

280 μ . Purified nitrogen was passed through the solution for at least 45 min before irradiation commenced, and a positive pressure of nitrogen was maintained throughout. Aliquots were removed without interrupting the photolysis and analyzed by infrared spectroscopy and thin layer chromatography. Even after 72 hr of irradiation, infrared analysis and thin layer chromatography showed only unchanged starting material. Upon work-up, pure crystalline starting material was the only compound present.

Quantum Yield Determinations. The apparatus used was that described earlier using a 200-w Hanovia lamp.⁴³ It consisted of five borosilicate glass cylinders of 100, 80, 39, and 28 mm joined together by appropriate ring seals and standard taper joints. The two interior tubes with cell spaces of 3 and 8 mm, respectively, contained 10 g of hexahydrated nickel sulfate per 30 ml of aqueous solution and 12.5 g of heptahydrated cobalt sulfate per 30 ml of aqueous solution. Light intensities were monitored just before and just

after sample irradiation. Quantum output rates for the 200-w mercury lamp used were determined by potassium ferrioxalate actinometry.⁴⁴ Reliably reproducible output rates of 1.5×10^{18} quanta/sec were recorded. After the irradiation the degree of reaction was determined by quantitative column chromatography using a liquid-liquid partition column. The conversions were run to 13% or less. Details of the measurements are given in Table II.

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Electrochemical Preparation of Bicyclobutanes and Other Strained Cycloalkanes

M. R. Rifi

Contribution from Union Carbide Chemicals and Plastics Operations Division, Research and Development Department, Bound Brook, New Jersey 08805.

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Abstract: As part of a study on the mechanism of the electrochemical cleavage of carbon-halogen bonds, it was discovered that 1,3-dihalocyclobutanes can be reductively cyclized to give bicyclobutanes in good yields. Thus, 1,3-dimethylbicyclobutane (II) was prepared from 1,3-dibromo-1,3-dimethylcyclobutane (I) in over 90% yield. Bicyclobutanes can be selectively prepared from cyclobutanes containing more than two halogens by controlling the electrode potential. By this technique, 1,1,3,3-tetrachloro-2,2,4,4-tetramethylcyclobutane (III) was electrolyzed at -2.0 ± 0.1 v (sce) to give 1,3-dichloro-2,2,4,4-tetramethylbicyclobutane (IV). The method of reductive cyclization is of general utility in the synthesis of small-ring compounds. Cyclopropane and cyclobutane were prepared from the corresponding α,ω -dihalides. Data obtained from polarography, as well as product analysis, suggest that anions are involved in these ring closures.

The first authentic bicyclobutane derivative was prepared by Wiberg and Ciula in 1959.¹ Since then, a host of bicyclobutanes have been prepared by numerous routes.²⁻¹²

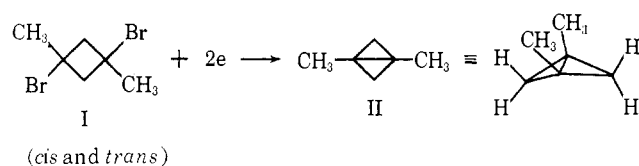
We have discovered that bicyclobutanes, as well as cyclopropane, cyclobutane, and spiropentane, can be prepared by the electrochemical reduction of appropriately substituted halides.

While 1,2-dihalides afford olefins upon electrolysis,¹³ the electrolytic cyclization of a 1,3- and 1,4-dihalide to

the corresponding cyclopropane and cyclobutane has not been reported. Therefore, it was of interest to study the electrolysis of α,ω -dihalides as a general preparative method for small-ring compounds.

Results

The electrolysis of 1-chloro-3-bromocyclobutane¹⁴ in dimethylformamide saturated with lithium bromide afforded a mixture of bicyclobutane (60%), cyclobutene (20%), and cyclobutane (10%). Similarly, 1,3-dibromo-1,3-dimethylcyclobutane¹⁵ was electrolyzed to give 1,3-dimethylbicyclobutane (II).



The structural assignment of II is based on its nmr spectrum which showed singlets at τ 8.67 (area 3), 9.0

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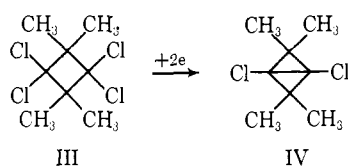
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(15) K. Griesbaum, W. Naegle, and G. G. Wanless, *J. Am. Chem. Soc.*, **87**, 3151 (1965).

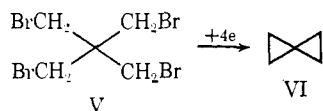
(area 1), and 9.48 (area 1). The fact that the two methylene protons have different chemical shifts is due to the noncoplanarity of the two cyclopropane rings. Compound II is reconverted to I by the action of bromine in carbon tetrachloride. While the chemistry of 1,3-dimethylbicyclobutane was being investigated, its preparation from the addition of carbene to dimethylacetylene was reported.¹⁶

It was of interest to determine whether bicyclobutanes could be prepared from cyclobutanes containing more than two halogens. This was readily accomplished by using controlled potential electrolysis coupled with a knowledge of the polarographic behavior of the compound. When 1,1,3,3-tetrachloro-2,2,4,4-tetramethylcyclobutane (III), synthesized by the action of phosphorus pentachloride on 2,2,4,4-tetramethylcyclobutane dione,¹⁷ was electrolyzed at a controlled potential of -2.0 ± 0.1 v (sce), 1,3-dichloro-2,2,4,4-tetramethylbicyclobutane (IV) was obtained.



The preparation and the chemistry of compound IV will be reported in a separate publication.

The electrolysis of straight-chain α,ω -dihaloalkanes was both simple and efficient. The electrolysis of 1,3-dibromo-2,2-bis(bromomethyl)propane¹⁸ (V) afforded spirocyclopentane (VI) in good yield.



The reduction of 1,3-dibromopropane gave cyclopropane as the only isolable product, whereas 1,3-dibromobutane gave a mixture of cyclobutane and *n*-butane. In contrast, no cyclopentane was detectable in the reduction of 1,5-dibromopentane under similar conditions.

Discussion

The yields of cyclic compounds in the electrolysis of 1,4-dibromobutane and 1,5-dibromopentane deserve comment. While in the Wurtz reaction the yield of cyclopropane is high compared to cyclobutane¹⁹ and cyclopentane,²⁰ the low yields of the latter compounds are comparable to each other. In the present system, cyclobutane was obtained in 25% yield, but we were unable to obtain any cyclopentane. This observation may be explained by a surface action phenomenon whereby cyclization takes place at the surface of the electrode. This would give higher yield of cyclization from the cyclobutane precursor which has a higher number of conformations favorable for cyclization.

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(17) H. Gilch, *J. Org. Chem.*, **30**, 4392 (1965).

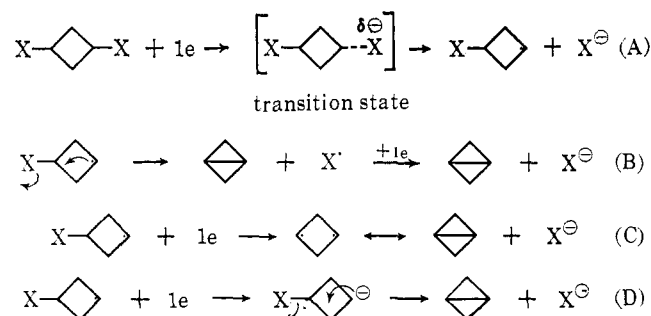
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Cleavage of the Carbon-Halogen Bond. The mechanism of the electrochemical cleavage of carbon-halogen bonds is not yet settled. While it has been argued that radicals may be involved,²¹ others have shown that cleavage in the presence of carbon dioxide produced the corresponding carboxylic acid.²² The data presented below seem most consistent with the proposal that anions rather than radicals are the intermediate species in the formation of small-ring compounds by electroreduction.

The possible mechanisms of the cleavage of the carbon-halogen bond in these cyclizations may be envisioned as follows.



Step A is most likely the rate-determining step²³ and is dependent on the halogen being cleaved, the ease of cleavage being $I > Br > Cl > F$. The formation of the radical anion has been reported^{24,25} as proceeding in either of two ways, *i.e.*, *via* attack of an electron from the cathode on the halogen atom or on the carbon atom. The author did not make a distinction between the two alternatives. Step B involves an improbable radical displacement reaction of a halogen radical. Such reactions are of high energy and seldom occur.²⁶ Furthermore, unless the halocyclobutyl radical diffuses rapidly from the vicinity of the electrode, *i.e.*, out of the double layer, it is likely to accept another electron rather than undergo cleavage of another bond.²⁷

The controlled potential electrolysis of 1-chloro-3-bromocyclobutane gave data that are more consistent with the formation of anions and eliminates the mechanism envisioned in step C. A polarogram of the compound in DMF- $Et_4N^+Br^-$ shows one wave at $E_{1/2} = -1.80$ v (sce). This wave must be attributed to the cleavage of the carbon-bromine bond, which is weaker than the carbon-chlorine bond. The over-all reaction was shown by coulometric analysis to require 2 electron equiv/mole. Since, as discussed above, the radical displacement (step B) seems unlikely and since the formulation of a diradical (step C) should exhibit two polarographic waves, it is concluded that the two electrons add to the carbon-bromine bond. This would

(21) P. J. Elving, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **14**, 99 (1953).

(22) S. Wawzonek, R. C. Duty, and J. H. Wagenknecht, *J. Electrochem. Soc.*, **111**, 74 (1964).

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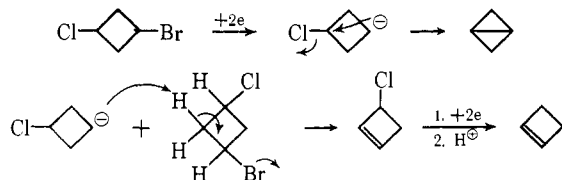
(24) J. W. Sease, P. Chang, and J. L. Groth, *ibid.*, **86**, 3154 (1964).

(25) F. L. Lambert, A. H. Albert, and J. P. Hardy, *ibid.*, **86**, 3156 (1964).

(26) E. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 691. For exceptions, see J. N. Pitts, *et al.*, *ibid.*, **79**, 6370 (1957).

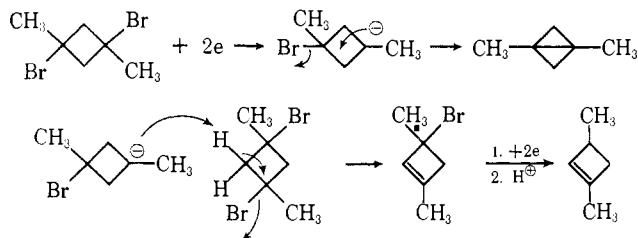
(27) This may be an oversimplified statement, for, although several calculations have been made to determine the difference in energies between allyl anions and radicals, no such calculations have been made for the simple alkyl species.

lead to the formation of chlorocyclobutyl carbanion and a bromide anion (step D). In an intramolecular displacement,¹ the carbanion can displace a chloride anion and effect the formation of bicyclobutane. Thus one is led to predict that the electrolysis of 1-chloro-3-bromocyclobutane at a controlled potential of about -2.0 v (sce) should lead to the formation of bicyclobutane. Indeed, when this compound was electrolyzed at a controlled potential of -2.0 ± 0.1 v (sce), bicyclobutane together with cyclobutene and cyclobutane were obtained. Thus our data seem to be most consistent with step D and the over-all reaction is envisioned as follows.



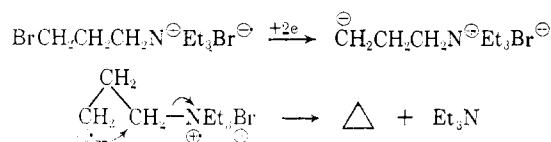
(note that allyl chlorides reduce at -1.9 v (sce)²⁸)

The above mechanism indicates that the formation of cyclobutene should depend on the concentration of the starting material. Indeed, it was observed that in the electrolysis of 1,3-dibromo-1,3-dimethylcyclobutane, as the concentration increased, the yield of 1,3-dimethylbicyclobutane decreased, and an olefinic compound was detected and identified by its nmr spectrum as 1,3-dimethylcyclobutene. Also detected was 1,3-dimethylcyclobutane.



The formation of cyclobutane and 1,3-dimethylcyclobutane in the two electrolyses is not easy to explain. Cyclobutane could have come from the reduction of cyclobutene since activated double bonds reduce at about -2.1 v (sec).²⁸ Possibly the strain energy of cyclobutene is sufficient to render it reducible at -2.0 v (sce).

Additional support for the anionic intermediate is obtained from the electrolysis of 3-bromopropyltriethylammonium bromide at -2.0 ± 0.1 v (sce). At this voltage the quaternary ammonium group is not affected electrochemically. The only products obtained were cyclopropane and triethylamine; no dimers or trimers of propane were detectable. The displacement of a triethylamine group by radicals has no precedent.



The proton source leading to the formulation of hydrocarbons in the electroreduction of these halides

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has not been elucidated. The following possibilities are considered: (1) although precautions were taken to obtain dry DMF, rigorous exclusion of moisture is difficult to ensure; (2) where $n\text{-Bu}_4\text{NClO}_4$ was used as a supporting electrolyte, it could serve as a proton source; (3) although unlikely, DMF may be a proton source.

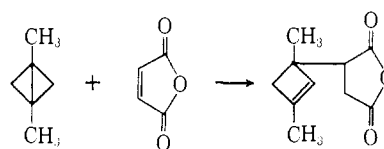
The data available at present do not allow the distinction between a concerted displacement reaction and one involving anions in solutions. The facts that the formation of cyclobutene is dependent on the concentration on the starting material and that the yield of bicyclobutanes is independent of the stereochemical nature, *i.e.*, *cis-trans* isomers, of the dihalocyclobutane, favor an anionic intermediate. However, the preferential formation of cyclopropane and cyclobutane over cyclopentane may be explained by a concerted reaction which takes place on the surface of the electrode. Furthermore, a positively charged species in a molecule such as a tetraalkylammonium halide may enhance a concerted mechanism by forcing the molecule to remain in the vicinity of the negatively charged electrode. This may be considered as a factor in forming cyclic products from longer chain α,ω -dihalides.

In conclusion, it is believed that the electrochemical reduction of the above halides involves either anionic intermediates or a concerted process but not radicals.

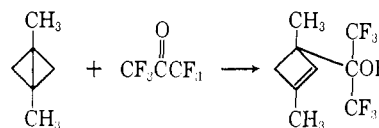
Some Reactions of 1,3-Dimethylbicyclobutane. While the bridged bond in 1,3-dimethylbicyclobutane is thermally stable, it is quite reactive chemically.²⁹ This observation, which is general for bicyclobutanes, has been explained as due to the inherent "unsaturation or π character" of the 1,3 bond.^{30,31}

We have found that 1,3-dimethylbicyclobutane exhibits an ultraviolet spectrum (cyclohexane) having λ_{max} 218 μm (ϵ 1800). Although our bicyclic compound was contaminated with 1,3-dimethylcyclobutene (3%) the observed spectrum cannot be attributed to this compound.³²

With electron-deficient molecules, 1,3-dimethylbicyclobutane reacts violently. For example, with maleic anhydride the following reaction was observed.



Hexafluoroacetone reacted in a similar manner.



These reactions are similar to those reported for 3-methylbicyclobutane carbonitrile.³³ The above prod-

(29) W. von E. Doering and J. E. Coburn, *Tetrahedron Letters*, 997 (1965).

(30) M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3970 (1966).

(31) K. B. Wiberg, G. M. Lampman, R. P. Ciula, C. S. Connor, P. S. Schertler, and J. Havnaish, *Tetrahedron Letters*, 2749 (1965).

(32) A. E. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press Inc., New York, N. Y., 1964, p 21.

(33) A. Cairncross and E. P. Blanchard, *J. Am. Chem. Soc.*, **88**, 487 (1966).

ucts were identified by their elemental analysis and infrared and nmr spectra.

1,3-Dimethylbicyclobutane reacts violently with tetracyanoethylene. At 0° a blue color appears and fades within a few seconds. At liquid nitrogen temperature the blue color persists and displays an esr signal. Attempts to isolate and identify any products have been unsuccessful. Only low molecular weight polymers were obtained upon warming.

Experimental Section

Solvent and Electrolytes. To obviate the necessity of using high hydrogen overvoltage metals as cathodes and to facilitate the study of the primary electrochemical reactions, an inert nonaqueous solvent was used. Such a solvent was dimethylformamide (DMF). This solvent was purified by refluxing over cupric sulfate for 24 hr, followed by vacuum distillation, 55° (15 mm). Finally, the solvent was passed through a 6-ft long, 1-in. diameter column filled with molecular sieves. The supporting electrolytes used were *n*-Bu₄NClO₄, Et₄NBr, and LiBr, in a concentration of approximately 0.1 M.

Reaction Conditions. All electrode potentials cited in this paper refer to the saturated calomel electrode (sce) as the reference. Liquid junction potentials are ignored. All electrolyses were run at room temperature; however, in some cases where voltages in the order of 40 to 50 v were used, the reaction mixture warmed up to 55°.

Apparatus. All electrolyses were carried out in cells of the type shown in Figure 1. Mercury was used as the cathode, while the anode was a platinum wire. Polarograms were recorded on Beckman 30 Electroscan and Sargent (XXI) polarographs.

1,3-Dimethylbicyclobutane (II). A solution of 50 g (0.2 mole) of 1,3-dibromo-1,3-dimethylcyclobutane in 230 ml of DMF-LiBr was introduced into the cathode chamber. The anode chamber was charged with a solution of 150 ml of DMF-LiBr. Forty volts was applied across the cell, thus allowing 0.5 amp to pass through the cell. Electrolysis was allowed to proceed for 16 hr, after which a colorless liquid was collected into the trap. Distillation from repetitive runs at atmospheric pressure afforded yields that varied from 9 to 15 g (55–94%) of a liquid, bp 54.5°, which decolorized Br₂-CCl₄ to regenerate the starting material. Its nmr spectrum (CCl₄) showed the following peaks: singlets at τ 8.67 (area 3), 9.0 (area 1), and 9.48 (area 1). When the concentration of the starting material was increased to about 1.6 M, the yield of 1,3-dimethylbicyclobutane dropped sharply and was difficult to purify even by vpc. The nmr of the mixture showed the presence of 1,3-dimethylcyclobutane and 1,3-dimethylbicyclobutane.

Bicyclobutane. A solution of 10 g (0.059 mole) of 1-chloro-3-bromocyclobutane in 20 ml of DMF-Et₄NBr was introduced into the cathode compartment. The anode compartment was charged with a solution of DMF-Et₄NBr (15 ml). Sufficient voltage (~40 v) was applied across the cell to maintain the cathode potential at -2.0 ± 0.1 v (sce) and was adjusted manually. This allowed the passage of 0.4 amp across the cell. Electrolysis continued (18–24 hr) until an aliquot from the cathode chamber showed no appreciable polarographic wave in DMF-Et₄NBr. This was indicative that the reaction was essentially completed. 1-Chloro-3-bromocyclobutane shows one wave in this solution with $E_{1/2} = -1.80$ v (sce). A colorless liquid was collected into the trap. The liquid was distilled into an nmr tube by allowing the Dry Ice-acetone trap to warm up slowly. What did not distil was shown to be DMF. An nmr spectrum (CCl₄) of the distilled product showed the presence of (1) bicyclobutane, a singlet at τ 9.56 (area 2), and a multiplet centered at 8.5 (area 4); (2) cyclobutene, a singlet at τ 4.03 (area 2) and a singlet at 7.42 (area 4); (3) cyclobutane, a singlet at τ 8.0. An estimation of the per cent yield of the three components from the nmr spectrum was found to be 60:20:10 bicyclobutane, cyclobutene, and cyclobutane, respectively.

Cyclopropane. A solution of 50 g (0.2 mole) of 1,3-dibromopropane in 1 l. of DMF-*n*-Bu₄NClO₄ was electrolyzed over a period of 12 hr. A voltage of 40–50 v was applied, thus allowing the pas-

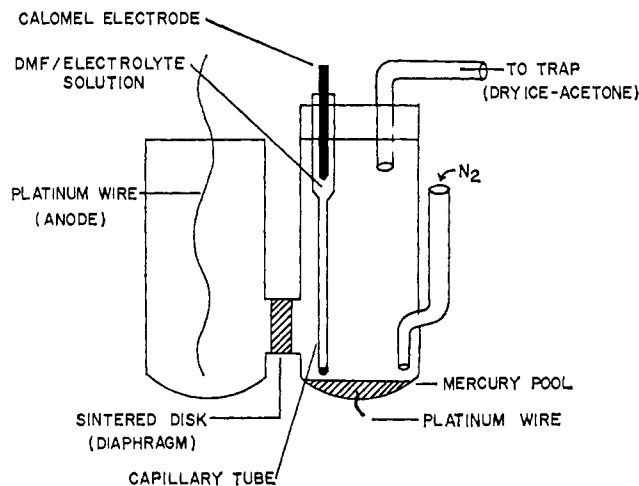


Figure 1. Electrolysis cell.

sage of 0.3–0.5 amp through the cell. A colorless liquid was collected into the trap and was shown to be pure cyclopropane from its nmr spectrum (neat), a singlet at τ 9.78. A trace of DMF was also collected in the trap. The cathode solution was examined and was found to contain only DMF. Due to the difficulty that is involved in determining the weight of cyclopropane obtained, the yield was not determined; however, it was established that it was the only product formed.

3-Bromopropyltriethylammonium bromide was prepared from the reaction of equal moles of triethylamine with 1,3-dibromopropane in refluxing ether. The salt, a white solid, precipitates during the reaction. Distillation of the ether solution affords more salt; total yield is 51%.

Anal. Calcd for C₉H₂₁NBr₂: C, 35.7; H, 6.94; N, 4.61; Br, 52.7. Found: C, 35.9; H, 7.00; N, 4.58; Br, 52.9.

Electrolysis of 3-Bromopropyltriethylammonium Bromide. A solution of 10 g (0.03 mole) of 3-bromopropyltriethylammonium bromide in 500 ml of DMF-*n*-Bu₄NClO₄ was electrolyzed at a cathode potential of -2.0 ± 0.1 v (sce). The total voltage applied varied between 25 and 30 v, thus allowing the passage of 0.3–0.5 amp across the cell. Electrolysis proceeded for 12 hr. A colorless liquid was collected into the trap and was identified as a mixture of cyclopropane, triethylamine, and DMF. Upon examination of the cathode solution, only DMF was detected.

Cyclobutane. A solution of 50 g (0.2 mole) of 1,4-dibromobutane in 1 l. of DMF-*n*-Bu₄NClO₄ was electrolyzed for 24 hr under a voltage of 40–50 v and a current of 0.3–0.5 amp. A colorless liquid was collected into the trap. An nmr spectrum of this liquid showed the presence of two compounds, cyclobutane and *n*-butane, with a 1:3 ratio. Vapor phase chromatography on a high-activity silica gel (2 m) column showed only two peaks with retention times 3.3 and 5.7 min. Upon integration, it was shown that the ratio of the two peaks was 3:1. The cathode solution was examined and was found to contain only DMF.

Electrolysis of 1,5-Dibromopentane. Fifty grams (0.2 mole) of 1,5-dibromopentane was electrolyzed under similar conditions to those described for 1,4-dibromobutane. The only compounds detected were *n*-pentane (80%) and a white solid whose nature has not yet been determined.

Reaction of 1,3-Dimethylbicyclobutane with Maleic Anhydride. 1,3-Dimethylbicyclobutane (1.7 g, 0.02 mole) was added slowly (1 hr) to a solution of 2 g (0.02 mole) of maleic anhydride in 15 ml of benzene which was cooled with an ice bath. During this time the solution acquired a yellow color. Distillation at atmospheric pressure removed most of the solvent. This process was followed by distillation under vacuum to give 3 g (85%) of a colorless liquid, bp 112° (2.5 mm). The nmr spectrum (CCl₄) showed peaks at τ 4.2, multiplet (area 1); 7.0, multiplet (area 3); 7.8, broad doublet (area 2); 8.25, singlet (area 3); and 8.8, singlet (area 3).

Anal. Calcd for C₁₀H₁₂O₂: C, 66.7; H, 6.67. Found: C, 66.1; H, 6.65.