The Preparation of 1-Nitropentane.—A solution of 135 g. (0.894 mole) of *n*-amyl bromide in 100 ml. of petroleum ether (45–55°), contained in a 500-ml. three-necked flask fitted with a reflux condenser, mercury-sealed Hershberg stirrer and thermometer, was chilled in an ice-bath to 3°. A 5% excess (145 g.) of silver nitrite was added as rapidly as possible, the ice-bath removed, and the temperature of the well-stirred mixture allowed to rise to 40° (1/2 hour). The temperature of the exothermic reaction was kept at 38–42° for 5.5 hours by external cooling. A bromide test on the reaction liquor was negative at the end of this time. (It was carried out by warming a sample with alcoholic potassium hydroxide, acidifying with dilute nitric acid, and adding a solution of silver nitrate).

The mixture was filtered, and the silver salts washed on the funnel with 7 × 50 ml. of petroleum ether (45–55°). Removal of the solvent and low-boiling by-products (mostly alkyl nitrite) was carried out up to a bath temperature of 83° (25 mm.). A 15-cm. Vigreux column was used. The pale yellow liquid residue weighed 80.3 g.

The crude product thus obtained was added dropwise to a stirred solution of 5 g. of urea in 250 ml. of concentrated sulfuric acid at 0°. The temperature was kept between 0–2° by the rate of addition and by chilling in an ice–salt-bath (twenty minutes for complete addition). The resulting yellow solution was stirred for 10 minutes longer at 0°, and then, with manual stirring, poured over 500 g. of cracked ice to which had been added 200 ml. of petroleum ether (45–55°). The container was chilled in a salt–ice-bath during this process. After separation of the layers, the aqueous layer was extracted with 2 × 150 ml. of petroleum ether (45–55°). The combined organic layers were washed with 3 × 800 ml. of saturated sodium chloride solution and dried over calcium chloride. Removal of the solvent under reduced pressure left 72.0 g. of pale yellow liquid which was rectified at 23 mm. through the column described above. Three fractions were taken. The combined fractions weighed 69.60 g., corresponding to 66.6% of that calculated.

Fraction	B.p., °C.	$n^{25}D$	Wt., g.	Color
1	75.0–75.5	1.4152	0.55	Colorless
2	75.5–76.0	1.4154	6.45	Colorless
3	76.0–76.1	1.4154	62.60	Colorless

COLLEGE PARK, MARYLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azo-bis Nitriles.[1] Decomposition of Azo Compounds. A Special Case of Carbon–Carbon Hyperconjugation in a Free Radical Reaction

BY C. G. OVERBERGER AND ALEXANDER LEBOVITS

RECEIVED JANUARY 9, 1954

Azo nitriles prepared from methyl cyclobutyl ketone, methyl cyclopentyl ketone and methyl cyclohexyl ketone have been prepared and characterized. The rates of decomposition have been measured and compared with the rate of decomposition of the azo nitrile from methyl cyclopropyl ketone. The evidence strongly indicates that the enhanced rate of decomposition of the methyl cyclopropyl azo nitrile is due to delocalization of the carbon–carbon bond in the cyclopropane ring (hyperconjugation). This is the first reported case of carbon–carbon radical hyperconjugation which has strong experimental support.

There is considerable evidence largely based on calculations of ionization potentials that hyperconjugation is of much greater importance in carbonium ion transition states than in radical ones.[2] Although there is some experimental indication that hyperconjugation of hydrogen atoms in radical transition states may influence the rate of some reactions, there is no experimental evidence for carbon–carbon hyperconjugation in a radical reaction.

This paper describes the preparation and decomposition of the azo nitriles derived from methyl cyclobutyl, methyl cyclopentyl and methyl cyclohexyl ketones and compares these results with those previously obtained from the decomposition of methyl cyclopropyl ketone.[3]

The evidence strongly supports a case of carbon–carbon radical hyperconjugation previously suggested.[3] These results again emphasize the value of radical formers which decompose by kinetically clean processes independent of solvent effects, for studying the effect of structure on reactivity.

A. Preparation of Azo Compounds

1. **Discussion.**—The azo compounds from methyl cyclobutyl, methyl cyclopentyl and methyl cyclohexyl ketones were prepared according to previously described procedures.[4] Methyl cyclobutyl ketone was prepared by reaction of cyclobutanecarbonyl chloride with the magnesium salt of malonic ester. This preparation represents a useful procedure for its synthesis.[5] The cyclopentyl and cyclohexyl ketones were prepared from the corresponding cycloalkylmagnesium bromides and acetic anhydride at low temperatures according to the general procedure of Newman and Smith.[6] No attempt is made here to record the numerous reported syntheses of these three cycloalkyl ketones; it is sufficient to state that they have not been reported prepared by the methods described here.

Both stereoisomers, the *dl* and *meso* forms of the azo compounds of methyl cyclobutyl ketone and methyl cyclopentyl ketone were isolated and characterized. Two stereoisomeric 1,2-disubstituted hydrazines were isolated from the reaction with methyl cyclopentyl ketone. Separation was effected by fractional crystallization. The separa-

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[1] This is the tenth in a series of articles concerned with the decomposition of azo compounds. For the ninth paper in this series, see C. G. Overberger, P. T. Huang and T. B. Gibb, Jr., THIS JOURNAL, **75**, 2082 (1953).

[2] E. C. Baugham, M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1941).

[3] C. G. Overberger and M. B. Berenbaum, THIS JOURNAL, **73**, 2618 (1951).

[4] C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

[5] H. G. Walker and C. R. Hauser, *ibid.*, **68**, 1386 (1946).

[6] M. S. Newman and A. S. Smith, *J. Org. Chem.*, **13**, 592 (1948)

tion of similar isomers from other unsymmetrical ketones was reported previously.[3]

The coupled products from the cyclopentyl and cyclohexyl azo compounds obtained in the kinetic experiments were also characterized. The products obtained from the decomposition of methyl cyclobutyl ketone will be reported separately.

It has also been demonstrated that the 1,2-disubstituted hydrazine nitrile from acetone can be successfully oxidized by means of sodium permanganate in acid solution in 62% yield.

Experimental[7]

Cyclobutanecarboxylic Acid.—The procedure was similar to that described by Cason and Rapaport[8] except that 5 times the quantities were used.

Methyl Cyclobutyl Ketone.—Cyclobutanecarbonyl chloride was prepared from cyclobutanecarboxylic acid and a 50–60% excess of phosphorus trichloride, 55%, b.p. 136.5–140° (atm.).

The general procedure of Walker and Hauser[5] for the preparation of methyl ketones from the magnesium salt of malonic ester and an acid chloride was used. The magnesium salt of ethyl malonate was prepared according to the procedure of the above reference from 80 g. (0.5 mole) of ethyl malonate, 12.16 g. (0.5 g. atom) of magnesium turnings in 61 ml. of ethanol and 178 g. of anhydrous ether. To this was added 32.3 g. (0.27 mole) of the cyclobutanecarbonyl chloride in ethereal solution with vigorous stirring as fast as the refluxing would permit. The reaction mixture was refluxed for 1/2 hour and allowed to stand overnight. The condensate was hydrolyzed and decarboxylated as described in reference 5. The reaction mixture was poured into 2.5 moles of sodium hydroxide in 400 g. of ice and water. The organic layer was separated, washed with sodium hydroxide solution followed by water and the aqueous layers were combined and extracted with ether. The ether layer was washed with water, added to the organic layer and dried. The residue was distilled through a Vigreux column, 14.9 g. (55.5%), b.p. 134.5–141° (763 mm.), $n^{25}\text{D}$ 1.4290 (b.p. 134.8–135.2° (750 mm.), $n^{25}\text{D}$ 1.4300, from acetic acid and cyclobutanecarboxylic acid over a manganous carbonate catalyst).[9]

A 2,4-dinitrophenylhydrazone[10] was prepared, m.p. 123.9–126.9° (m.p. 119.9–121.3° uncor.).[9]

Methyl Cyclopentyl Ketone.—The procedure of Newman and Smith[6] for the preparation of ketones from anhydrides at low temperatures was utilized. The Grignard reagent from 40 g. (1.65 g. atoms) of magnesium turnings, 164.5 g. (1.1 moles) of cyclopentyl bromide in 440 g. of ether was prepared. This solution was added to 115 g. (1.13 moles) of acetic anhydride in 204 g. of ether at −70° with vigorous stirring over a 75-minute period. The reaction mixture was allowed to warm to −10°, water was added and the ether layer separated. The aqueous layer was extracted with ether, the ether solutions combined and shaken with potassium hydroxide solution followed by washing with water. All aqueous solutions were again extracted with ether and the combined ethereal solutions dried over anhydrous magnesium sulfate. The residue was distilled through a Vigreux column followed by redistillation of several fractions. 53 g. (43%), b.p. 85.3–88.3° (78.5–79 mm.), $n^{25}\text{D}$ 1.4409 (b.p. 94.8–95.0° (99 mm.), $n^{25}\text{D}$ 1.4411, prepared from acetic acid and cyclopentanecarboxylic acid).[9]

The 2,4-dinitrophenylhydrazone[10] was prepared, m.p. 126.9–127.7° (m.p. 126.9–127.3, uncor.).[9]

Methyl Cyclohexyl Ketone.—Methyl cyclohexyl ketone was prepared by a procedure similar to that described previously for methyl cyclopentyl ketone (62.3%), b.p. 71–74.2° (17–18 mm.), $n^{25}\text{D}$ 1.4482 (b.p. 76.2–77.0° (25 mm.), $n^{25}\text{D}$ 1.4491, prepared from acetic acid and cyclohexanecarboxylic acid).[9]

The 2,4-dinitrophenylhydrazone[10] was prepared, m.p. 140.2–141.8 (m.p. 136.0–136.6°, uncor.).[9]

When acetyl chloride was substituted for acetic anhydride in this procedure, the yields were poor.

2,2′-Azo-bis-2-cyclobutylpropionitrile.—This compound was prepared by previously described procedures.[4] The crude hydrazine nitrile was obtained from 10.04 g. (0.102 mole) of methyl cyclobutyl ketone, 7.28 g. (0.056 mole) of hydrazine sulfate, 5.86 g. (0.12 mole) of sodium cyanide and 100 ml. of water. The reaction mixture was shaken for five days and the oil which formed extracted with ether. The crude hydrazine obtained after drying of the ether solution and removal of the solvent was dissolved in 150 ml. of alcohol, 75 ml. of water and 75 ml. of concentrated hydrochloric acid was added and the compound oxidized with bromine as previously described. The reaction mixture was poured into a large volume of ice-water and the solid removed by filtration. Decolorization in ether solution with "Norite" followed by recrystallization from an ether–petroleum ether (b.p. 33–35°) mixture at Dry Ice temperatures gave 6.1 g. (49% based on cyclobutyl methyl ketone) of crystals having a wide melting range.

Repeated recrystallization from a mixture of ether and petroleum ether gave rod-shaped crystals, m.p. 82.3–82.9° dec. (softens at 82°).

Anal.[11] Calcd. for $C_{14}H_{20}N_4$: C, 68.81; H, 8.25; N, 22.94. Found: C, 68.81; H, 8.00; N, 22.81.

From the mother liquor of the above recrystallization, 4.5 g. of crystals, as needles was obtained which were recrystallized from petroleum ether. Besides an additional amount of the isomer melting at 82.3–82.9°, a second more soluble isomer was obtained, m.p. 38–42°.

Anal. Calcd. for $C_{14}H_{20}N_4$: C, 68.81; H, 8.25; N, 22.94. Found: C, 68.93; H, 8.38; N, 22.80.

Numerous attempts were made to isolate the solid 1,2-disubstituted hydrazine nitrile precursors, either as the free base or as a salt without success. An impure hydrochloride salt was obtained but was not purified. Good yields of these pure azo isomers are difficult to obtain because of the necessary fractional crystallizations.

1,2-Di-(1-cyclopentyl-1-cyano)-ethylhydrazine.—The previously described procedure was employed. A reaction mixture of 20 g. (0.178 mole) of methyl cyclopentyl ketone, 9.6 g. (0.195 mole) of sodium cyanide, 12.7 g. (0.098 mole) of hydrazine sulfate and 200 ml. of water was shaken for six days. The aqueous layer was removed, extracted with ether and the ether was combined with the semi-solid oil which had formed in the reaction. The latter did not dissolve completely in the ether and a crystalline residue remained. This residue was washed with small portions of fresh ether and then dissolved in acetone. From the acetone solution, on cooling, crystals in the form of square plates were obtained. From the mother liquor several additional crops of crystals were obtained, total yield 5.87 g., m.p. 128.7–134° (24%). An analytical sample was prepared by recrystallization from ether and melted at 133.9–134.9° dec.

Anal. Calcd. for $C_{16}H_{26}N_4$: C, 70.02; H, 9.56; N, 20.42. Found: C, 70.09; H, 9.50; N, 20.52.

All the ether wash solutions described previously were combined, washed with water, decolorized with charcoal and dried over anhydrous magnesium sulfate. After adding petroleum ether and cooling to Dry Ice temperatures, 7.11 g. (29%) of crystals, m.p. 90–96°, was obtained. Repeated recrystallizations of this isomer from a wide variety of solvents failed to effect a narrower range of melting. From one of many experiments, crystals were obtained after many recrystallizations melting at 89.5–94°. Although the analysis of this compound demonstrates the correct empirical formula, it is likely that some high melting isomer may be present.

Anal. Calcd. for $C_{16}H_{26}N_4$: C, 70.02; H, 9.56; N, 20.42. Found: C, 70.09; H, 9.65; N, 20.34.

2,2′-Azo-bis-2-cyclopentylpropionitrile.—A sample of the high melting hydrazine from methyl cyclopentyl ketone, 0.53 g. (0.00195 mole), m.p. 135.0–136.2° dec., oxidized as previously described, gave a near quantitative yield of azo compound, m.p. 98.1–98.7° (softens 97.1°). Recrystallization from an ether–petroleum ether mixture at 0° gave needles, m.p. 98.2–99.7° dec.

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(7) All melting points are corrected.

(8) J. Cason and H. Rapaport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 304.

(9) R. P. Mariella and R. R. Raube, THIS JOURNAL, **74**, 518 (1952).

(10) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(11) Analyses by Dr. K. Ritter, Zurich, Switzerland; Dr. F Schwarzkopf, New York, N. Y.

Anal. Calcd. for $C_{16}H_{24}N_4$: C, 70.53; H, 8.89; N, 20.57. Found: C, 70.52; H, 8.85; N, 20.29.

The low melting isomer was obtained from the mixture of stereoisomers. In a separate experiment similar except for minor details, 45% of solid azo compound was obtained, m.p. 70–86°. Repeated recrystallization from a mixture of ether and petroleum ether allowed the removal of the isomer melting *ca.* 98° since it is more insoluble. The more soluble isomer was obtained on successive recrystallizations, m.p. 72.2–74.5° (softens 70.5°).

Anal. Calcd. for $C_{16}H_{24}N_4$: C, 70.53; H, 8.89; N, 20.57. Found: C, 70.64; H, 8.74; N, 20.44.

2,2′-Azo-bis-2-cyclohexylpropionitrile.—The procedure was similar to that described for the preparation of the azo compound from methyl cyclobutyl ketone. The hydrazine was not isolated as a solid although numerous attempts were made. Repeated recrystallization of the solid product gave 31.7% yield of three solid fractions. The first of these fractions, m.p. 109–109.5° dec. (softens 108.2°) on repeated recrystallization from an ether–petroleum ether mixture gave the same melting point.

Anal. Calcd. for $C_{18}H_{28}N_4$: C, 71.96; H, 9.39; N, 18.65. Found: C, 71.93; H, 9.50; N, 18.65.

Decomposition Products from Azo Compounds. (1) **Decomposition Product from 2,2′-Azo-bis-2-cyclopentylpropionitrile.**—The colorless solutions from all kinetic experiments, 1.0992 g. (0.00403 mole) of azo nitrile were combined and the solvent removed to a volume of 9.7 ml. under reduced pressure. On cooling to Dry Ice temperatures, successive crops of crystals were obtained, 0.465 g., m.p. 98–115° (47.2%). Repeated crystallization from ethano gave a high melting isomer, m.p. 129–131°, most probably the product arising from the coupling of the two radicals.

Anal. Calcd. for $C_{16}H_{24}N_2$: N, 11.47. Found: N, 11.54.

An oil residue from the initial crystallization of solid was not identified.

Decomposition Product from 2.2′-Azo-bis-2-cyclohexylpropionitrile.—A solution of 2.059 g. (0.0069 mole) of azo compound and 150 g. of benzene was refluxed for 14 hours. The solvent was removed under reduced pressure. The residue, a solid, was dissolved in petroleum ether and fractionally recrystallized (7 fractions). The first crop, 942 mg. (50%), m.p. 122–140°, was sublimed at a bath temperature of 120–130° at 0.5 mm. Pure product could not be isolated from the other fractions. The sublimate on recrystallization from petroleum ether melted at 121–124°.

Anal. Calcd. for $C_{18}H_{28}N_2$: N, 10.28. Found: N, 10.57.

Oxidation of Hydrazine from Acetone with Acidic Sodium Permanganate.—To a solution of 40 ml. of glacial acetic acid and 3 ml. of concentrated sulfuric acid was added 0.989 g. (0.006 mole) of the 1,2-hydrazine nitrile from acetone $[(CH_3)_2(CN)C{-}NH{-}]_2$ and the solution cooled in ice. A solution of 2.6 g. of sodium permanganate trihydrate in 50 ml. of water was prepared and 25 ml. of this solution was added. Manganese dioxide immediately precipitated. The excess permanganate and the manganese dioxide formed were reduced with sodium bisulfite and the solution poured into ice-water. The azo compound which precipitated was removed by filtration, washed with water and dried in a vacuum desiccator. 0.608 g. (62%), m.p. 102.1–103.2° (103–104°).[4]

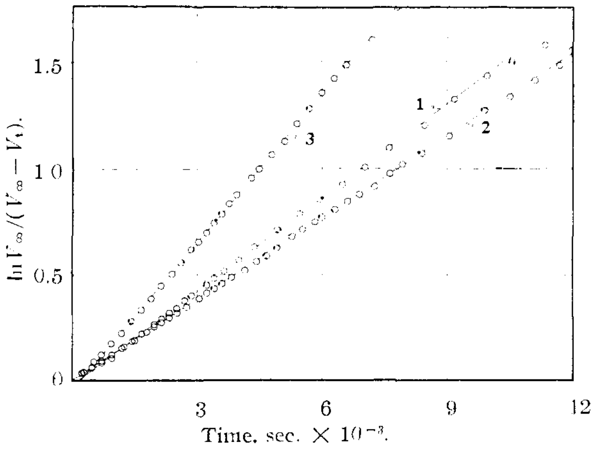


Fig. 1. Decomposition of azonitriles in toluene at 80.5°: 1, azonitrile from methyl cyclobutyl ketone, m.p. 81.5-82.5°; 2, azonitrile from methyl cyclopentyl ketone, m.p. 96.3-97.6°; 3, azonitrile from methyl cyclohexyl ketone, m.p. 108.6-109.4°.

B. Kinetic Measurements

I. Procedure.—The procedure for measuring rates of decomposition has been described previously.[3,4]

II. Results.—The rates of decomposition of the compounds, $R(CH_3)(CN)C{-}N{=}N{-}C(CN)(CH_3){-}R$ where R = cyclo-C_4H_7, cyclo-C_5H_9 and cyclo-C_6H_{11} as measured by nitrogen evolution are reported in Table I. Rate constants for both stereoisomers of compounds R = cyclo-C_4H_7 and cyclo-C_5H_9 are included. Table I contains average rate constants for each compound for decompositions carried out in toluene at 80.5°. Previous work has shown that the effect of solvent and concentration on the rate of decompositions of similar compounds is negligible.[3,4] In Fig. 1, plots of $\ln V_\infty/(V_\infty - V_t)$ *vs.* time are reproduced for a typical decomposition of one of the stereoisomers of each azo compound.

TABLE I

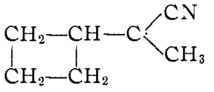
DECOMPOSITION OF AZO COMPOUNDS IN TOLUENE AT 80.5°[a]

$(R{-}C(CH_3)(CN){-}N_2$

R	Azo nitrile, m.p., °C.	k, sec.$^{-1}$ × 10^4	No. of runs	Concn. range, mole/l.	Av. dev.
Cyclo-C_3H_5[b]	64–65	33[d]	7		
Cyclo-C_4H_7	81.5–82.5	1.51	3	0.0157–0.0270	0.01
Cyclo-C_4H_7	38–42	1.51	1	.0238	
Cyclo-C_5H_9	96.3–97.6	1.30	3	.0188–0.0277	.005
Cyclo-C_5H_9	72.2–74.5	1.31	1	.0256	
Cyclo-C_6H_{11}	108.6–109.4[c]	2.27	4	.0106–0.0232	.10

[a] If R = CH_3, k = 1.60–1.72 sec.$^{-1}$ × 10^4, ref. 4. [b] Reported in reference 3, high melting isomer. [c] A number of samples used to determine the average rate constant melted several degrees higher. [d] Corrected to 80.2°, one stereoisomer, ref. 3.

III. Discussion of Results.—The results demonstrate that there is no major enhancement in the rate of decomposition of the three methyl cycloalkyl ketones described here when compared with the azo compound derived from acetone. This lends strong support to the theory that there is no difference in the steric interaction between the two halves of the molecule in the *trans* azo configuration of these compounds. This point has been discussed in previous papers. It is again noted that the two stereoisomeric forms decompose at the same rate as has previously been reported for other isomer pairs.[3] The slight enhancement of rate for the azo compound from methyl cyclohexyl ketone might conceivably be due to slight steric interaction of the type suggested above and previously discussed. In an earlier paper, we had suggested that the increased rate of decomposition for the azo nitrile derived from methyl cyclopropyl ketone was due to transition state resonance of the type involving delocalization of the carbon–carbon bonds of the cyclopropyl ring. The possibility of back strain or even steric interaction between the two halves of the molecule (front strain) could, however, not be ruled out at that time. The fact that the azo nitrile from methyl cyclobutyl ketone did not show this enhancement of rate strongly supports the suggestion that this is a true case of hyperconjugation and not back strain—no other simple conclusion can be drawn from the evidence. The evidence indicates that the formation of radical I is not accompanied by stabilization involving delocalization of the carbon–carbon bonds of the cyclobutyl ring. The cyclopropyl case is similar in principle to the solvolysis of cyclopropylcarbinyl chloride where it has been demonstrated that extensive stabilization of the cyclopropylcarbinylcarbonium ion is responsible for the high reactivity of the chloride. There is undoubtedly a difference of degree in the radical case and there remains a question whether electron distributions such as A, B, C and D contribute more or less than types indicated by E and F. It is not possible at present to assess the relative contribution of a distribution such as C, and thus whether any increase in the decomposition rate of the cyclopropyl compound is due to a driving force of a rearrangement to products resulting from structure C.



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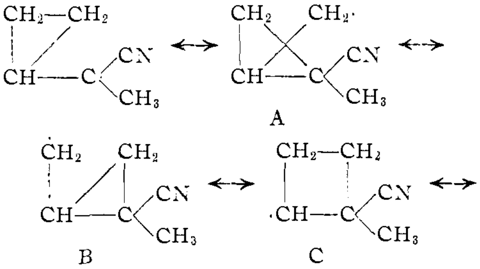

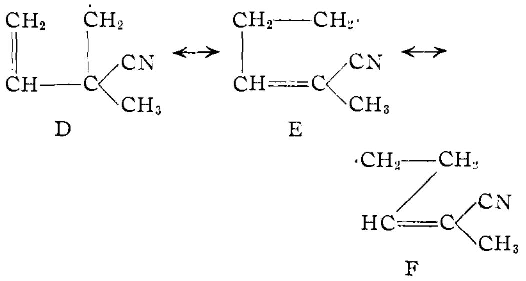

The distributions depicted by A, B, C and D represent structures formally similar to those suggested for the symmetrical cyclopropylcarbinylcarbonium ion for which considerable evidence was amassed.[12]

Roberts and Mazur[12] in discussing the symmetrical cyclopropylcarbinylcarbonium ion point out that the three extra Sp^3 orbitals of each of the methylene groups are positioned so that they do overlap and can form one stable molecular orbital holding two electrons and two vacant considerably less stable orbitals. In the corresponding radical form there is an excess electron which could necessarily go into a less stable orbital. Thus, distributions such as A, B and C may contribute very little since they are less probable. They reported no interconversion to cyclopropyl derivatives when cyclobutane was chlorinated in the light in the vapor phase to give cyclobutyl chloride.

It is noteworthy that Mariella and Raube[9] in a study of the ultraviolet absorption spectra of cycloalkyl methyl ketones have concluded that some interaction of the carbonyl group with the ring may occur in some excited states with cycloalkyl groups higher than cyclopropyl.

(12) J. D. Roberts and R. H. Mazur, THIS JOURNAL, **73**, 2509 (1951); **73**, 3542 (1951).

BROOKLYN, NEW YORK

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

Optical Bleaching Agents. I. Derivatives of Dichlorodiaminostilbenedisulfonic Acid

BY D. W. HEIN AND ELLIOT S. PIERCE

RECEIVED OCTOBER 22, 1953

Two new dye intermediates, 5,5-dichloro- (III) and 6,6′-dichloro-4,4′-diaminostilbene-2,2′-disulfonic acid (IV) were prepared, and several new optical bleaching agents were prepared from them, mainly by acylation with substituted benzoyl chlorides. The fluorescent properties and ultraviolet absorbency characteristics of the products were compared with those of the corresponding acyl derivatives of 4,4′-diaminostilbene-2,2′-disulfonic acid.

The use of fluorescent colorless dyes in laundry soaps to counteract the gray or yellow tinges of white fabrics and to brighten colored fabrics is well established.[1] Previously, it was general practice to neutralize the yellow tinge of white fabrics by the use of a blue dye ("bluing"). Unless a careful balance was struck between the relative amounts of blue and yellow colors, there was always a residual blue or yellow tinge depending upon which was in excess. Even when a careful balance was struck between the blue and yellow components, there was always some graying or dulling since the total amount of light reflected from the surface of the cloth was less than when no "bluing" was used. This was due to the fact that the blue dye absorbed some of the impinging light.

Optical bleaches are fluorescent colorless dyes which operate by absorbing ultraviolet light and re-emitting this energy as blue light. By their use, the natural yellow tinge of the fabric is neutralized by resupplying the blue light absorbed by the yellow substance. Since the total amount of light coming from the surface of the fabric is greater than when the optical bleach is absent, a true

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(1) T. F. Cooke, H. E. Millson and E. I. Stearns, *Soap Sanit. Chemicals*, **XXVI**, No. 3, 37 (1950); *ibid.*, **XXVI**, No. 4, 48 (1950).