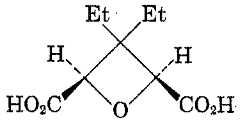
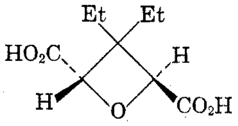
other protons. Only structures Ia and Ib will accommodate this spectrum.



Ia



Ib

The spectrum also permits assignment of configuration, for in the ester of *B*, the methyl bands at 9.1 have the normal three components, whereas the corresponding band of *A* has five components of which part must originate from a chemical shift. Thus, the ethyl groups of *B* have the same environment and those of *A* have different environments, and correspondingly, *A* must be the *cis* isomer and *B* the *trans* isomer. This assignment is also in agreement with the ratio of ionization constants ($K_1/K_2 = 40$ for *A*, and 9 for *B*).

A consideration of the factors which favor the formation of a keto acid or a trimethylene oxide in the reaction by which the acids Ia and Ib are formed (the reaction of the α,α'-dibromoglutaric esters with strong base) will be postponed until the structures of all of the compounds in Thorpe's series have been reinvestigated.

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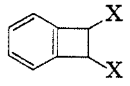
1,2-Bisdimethylaminobenzocyclobutene and its Rearrangement to α-Dimethylamino-*o*-Tolualdehyde

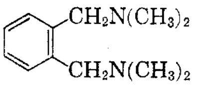
Sir:

Recently derivatives of benzocyclobutene have been studied by several groups of workers.[1-4] 1,2-Diiodobenzocyclobutene (I) has been prepared by Cava and co-workers[1,2] and has been shown to exist as *cis* and *trans* isomers.[3] It has been stated that I is inert to nucleophilic attack.[2]

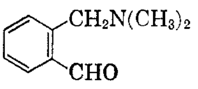
Treatment of pure *trans* I with excess dimethylamine yielded two equivalents of dimethylammonium iodide and a highly reactive liquid, b.p. 100–102°/2.5 mm., n_D^{25} 1.5094, for which we suggest the 1,2-bisdimethylaminobenzocyclobutene structure (II). The liquid II began to decompose within 15 minutes after distillation, making it impossible to obtain direct analytical data. Reduction of II with Raney nickel in dry petroleum ether yielded α,α'-dimethylamino-*o*-xylene (III), b.p. 80–82/4.2 mm., n_D^{25} 1.5024, which when treated with picric acid yielded a dipicrate, m.p. 192.6–194.1°. *Anal.* Calcd. for $C_{24}H_{26}N_8O_{14}$ ($C_{12}H_{20}N_2$ + $2C_6H_3N_3O_7$): C, 44.31; H, 4.03; N, 17.23. Found: C, 44.61; H, 4.09; N, 16.93. The infrared spectrum of III was identical to that of an authentic sample of α,α'-dimethylamino-*o*-xylene prepared by the method of von Braun and Cahn,[5] and a mixture melting point of the two dipicrates showed no depression.



I, X = I
II, X = N(CH₃)₂



III



IV

Treatment of II with dilute acid followed by isolation of the basic material yielded α-dimethylamino-*o*-tolualdehyde (IV), b.p. 84–86°/2.5 mm., n_D^{23} 1.5356. *Anal.* Calcd. for $C_{10}H_{13}NO$: C, 73.59; H, 8.03. Found C, 73.65; H, 8.13. The infrared spectrum of IV contained a conjugated carbonyl band at 1690 cm.$^{-1}$ and a band characteristic of *ortho* disubstitution at 760 cm.$^{-1}$ The ultraviolet spectrum is similar to that of other aromatic aldehydes $\lambda_{max}^{isooctane}$ 284 mμ (log ϵ = 3.11), 243 mμ (log ϵ = 4.05). The compound IV reduced Tollen's reagent and formed a *2,4-dinitrophenylhydrazone*, m.p. 175–176°. *Anal.* Calcd. for $C_{16}H_{17}N_5O_4$: C, 55.97; H, 4.99; N, 20.40. Found: C, 55.94; H, 4.96; N, 20.34. A *picrate* was also formed, m.p. 148–149°. *Anal.* Calcd. for $C_{16}H_{16}N_4O_8$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.22; H, 4.19; N, 14.31.

That dimethylamine was lost in the reaction of II to form IV was shown by treatment of II with picric acid in 95% alcohol. After five recrystallizations, analytically pure dimethylamine picrate was isolated. A mixture melting point of this picrate with that of an authentic sample of dimethylamine picrate showed no depression.

Cava has suggested that in the conversion of 1,2-dibromobenzocyclobutene to I there is elimination of bromine to form benzocyclobutadiene, followed by addition of iodine to the highly reactive double bond.[2] The possibility of a nucleophilic displacement of bromine by iodide ion was ruled out. The present results can be rationalized by a similar mechanism by postulating a *cis* elimination of hydrogen iodide followed by addition of dimethylamine to the benzocyclobutadiene intermediate. This would have to be followed by a second elimination and addition to give II. An alternative mechanism involving direct nucleophilic displacement of the iodine atoms is also possible.

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(3) W. E. Coleman and F. R. Jensen, *J. Org. Chem.*, **23**, 869 (1958).

(4) W. E. Coleman and F. R. Jensen, *J. Am. Chem. Soc.*, **80**, 6149 (1958).

(5) J. von Braun and R. S. Cahn, *Ann.*, **436**, 262 (1924).

Attack of water or hydroxide ion on singly protonated II, followed by ring opening, a proton shift and hydrolysis of the resulting amino alcohol, could give the aldehyde IV.

Further work is being carried out on the mechanism of formation of II, on its reactions and on the possibility of reactions of I with other nucleophilic reagents.

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α-Oximino Ketones. I. The "Normal" and "Abnormal" Beckmann Rearrangements

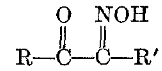
Sir:

The Beckmann rearrangement of α-oximino ketones possessing the *anti* or α-configuration is commonly described[1,2,3] as proceeding "normally," to a secondary amide and/or the hydrolysis products thereof, when brought about by an acid or an acid chloride, but "abnormally," to a nitrile and a carboxylic acid, when brought about by an acylating agent and base[1,4] (rearrangement of the "second order"[5]). It was reported originally that rearrangement of α-oximino ketones in polyphosphoric acid was "normal",[6] but more recent work[7,8] has shown that actually the "abnormal" route is followed.

In this laboratory both types of rearrangement have been studied by submitting several unsymmetrical α-oximino ketones to the action of 85% sulfuric acid ("normal") and benzenesulfonyl chloride and aqueous base ("abnormal"). All products obtained are reported in Table I, except that no attempt was made to isolate two-carbon materials. Of particular interest are the first two pairs of α-oximino ketones, since if a secondary amide intermediate were formed in the "normal" reaction, both 2-oximino-1-phenyl-1-propanone and 1-oximino-1-phenyl-2-propanone should give *N*-acetylbenzamide or the same hydrolysis products therefrom, and 1,3-diphenyl-2-oximino-1-propanone and 1,3-diphenyl-1-oximino-2-propanone should give *N*-benzoylphenylacetamide or the same hydrolysis products.

TABLE I

BECKMANN REARRANGEMENTS OF α-OXIMINO KETONES



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{\overset{\displaystyle NOH}{\|}}{C}{-}R'$$

α-Oximino Ketone		Products and Yields from	
R	R′	85% H_2SO_4	$PhSO_2Cl$ + NaOH
Ph	Me[a]	$PhCO_2H$ (84%)	$PhCO_2H$ (91%)
Me	Ph[b]	$PhCONH_2$ (92%)	PhCN (87%)
Ph	CH_2Ph[c]	$PhCH_2CONH_2$ (47%)	$PhCH_2CN$ (68%)
		$PhCO_2H$ (86%)	$PhCO_2H$ (74%)
$PhCH_2$	Ph[d]	$PhCONH_2$ (61%)[e]	PhCN (77%)
		$PhCH_2CO_2H$ (68%)	$PhCH_2CO_2H$ (74%)
Me	Bu[f]	$BuCONH_2$ (59%)	BuCN (70%)
Me	CH_2Ph[g]	$PhCH_2CONH_2$ (83%)[h]	$PhCH_2CN$ (87%)
Pr	Et[i]	$EtCONH_2$ (19%)	EtCN (45%)
		$PrCO_2H$ (78%)	$PrCO_2H$ (84%)

[a] Purchased from Distillation Products Industries, Rochester, N. Y. [b] M.p. 162–163°. H. Rheinboldt and O. Schmitz-Dumont, *Ann.* **444,** 113 (1925) report 164–165°. [c] M.p. 126–127.5°. W. Schneidewind, *Ber.*, **21,** 1323 (1888) reports 125–126°. [d] M.p. 114–114.5°. *Anal.* Calcd. for $C_{15}H_{13}O_2N$: C, 75.29; H, 5.48; N, 5.85. Found: C, 75.46; H, 5.43; N, 5.81. [e] An 8% yield of $PhCO_2H$ was obtained also. [f] M.p. 59–60°. *Anal.* Calcd. for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.85; H, 9.25; N, 9.77. [g] M.p. 80–81°. G. Ponzio, *Gazz. chim. ital.*, **35,** 394 (1905) reports 80–81°. [h] A 12% yield of $PhCH_2CO_2H$ was obtained also. [i] B.p. 62–63° (0.45 mm.), n_D^{35} 1.4548. *Anal.* Calcd. for $C_7H_{13}O_2N$: C, 58.72; H, 9.15; N, 9.78. Found: C, 58.97; H, 9.30; N, 9.51.

The results obtained show that in both so-called types of rearrangement the nitrogen in the products was attached to the radical which originally bore the oxime carbon, and the conclusion seems inescapable that both reactions proceeded by the same path, except that hydrolysis of the nitrile took place in sulfuric acid. Additional confirmation for this view was obtained when other typical catalysts for the "normal" reaction were examined: Phosphorus pentachloride gave valeronitrile (70%) from 3-oximino-2-heptanone, and phenylacetonitrile (86%) from 2-oximino-1-phenyl-3-butanone; thionyl chloride gave benzonitrile (88%) from 1-oximino-1-phenyl-2-propanone. Trifluoroacetic acid, which has been shown[9–11] to give normal amide products from simple ketoximes, gave

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