[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

The Action of Diazomethane on Schiff's Bases

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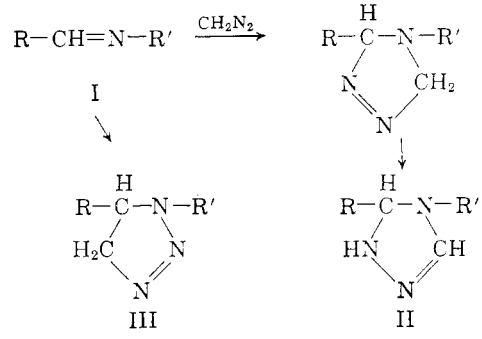
A study of the reaction of diazomethane with various Schiff's bases has been carried out in the hopes of obtaining ethylenimines; the results were largely negative. The addition of diazomethane to benzalanilines to give 1,2,3-triazolines has been investigated with emphasis on the conditions for good yield and on the kinetics. The mechanism of this addition reaction is discussed.

INTRODUCTION

The formation of three-membered ring systems from the reaction of double bond containing compounds and diazomethane derivatives has long been known. From certain olefins, a pyrazoline ring may be formed first and this may then be pyrolyzed to give a cyclopropane.[1] It has also been found[2] that both carbene and dichlorocarbene react with olefins to give cyclopropane derivatives. It is also known that diazomethane adds to the carbonyl group of aldehydes and ketones[3] to give an ethylene oxide or the higher homologous aldehydes and ketones. From the above considerations, the double bond in a Schiff's base might be expected to react with diazomethane either directly or indirectly to form an ethylenimine; with this in view an investigation of the action of diazomethane on Schiff's bases, both aliphatic and aromatic, was undertaken.

The reaction of aliphatic Schiff's bases with diazomethane itself and also with carbenes was studied; the carbene was generated either photolytically or catalytic decomposition of diazomethane was effected by use of boron trifluoride etherate.[4] In none of the cases studied here was it possible to obtain a definite reaction product corresponding to an ethylenimine. Also, no ethylenimine was detected in a petroleum ether solution of benzalaniline and diazomethane which had been exposed to light for four and a half hours. This anil, however, has been shown[5] to add dichlorocarbene (obtained from chloroform and sodium methoxide) to give 1,2-diphenyl-3,3-dichloroethylenimine. Dichlorocarbene obtained by the action of sodium methoxide on hexachloroacetone[6] also reacts with benzalaniline to yield the same ethylenimine.

Diazomethane itself reacts with some anils to give stable addition products. Mustafa[7], who first noticed the reaction, assigned to the addition product a 1,2,4-triazoline structure (*II*) solely on the basis of his observation that when heated or hydrolysed with acid these compounds decomposed with evolution of diazomethane and regeneration of I.



However, the triazoline addition product was later shown to have a 1,2,3-triazoline structure (III) by Buckley.[8] He compared the products obtained by Mustafa with those obtained by the addition of phenyl azide to olefins and found them to have identical melting points and infrared absorption spectra.

Kinetic studies of the addition reactions of diazomethane with various anils have now been carried out along with the synthesis of various substituted triazolines. It was found that water and methanol both catalyze the otherwise slow reaction in ether. The solvents used have a considerable effect on the yield of the reaction; *e.g.*, addition takes place to a greater extent in dioxane than in diethyl ether.

Wolff[9] and later Alder and Stein[10] suggested that the thermal decomposition of 1,5-diphenyl-1,2,3-triazoline yields a mixture of 1,2-diphenylethylenimine and the anil of acetophenone. The ethylenimine as such was not, however, isolated and characterized by these workers. Their conclusion was based on the observation that the product obtained by the pyrolysis of the triazoline had two nitrogen atoms less than the original compound and also that the triazoline was hydrolyzed by acid with evolution of nitrogen and formation

(1) *Cf.* E. P. Kohler and L. L. Steele, *J. Am. Chem. Soc.*, **41**, 1093 (1919).
(2) *Cf.* (a) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6163 (1954); (b) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409 (1956).
(3) F. Arndt and B. Eistert, *Ber.*, **61**, 1107, 1118 (1928); **68**, 196 (1935).
(4) H. Meerwein, *Angew. Chem.*, **A60**, 78 (1948).
(5) E. K. Fields and J. M. Sandri, *Chem. & Ind.*, 1216 (1959).
(6) P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **25**, 1431 (1960).
(7) A. Mustafa, *J. Chem. Soc.*, 234 (1949).
(8) G. D. Buckley, *J. Chem. Soc.*, 1850 (1954).
(9) K. L. Wolff, *Ann.*, **394**, 68 (1912).
(10) K. Alder and G. Stein, *Ann.*, **501**, 1 (1933).

of an amino alcohol, which could have been formed from an ethylenimine intermediate. A reinvestigation by us of the pyrolysis of 1,5-diphenyl-1,2,3-triazoline failed to give 1,2-diphenylethylenimine. Careful fractional crystallization of the hydrochlorides obtained by treatment of the pyrolysis product with gaseous hydrogen chloride in ether solution gave only aniline hydrochloride. Thermal decomposition of 1-phenyl-5-(*o*-nitrophenyl)-1,2,3-triazoline in *o*-dichlorobenzene at 140–150° also did not yield an ethylenimine. The reaction product after acid hydrolysis consisted only of aniline, as shown by infrared spectra.

EXPERIMENTAL

Materials. The anils were synthesised by known methods, using condensation of the appropriate aldehydes with the amines. In the case of benzal-*p*-nitroaniline[11] a modified method was used. The mixture of *p*-nitroaniline and benzaldehyde was heated at 150–160° for 8 hr. in the presence of dry nitrogen in an open round-bottom flask, and the water formed in the reaction was allowed to evaporate continuously. The water, if allowed to condense back into the reaction mixture, caused hydrolysis of the anil and a deep yellow product with a considerably lower melting point resulted, from which the pure anil could not be obtained even after repeated recrystallization. All the anils were crystallized from suitable solvents shortly before use and air dried. Benzal-*p*-chloroaniline was dried *in vacuo* at 40–45° for 2 hr. The *o*-nitrobenzaldehyde needed in the preparation of the *o*-nitrobenzal-anilines was made by oxidation of *o*-nitrotoluene.[12]

Syntheses of 1,2,3-triazolines. In a typical reaction, the anil (0.05 mole) was dissolved in an ethereal solution (200 ml.) of diazomethane (0.1 mole) (not dried)[13] and 6 ml. of methanol (reagent grade) added as catalyst. The reaction mixture was then allowed to stand in a stoppered flask at room temperature for 4 days. At the end of this period, the major portion of the ether and unchanged diazomethane was removed by careful distillation. The residue was then cooled, and the sparingly soluble triazoline crystallized out first in preference to the unchanged anil. The triazolines were recrystallized from appropriate solvents as indicated below. All the triazolines melted with vigorous decomposition, evolving gas and forming deep orange-red melts.

When dioxane was used as solvent for the reaction, the anil was dissolved in dioxane containing diazomethane (not dried) and, at the end of 4 days, the reaction mixture was diluted with water until a heavy cloudiness appeared. It was then cooled in ice, when the triazoline was thrown out as a fine crystalline material.

The compounds 1,5-diphenyl-1,2,3-triazoline and 1-phenyl-5-*p*-chlorophenyl-1,2,3-triazoline are known compounds[7,8]; the melting points of our products agreed with the literature values. The six triazolines listed below with their properties are new compounds.

1-p-Nitrophenyl-5-phenyl-1,2,3-triazoline. Pale yellow glistening needle-like crystals from acetone; m.p. 152–153°.

Anal. Calcd. for $C_{14}H_{12}N_4O_2$: C, 62.68; H, 4.48; N, 20.89. Found: C, 62.75; H, 4.51; N, 21.09.

1-Phenyl-5-p-nitrophenyl-1,2,3-triazoline. Pale yellow fluffy needle-like crystals from benzene or from acetone-petroleum ether mixture; m.p. 130–130.5°. Turns orange on exposure to air.

Anal. Calcd. for $C_{14}H_{12}N_4O_2$: C, 62.68; H, 4.48; N, 20.89. Found: C, 62.55; H, 4.29; N, 20.93.

1-Phenyl-5-o-nitrophenyl-1,2,3-triazoline. Stout, yellow crystals from benzene; m.p. 149–150°.

Anal. Calcd. for $C_{14}H_{12}N_4O_2$: C, 62.68; H, 4.48; N, 20.89. Found: C, 61.84; H, 4.62; N, 21.06.

1-p-Chlorophenyl-5-phenyl-1,2,3-triazoline. Very pale yellow, stout hexagonal crystals from ether; m.p. 130–132°.

Anal. Calcd. for $C_{14}H_{12}N_3Cl$: C, 65.24, H, 4.69; N, 16.31; Cl, 13.76. Found: C, 64.14; H, 4.59; N, 16.71; Cl, 13.14.

1-p-Methoxyphenyl-5-o-nitrophenyl-1,2,3-triazoline. Bright orange-yellow crystals from acetone; m.p. 140–140.5°.

Anal. Calcd. for $C_{15}H_{14}N_4O_3$: C, 60.40; H, 4.70; N, 18.79. Found: C, 60.36; H, 4.80; N, 18.88.

1-p-Nitrophenyl-5-p-methoxyphenyl-1,2,3-triazoline. Shiny yellow gritty crystals from acetone; m.p. 157–158°.

Anal. Calcd. for $C_{15}H_{14}N_4O_3$: C, 60.40; H, 4.70; N, 18.79. Found: C, 60.66; H, 4.66; N, 18.99.

Rate measurements. The kinetic runs were carried out in dioxane solution at 24.95° ± 0.10°. The reaction course was studied as follows: 10-Ml. aliquots (in duplicates) at appropriate time intervals were quenched into a measured volume of a cold solution of benzoic acid (U.S.P. grade recrystallized form ethanol) of known strength in dioxane. The diazomethane reacted rapidly with the benzoic acid and there was no need to shake the mixture for more than 3 min. The solution was then diluted with 100 ml. of cold distilled water and the excess benzoic acid was titrated with standard alkali using phenolphthalein as indicator. This is essentially the procedure used in determining diazomethane concentrations in ethereal solution.[13] The same amount (10 ml.) of dioxane was used for rinsing the sides of the flask during titration in all the runs. The end point of the titration is indicated by a dull orange-yellow color in the case of anils with yellow color, and by a pink color in the case of colorless anils. The amount of benzoic acid reacting with the diazomethane can be used to calculate the diazomethane concentration at a given time. At the end of each run, duplicate aliquots were quenched in benzoic acid; one was titrated immediately and the other was allowed to stand for 40 min. in the cold (10–15°) and then titrated. Both gave identical results; thus under these conditions, no hydrolysis of anil or triazoline by benzoic acid occurred.

Dioxane (Eastman Kodak, white label) was left overnight over potassium hydroxide pellets and then distilled, b.p. 98–99°. The same dioxane was used in all the kinetic runs. Diazomethane solution of approximately 2% strength was prepared by slow distillation of a dilute ethereal solution of diazomethane and collecting the distillate in an equal volume of dioxane. The amount of diethyl ether present in a run was thus reduced to a minimum.

Solutions for the runs were prepared by dissolving weighed amounts of anil in 80 or 230 ml. of dioxane in 100 or 250 ml. volumetric flasks, respectively, and allowing them to stand at 24.95° for 1–2 hr. An approximately 2% solution of diazomethane, also at 24.95°, was then added to the anil solution and the mixture made up to total of 100 or 250 ml. as the case may be. The amount of diazomethane used was such

TABLE I

REACTION OF DIAZOMETHANE WITH BENZAL-*p*-NITROANILINE[a]

$[CH_2N_2]$[b]	[Anil][b]	k_1[c]	k_2[d]
0.0338	0.451	0.204	0.45
0.0141	0.429	0.198	0.46
0.0048	0.399	0.193	0.48
0.0186	0.496	0.327	0.66[e]
0.0154	0.248	0.139	0.56
0.0094	0.111	0.071	0.64

[a] In dioxane at 24.95°. [b] Units are mole liter.$^{-1}$ [c] Units are hr.$^{-1}$ [d] Units are liter mole^{-1} hr.$^{-1}$ [e] Using a different dioxane sample.

(11) W. v. Miller and J. Plöchl, *Ber.*, **25**, 2020 (1892).

(12) S. M. Tsang, E. H. Wood and J. R. Johnson, *Org. Syntheses*, **Coll. Vol. III**, 641 (1955).

(13) Prepared from nitrosomethyl urea; *cf.*, F. Arndt, *Org. Syntheses*, **Coll. Vol. II**, 165 (1943).

TABLE II

YIELDS[a] AND RATES[b] FOR TRIAZOLINE FORMATION

Substituent					
C-Phenyl	*N*-Phenyl	Time[c]	Catalyst[d]	Yield, %	k_2[e]
H	H	240	M	10	3.5×10^{-2}
H	*p*-NO_2	21[f]	W	64	4.5×10^{-1}
		42[f]	W	75	
H	*p*-Cl	96	M	22	6.4×10^{-2}
H	*p*-CH_3	—	—	—	1.2×10^{-2}
p-NO_2	H	25	W or M	0	7.6×10^{-2}
		96	M	25	
		96[f]	W	45	
o-NO_2	H	18	None	5	—
		21	M or W	25	
		21	M plus W	25	
		96	M	56	
p-Cl	H	240	M	<10	1.5×10^{-2}
o-NO_2	*p*-OCH_3	21	M or W	7	—
		96	M or W	20	
p-OCH_3	*p*-NO_2	96[f]	W	53	—

[a] The data in the columns labelled time, catalyst and yield are for experiments in diethyl ether at room temperature to test for best synthetic conditions. [b] Rates are for dioxane solution at 24.95°. [c] Time in hours. [d] M is methanol and W is water. [e] Units are liter $mole^{-1}$ $hr.^{-1}$ [f] In dioxane as solvent.

that the concentration of the latter permitted accurate measurements by the titration procedure adopted. The standard alkali solutions used were diluted (0.03–0.05*N*) to permit greater accuracy in the experimental procedure.

Pseudo first order rate constants k_1 were calculated by dividing the factor 0.693 by the half-life of the reaction; this was obtained from the plot of log CH_2N_2 concentration against time. The second-order rate constants k_2 were obtained by dividing the k_1 values by the anil concentration which was in large excess. Some data which illustrate concentrations, etc., of the kinetic runs are shown in Table I.

RESULTS AND DISCUSSION

Ethylenimine synthesis. The initial purpose of the present investigation was to find new ways to prepare ethylenimines (aziridines). Methods tried included: (a) reaction of diazomethane with anils under a variety of conditions including boron trifluoride catalysis and light activation, (b) reaction of aliphatic Schiff's bases with dichlorocarbene, and (c) pyrolysis of the 1,2,3-triazolines formed by the direct addition of diazomethane to aromatic anils. No ethylenimine was isolated nor was any identified (in the liquid product mixtures) by either infrared or gas chromatography. It seems safe to conclude that the reaction of diazomethane or other carbene-formers with anils to give ethylenimine shows little promise as a general synthetic route. The only exception presently known is the formation of 1,2-diphenyl-3,3-dichloroethylenimine.[5,6]

In view of the nature of the results obtained on ethylenimine synthesis, we have merely listed general areas of experimentation that were carried out. Details may be obtained from the authors as to conditions and results; however, publication of these details seems to be unwarranted at the present time.

Triazoline synthesis. The method of synthesis of triazolines was mentioned previously. It was observed during these preparations that the yields depended significantly on the reaction time and on the substituent groups of the aromatic rings. This strongly suggested that the reaction of diazomethane with a benzalaniline has a rate convenient for measurment. In Table II data on yields for eight triazolines are presented; among the factors studied were solvent, catalyst (water or methanol), and time. These results will be discussed after the kinetic data are presented.

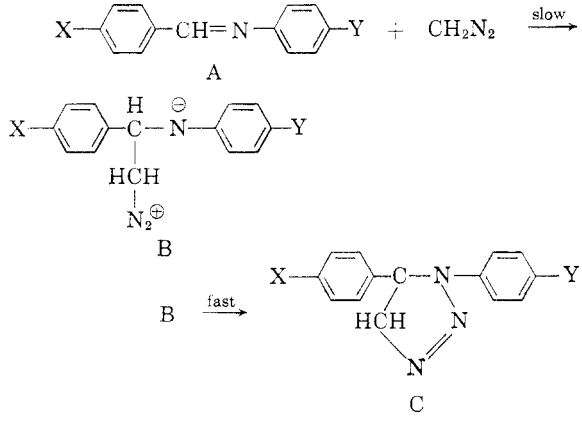
Kinetics. The results are summarized in the tables. In Table I are presented the first and second order rate constants for the addition reaction of diazomethane with benzal-*p*-nitroaniline at 24.95° at several different anil concentrations (always in excess). The reaction in first order in diazomethane concentration as good straight lines were obtained when the logarithm of the concentration of diazomethane was plotted against time; also the rate constant is independent of diazomethane concentration. The first order rate constants are dependent on first power of the anil concentration as seen from the data in Table I; the reaction thus follows simple second order kinetics.

The last column of Table II gives the second order rate constants for the reaction of diazomethane with benzal aniline and five anils having substituents on the *N*-phenyl and C-phenyl groups. Also given for comparison are the yields of triazolines obtained in the synthetic experiments; the parallelism between rate and yield is striking.

These results indicate conclusively that the diazomethane molecule is acting as a nucleophile in attacking the anil for the rate of reaction is increased by placing electron-withdrawing groups on the benzene rings of the anil and is decreased by the presence of electron-releasing groups. The results also show that substituents on the *N*-phenyl

group of the anil have a large polar effect whereas those on the C-phenyl have only a small polar effect. But the results do not of themselves indicate the site of attack, as either end of the diazomethane molecule could conceivably add to the anil in the rate step. It is possible, however, to give a satisfactory answer to this question of site, for several pieces of evidence (chemical data and kinetic studies) agree with a single mechanistic postulation.

Mechanism. Consider the mechanism



where the reaction is made of two steps, a slow and rate-determining step (A → B) and a subsequent rapid ring closure (B → C). There is a zwitterion intermediate B formed in the first step, which step is the nucleophilic attack by the carbon in diazomethane on the double bond carbon of the anil. It is pertinent to note here that the carbon of diazomethane has often been postulated to have nucleophilic character.[8,14] Also, double bonds are usually attacked at the position β to the activating group,[15] which certainly in our case is the *N*-phenyl group. There is little doubt that it is the carbon-carbon bond which is formed in the rate step.

The reaction coordinate diagram may be represented as shown in Fig. 1. The transition state is presumably close in energy content to the intermediate B, which fact suggests that the Hammond postulate[16] can be employed in discussion of the mechanism. One would, on the basis of this postulate, expect the transition state to have properties similar to the zwitterion intermediate. Some of the observations consistent with this are as follows: (a) The rate is dependent on solvent nature and the addition of a little water or methanol has a definite accelerating effect on the rate. (b) Electron-withdrawing substituents on the *N*-phenyl have a strong effect because of the high electron density on the nitrogen attached to this ring. The results should be, and are, particularly striking where conjugation of the type can occur. (c) The resonance

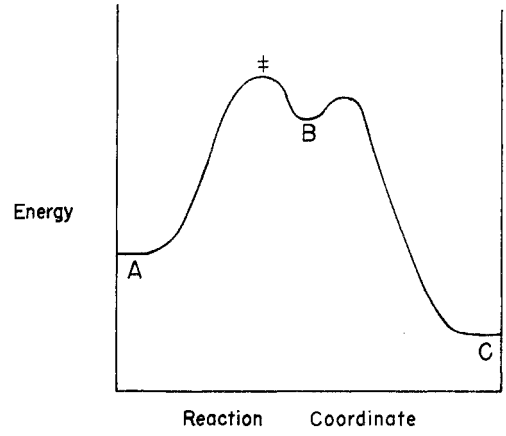
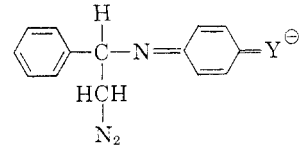
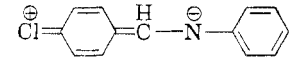


Fig. 1. Proposed reaction coordinate diagram for the reaction of aromatic Schiff's bases with diazomethane. Letters A, B, and C refer to reactants, zwitterion intermediate and product, respectively



between the C-phenyl ring and the double bond is broken as the new carbon-carbon bond is formed; thus electron-withdrawing substituents on C-phenyl should enhance the rate but not to a large extent. Such is the observation. The low rate (slower than benzalaniline itself) observed in the case of *p*-chlorobenzalaniline is presumably due to mesomeric double-bonding of the type which would



result in a lowering of the energy of the ground state A.

The observation that a comparatively high yield is obtained when the nitro-group on C-phenyl is in the *ortho* position is interesting. One possible explanation is that steric inhibition of resonance in the *ortho* case has raised the ground state energy, thus decreasing the activation energy. Unfortunately it was not possible for us to do any further experiments; therefore we were not able to test this particular hypothesis or to evaluate activation parameters for the addition reaction.

General significance. The mechanism of the addition of diazomethane to anils as postulated here is of general significance for certain other reactions have related mechanisms. One of these is the Michael addition,[15] which involves the attack of a carbanion on an activated double bond. Another is the attack of peroxy anions on double bonds.[17] In each case the site of attack by the nucleophile is the carbon which is *beta* to the acti-

(14) E. R. Alexander, *Ionic Organic Reactions*, Wiley, New York, 1950, p. 52.

(15) E. S. Gould, *Mechanism and Structure in Organic Chemistry*, Henry Holt, New York, 1959, p. 393.

(16) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(17) H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).

vating group. A related mechanism applies for the addition of diazomethane and diphenyldiazomethane to the double bond in maleic and fumaric esters[18] and maleic anhydride. The same addition product is obtained from the two esters and these when heated split off nitrogen to yield a *trans*-cyclopropane dicarboxylic acid. However, addition of diphenyldiazomethane to maleic anhydride yields a pyrazoline from which a *cis*-cyclopropane dicarboxylic acid is obtained. These results can be explained on the basis of an intermediate zwitterion addition product. In the case of the esters, as the C=C double bond is converted to a single bond in the intermediate, freedom of rotation is achieved resulting in identical pyrazolines, whereas in the case of the anhydride, no rotational freedom is achieved in the intermediate because of its cyclic nature. It has also been shown recently that the addition reactions of *p*-substituted diphenyldiazomethane to maleic ester and related compounds have rates consistent with the diazomethane acting as a nucleophile[19] and with there being an intermediate present in the reaction.

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(18) *Cf.* J. van Alphen, *Rec. Trav. Chim.*, **62**, 210 (1943).

(19) N. B. Mehta, R. E. Brooks, and R. Baltzly, A.C.S. Meeting, Sept. 1960, New York City; paper #89, Abstracts of the Organic Chemistry Division.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF VIRGINIA]

2-Phenylcyclobutylamine

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The DL-*cis* and -*trans* isomers of 2-phenylcyclobutylamine have been synthesized in a sequence of reactions involving DL-*cis*- and -*trans*-2-phenylcyclobutanecarboxylic acids and 2-phenylcyclobutanone. An improved route to 2-phenylcyclobutane-1,1-dicarboxylic acid is also reported.

The discovery[2] of the potent inhibition of monoamine oxidases[3] by 2-phenylcyclopropylamine[4] (tranylcypromine) made it of interest to compare the effect of ring-homologous phenylcycloalkylamines on such enzymes. 2-Phenylcyclopentylamine,[5] 2-phenylcyclohexylamine,[6] and 2-phenylcycloheptylamine[7] have been described in the literature and 3-phenylcyclobutylamine has recently been reported.[8] This article describes the synthesis of *cis*- and *trans*-2-phenylcyclobutylamines.

Since cyclobutanecarboxylic acids have been successfully degraded to amines,[9] 2-phenylcyclobutanecarboxylic acid appeared to be a suitable starting material for our purpose. An oily 2-phenylcyclobutanecarboxylic acid,characterized as the *p*-toluidide, has been synthesized by Burger and Hofstetter[10] by decarboxylation of 2-phenylcyclobutane-1,1-dicarboxylic acid. However, the yields both in the lengthy synthesis of this dicarboxylic acid and in the decarboxylation were so low that they severely limited that sequence for preparative purposes. A new and more rewarding synthesis of 2-phenylcyclobutane-1,1-dicarboxylic acid has therefore been developed.

Diethyl cinnamylmalonate (I) was prepared by the alkylation of diethyl malonate with cinnamyl chloride.[11] Addition of hydrogen bromide to this unsaturated ester gave diethyl (3-bromo-3-phenylpropyl)malonate (II) and this was cyclized to diethyl 2-phenylcyclobutane-1,1-dicarboxylate (III) with sodium hydride in tetrahydrofuran. Alkaline hydrolysis of III led to 2-phenylcyclobutane-1,1-dicarboxylic acid (IV) in a yield of 80% based on I. The compound was identical with that previously reported.[10]

$$C_6H_5CH{=}CHCH_2Cl \xrightarrow{Na^+\bar{C}H(CO_2C_2H_5)_2} C_6H_5CH{=}CHCH_2CH(CO_2C_2H_5)_2 \quad (I) \xrightarrow{HBr}$$

[1] Smith, Kline & French Laboratories Postdoctoral Fellow, 1959–61.

(2) R. E. Tedeschi, D. H. Tedeschi, P. L. Ames, L. Cook, P. A. Mattis, and E. J. Fellows, *Proc. Soc. Exptl. Biol. Med.*, **102**, 380 (1959).

(3) S. Sarkar, R. Banerjee, M. S. Ise, and E. A. Zeller, *Helv. Chim. Acta*, **43**, 439 (1960).

(4) A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).

(5) See, for example, T. R. Govindachari, K. Nagarajan, B. R. Pai, and N. Arumugan, *J. Chem. Soc.*, 4280 (1956).

(6) See, for example, R. T. Arnold and P. N. Richardson, *J. Am. Chem. Soc.*, **76**, 3649 (1954).

(7) A. Burger, C. R. Walter, W. B. Bennett, and L. B. Turnbull, *Science*, **112**, 306 (1950).

(8) A. Burger and R. Bennett, *J. Med. and Pharm. Chem.*, **2**, 687 (1960).

(9) E. R. Buchmann, A. O. Reims, T. Skei, and M. J Schlatter, *J. Am. Chem. Soc.*, **64**, 2696 (1942).

(10) A. Burger and A. Hofstetter, *J. Org. Chem.*, **24**, 1290 (1959).