relatively stable conjugate acid, and the interception of CE′ by means of a Favorskii-type reaction with methoxide–methanol.



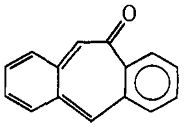
CE



CE±



CE′



BE

The symmetrical dibromide (DBK) of ketone K is readily available,[2] but did not prove a suitable precursor for CE (or CE′). Direct bromination of K is not feasible because of facile dibromination and the chromatographic instability of both the mono- and dibromides. Monobromination of the enol acetate of K (EA) does, however, afford pure monobromide (MBK). Conversion of K to EA required 40 hr of refluxing with isopropenyl acetate–toluenesulfonic acid. Bromination (Br_2) of EA at −78° in methylene chloride–chloroform gave MBK, mp 105–108° dec.[3]

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(1) N. L. Bauld and Y. S. Rim, *J. Amer. Chem. Soc.*, **89**, 179 (1967).

(2) T. L. Gilchrist and C. W. Rees, *J. Chem. Soc. C*, 1973 (1969).

(3) All substances reported as isolated gave satisfactory elemental analyses, nmr, and mass spectral data.