recrystallized several times from ethanol, yield 80–90%, m.p. 46–47°.

Anal. Calcd. for $C_{19}H_{24}N_2O_6$: C, 60.6; H, 6.4. Found: C, 60.7; H, 6.5.

The phenylurethan of VI was obtained in 90% yield, and after recrystallizations from hexane–pentane mixtures it melted at 84–85°.

Anal. Calcd. for $C_{19}H_{27}NO_2$: C, 75.8; H, 9.1. Found: C, 76.0; H, 9.2.

The α-naphthylurethan of VI, obtained in 85% yield, melted at 72–73° after recrystallization from hexane.

Anal. Calcd. for $C_{23}H_{29}NO_2$: C, 78.6; H, 8.3. Found: C, 78.8; H, 8.3.

cis-Hexahydrobenzylcyclopentanol (VII).—Catalytic hydrogenation of a solution of 17.6 g. (0.1 mole) of pure *cis*-2-benzylcyclopentanol (III) in 150 cc. of methanol containing 2 cc. of concentrated hydrochloric acid and 0.2 g. of platinum oxide proceeded rapidly with an uptake of just 0.3 mole of hydrogen. After removing catalyst and solvent, the residue in ether was washed with a little dilute aqueous alkali to remove any acid. After drying the ether layer, the ether was removed and the product was distilled *in vacuo*. The yield of pure VII was 17 g. (95%), b.p. 130–131° at 10 mm., and with no observable foreruns or distillation residues.

This product gave a good carbon–hydrogen analysis, formed a 3,5-dinitrobenzoate melting at 103–104° in 80% yield, and gave an α-naphthylurethan melting at 111–112° in 85% yield. Analytical results and melting points for other samples of these compounds are reported under the description of one of the products of the catalytic hydrogenation of 2-benzylcyclopentanone (II) with platinum oxide in the presence of acid.

The further hydrogenation of the pure *cis*- and *trans*-2-benzylcyclopentanols (III and IV) in the presence of acid and platinum oxide leads only to the pure hexahydro derivatives, VII and VI, respectively, uncontaminated with any lower boiling (hydrocarbon), material. This strongly suggests that in the mixture of products obtained during the reduction, under similar conditions, of 2-benzylcyclopentanone (II) the lower boiling hydrocarbon product VIII must result in some other route from II, not mediated by the alcohol III. What this alternate pathway might be in this case still remains obscure.

Acknowledgment.—The authors are indebted to S. W. Blackman for the microanalytical results included here.

TUCKAHOE 7, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

Reactions with Diazoalkanes. V. Action of Diazoalkanes and of Aryl Azides on N-Arylmaleimides

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Diazomethane and ethyl diazoacetate add to the C=C bond in N-arylmaleimides (Ia–f) at 0° to yield the corresponding bicyclic pyrazoline derivatives (II; *cf.* Scheme 1). The cyclopropane derivatives (IV) are obtained by the action of diphenyldiazomethane and of 9-diazofluorene on Ia–f in boiling benzene solution; the pyrazoline derivatives (III) are only obtained when these reagents are allowed to react with Ia and Ib at 0°, respectively (*cf.* Scheme 2). N-Phenylcitraconimide (VIIa) behaves similarly toward diazoalkanes (*cf.* Scheme 4). Δ^2-1,2,3-Triazoline derivatives (V) are readily obtained by the action of aryl azides on Ia–g and undergo loss of nitrogen with the formation of the corresponding aziridine derivatives (VI) (*cf.* Scheme 3). The behavior of 2,3-dichloro-N-phenylmaleimide (VIIb) toward sodium azide simulates that of 2,3-dichloro-1,4-naphthoquinone toward the same reagent, yielding 2,3-diazido-N-phenylmaleimide (XI).

In continuation of previous work,[1] the action of diazoalkanes on N-arylmaleimides has now been investigated. When Ia-f are allowed to react with ethereal diazomethane solution and/or ethereal solution of ethyl diazoacetate at 0°, the corresponding bicyclic pyrazoline derivatives (II) (*cf.* scheme 1) are obtained. The action of diphenyldiazomethane and of 9-diazofluorene on Ia and on Ib, respectively, in cold benzene solution leads to the formation of the pyrazoline derivatives (III), whereas their action on Ia-f in boiling benzene solution yields the corresponding cyclopropane derivatives (IV; *cf.* Scheme 2).

Similarly, N-phenylcitraconimide (VIIa) gives the pyrazoline derivatives (VIIIa or VIIIb) with diazomethane and with ethyl diazoacetate in the cold and the corresponding cyclopropane derivatives[2] (IX) with diphenyldiazomethane and with 9-diazofluorene in boiling benzene solution.

Whereas VIIa reacts readily with diphenyldiazomethane and with 9-diazofluorene (Scheme 4), 2,3-dichloro-N-phenylmaleimide (VIIb) is stable or almost stable toward the action of these reagents under the given experimental conditions.

The pyrazoline derivatives (II, III and VIIIa or VIIIb) are analogous. II (X = C_6H_5, R = H), which can be taken as an example, is colorless, melts with evolution of gas and gives the correct analytical values. When heated in vacuum above its melting point, it gives 2,3-cyclopropane-(N-phenyl)-dicarboximide (IV, X = C_6H_5, R = R′ = H). Similarly, the pyrolysis of II (X = C_6H_5, R = $COOC_2H_5$) gives a product believed, by analogy, to be 1-carbethoxy-2,3-cyclopropane-(N-phenyl)-dicarboximide (IV, X = C_6H_5, R = $COOC_2H_5$, R′ = H).

Reactions with Aryl Azides.—Similarities between diazoalkanes and their isoteric azides have been described. The addition of diazomethane and of phenyl azide to olefinic linkages in fumaric ester[3] and in toluoquinone[4] provides a good example.

We have now investigated the behavior of the C=C bond in Ia-g and in X toward the action of aryl azides. Whereas X failed to react with phenyl azide under the given experimental conditions, Ia-g react readily with aryl azides to give the addi-

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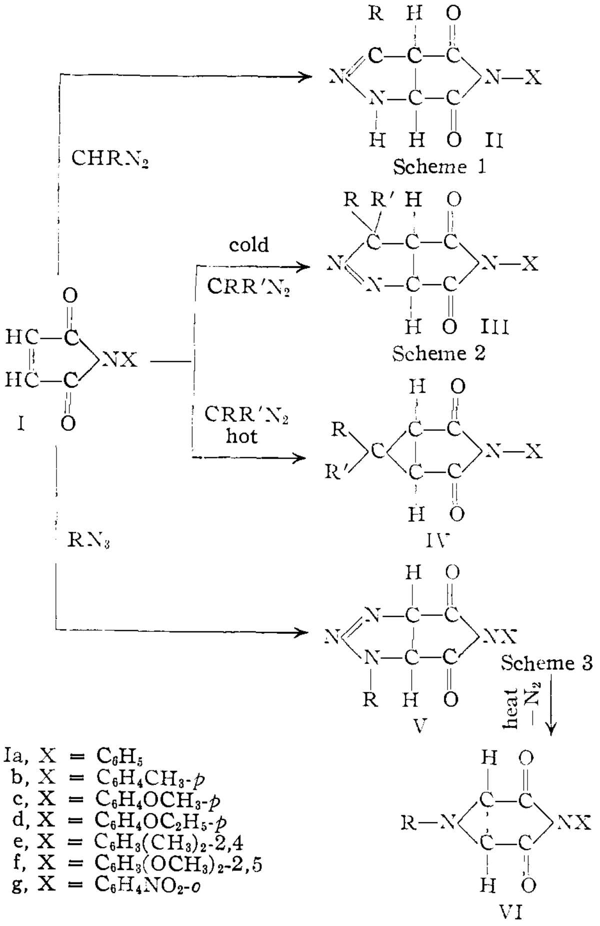
[1] For previous work on diazoalkanes see A. Mustafa, *J. Chem. Soc.*, 234 (1949); A. Mustafa and M. K. Hilmy, *ibid.*, 3254 (1951); 1434 (1952); A. Mustafa and A. H. E. Harhash, THIS JOURNAL, **76**, 1383 (1954).

[2] For the formation of cyclopropane derivatives by the action of diazoalkanes on olefinic compounds compare A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952); L. Horner and L. Lingnau, *Ann.*, **591**, 21 (1955).

[3] L. Wolff, *Ann.*, **394**, 23, 59 (1912).

[4] G. Caronna and S. Palazzo, *Gazz. chim. ital.*, **82**, 292 (1952).



I II III IV V VI

Scheme 1

Scheme 2

Scheme 3

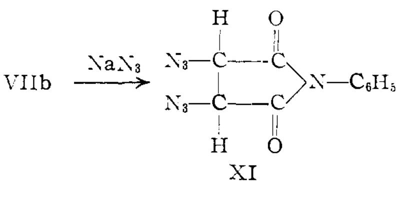
Ia, X = C_6H_5
b, X = $C_6H_4CH_3$-*p*
c, X = $C_6H_4OCH_3$-*p*
d, X = $C_6H_4OC_2H_5$-*p*
e, X = $C_6H_3(CH_3)_2$-2,4
f, X = $C_6H_3(OCH_3)_2$-2,5
g, X = $C_6H_4NO_2$-*o*

tion products (V) (*cf.* Scheme 3), thus showing that the olefinic linkage in I is in a more strained cyclic compound[5] than that in X.

The Δ^2-1,2,3-triazoline derivatives (V) are colorless, give the correct analytical values and undergo loss of nitrogen when heated above their melting points, yielding the corresponding aziridine derivatives[6] (VI; *cf.* Scheme 3).

The behavior of the olefinic linkage in I and in X toward aryl azides simulates its behavior toward diazoalkanes, thus favoring the finding that the ring in I is quinonoid and the C=C bond is olefinic and the ring in Xa is aromatic.[7]

Whereas, VIIa and/or VIIb does not react with phenyl azide under the given experimental conditions, VIIb reacts with sodium azide to give 2,3-diazido-N-phenylmaleimide (XI).[8]



XI

Experimental

The N-arylmaleimides needed in this investigation were prepared by the procedure of Searle.[9] By a similar procedure, N-2,4-dimethylphenylmaleimide (Ie) and N-2,5-dimethoxyphenylmaleimide (If) have now been prepared. Ie forms yellow crystals, m.p. 76°, from ethyl alcohol, and is obtained in 63% yield.

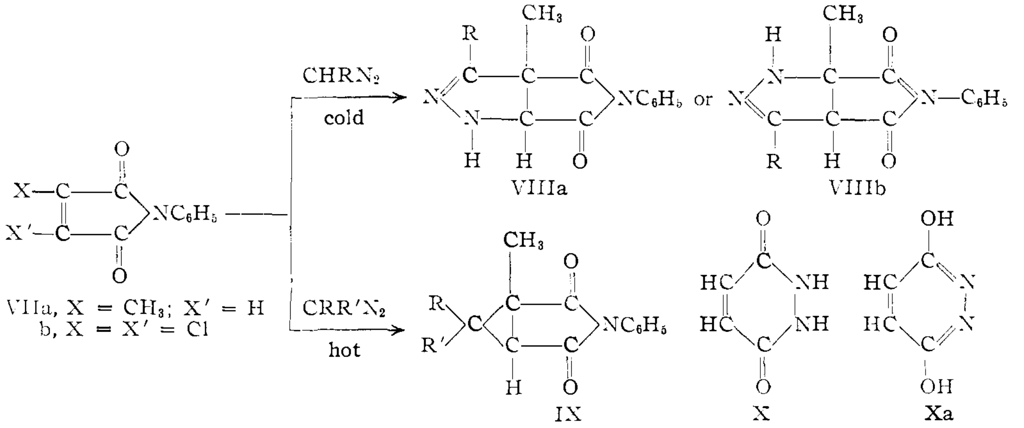
Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.64; H, 5.47; N, 6.96: Found: C, 71.37; H, 5.25; N, 6.73.

Ie is easily soluble in ethyl acetate and in benzene, but sparingly soluble in light petroleum (b.p. 40–60°) and gives a yellow solution with cold sulfuric acid.

If forms yellow crystals from dilute ethyl alcohol, m.p. 122°, yield *ca.* 53%. It possesses the same properties as Ie, but dissolves with brown color in cold sulfuric acid.

Anal. Calcd. for $C_{12}H_{11}NO_4$: C, 61.81; H, 4.81; N, 6.0. Found: C, 61.72; H, 4.74; N, 5.82.

Action of Diazoalkanes on N-Arylmaleimides (Ia-f).—(A) One gram of each of Ia-f was treated with each of solutions of diazomethane (prepared from 4 g. of nitrosomethylurea) in 40 ml. of ether, ethyl diazoacetate (from 4 g. of glycine ethyl ester hydrochloride) in 40 ml. of ether, diphenyldiazomethane[10] (prepared from 3 g. of benzophenonehydrazone) in 30 ml. of benzene and 1.5 g. of 9-diazofluorene[11] in 50 ml. of benzene.



VIIa, X = CH_3; X' = H
b, X = X' = Cl

VIIIa VIIIb IX X Xa

The reaction mixture, in the case of diazomethane and ethyl diazoacetate, was kept at 0° overnight and then

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(5) The addition of phenyl azide to olefinic linkages in strained cyclic compounds has been used occasionally to detect and characterize the olefins (*cf.* J. H. Boyer and F. C. Canter, *Chem. Revs.*, **54**, 42 (1954); *cf.* also K. Alder and R. Ruhrmann, *Ann.*, **566**, 1 (1950)).

(6) That the adducts of aryl azides with olefins undergo loss of nitrogen with the formation of three-membered ring (aziridines) has been demonstrated by F. D. Chattaway and G. D. Parkas (*J. Chem. Soc.*, **127**, 1307 (1925)) and T. Curtius and W. Dorr (*J. prakt. Chem.*, **125**, 425 (1930)).

(7) F. Arndt, L. Loewe and L. Ergner, *Rev. faculté Sci. Univ. Istanbul*, **13A**, 103 (1948); *C. A.*, **43**, 579a (1949).

(8) *Cf.* the action of sodium azide on 2,3-dichloro-1,4-naphthoquinone, yielding 2,3-diazido-1,4-naphthoquinone (K. Fries and P. O. Ochwat, *Ber.*, **56**, 1291 (1923)).

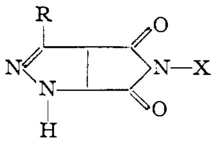
(9) N. E. Searle, *C. A.*, **42**, 7340 (1948).

(10) H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916).

(11) A. Schönberg, W. Awad and N. Latif, *J. Chem. Soc.*, 1368 (1951).

TABLE I

PYRAZOLINE DERIVATIVES

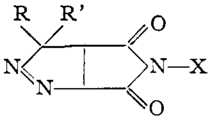


Maleimide derivs.	Diazo-alkane[c]	Pyrazoline[a] derivs. (X)	M.p.,[b] °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ia	1	C_6H_5	178	88	$C_{11}H_9N_3O_2$	61.39	61.25	4.18	4.03	19.53	19.27
	2	C_6H_5	193	81	$C_{14}H_{13}N_3O_4$	58.53	58.19	4.53	4.41	14.63	14.53
Ib	1	$C_6H_4CH_3$-*p*	178	85	$C_{12}H_{11}N_3O_2$	62.88	62.75	4.80	4.63	18.34	18.14
	2	$C_6H_4CH_3$-*p*	193	84	$C_{15}H_{15}N_3O_4$	59.80	59.75	4.98	4.82	13.95	13.86
Ic	1	$C_6H_4OCH_3$-*p*	184	85	$C_{12}H_{11}N_3O_3$	58.77	58.57	4.48	4.39	17.14	16.93
	2	$C_6H_4OCH_3$-*p*	154	65	$C_{15}H_{15}N_3O_5$	56.78	56.72	4.73	4.57	13.24	13.08
Id	1	$C_6H_4OC_2H_5$-*p*	172	70	$C_{13}H_{13}N_3O_3$	60.23	60.03	5.01	4.87	16.21	16.15
	2	$C_6H_4OC_2H_5$-*p*	164	60	$C_{16}H_{17}N_3O_5$	58.00	57.83	5.13	4.95	12.70	12.71
Ie	1	$C_6H_3(CH_3)_2$-2,4	143	85	$C_{13}H_{13}N_3O_2$	64.19	64.03	5.34	5.25	17.28	17.08
	2	$C_6H_3(CH_3)_2$-2,4	146	75	$C_{16}H_{17}N_3O_4$	60.95	60.86	5.39	5.18	13.33	13.24
If	2	$C_6H_3(OCH_3)_2$-2,5	124	65	$C_{16}H_{17}N_3O_6$	55.33	55.08	4.90	4.85	12.10	11.89

[a] In all pyrazoline derivatives obtained by the action of 1 on the corresponding maleimides R = H; those derived from 2 have R = $COOC_2H_5$. [b] Melting points are uncorrected. The pyrazoline derivatives melt with decomposition. [c] 1, diazomethane; 2, ethyl diazoacetate.

TABLE II

Δ^1-PYRAZOLINE DERIVATIVES



Maleimide derivs.	Diazo-alkane[c]	Δ^1-Pyrazoline derivs.[a] (X)	M.p.,[b] °C.	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ia	1	C_6H_5	143	75	$C_{23}H_{17}N_3O_2$	75.20	75.03	4.63	4.51	11.44	11.42
	2	C_6H_5	201	68	$C_{23}H_{15}N_3O_2$	75.61	75.37	4.10	3.95	11.50	11.26
Ib	2	$C_6H_4CH_3$-*p*	197	71	$C_{24}H_{17}N_3O_2$	75.98	75.82	4.48	4.27	11.08	10.96

[a] R = R′ = C_6H_5 in the case of pyrazoline derivatives obtained by the action of (1) on the corresponding maleimides, whereas R and R′ = $C_{13}H_8$ (9-fluorenylidene) in the case of (2). [b] Melting points are uncorrected. The pyrazoline derivatives melt with decomposition. [c] 1, diphenyldiazomethane; 2, 9-diazofluorene.

treated with a fresh amount of the diazoalkane, whereas, in the case of diphenyldiazomethane and 9-diazofluorene, it was kept at room temperature for the same time period. The final reaction products were collected, washed with cold ether (*ca.* 20 ml.) and recrystallized from a chloroform and ether mixture.[12]

The pyrazoline derivatives (Tables I and II) are colorless, easily soluble in cold chloroform, but not easily soluble in ether and light petroleum. They are insoluble in cold aqueous sodium hydrazide solution (10%), but soluble in hot, and give a yellow color with cold sulfuric acid which changes to orange in the case of the pyrazoline derivtives obtained from Id and Ie, respectively.

Treatment of citraconimide (VIIa)[13] with ethereal diazomethane solution and/or ethyl diazoacetate ethereal solution was carried out as described above. The reaction product (VIIIa or VIIIb, R = H) forms colorless crystals from chloroform and ether mixture[12] and melts at 180° dec. It is easily soluble in cold chloroform and benzene, but sparingly soluble in ether and light petroleum; yield *ca.* 88%.

Anal. Calcd. for $C_{12}H_{11}N_3O_2$: C, 62.88; H, 4.80; N, 18.34. Found: C, 62.73; H, 4.71; N, 18.16.

VIIIa or VIIIb (R = $COOC_2H_5$) is obtained in *ca.* 85% yield, m.p. 170°, dec., as colorless crystals from the same solvent and its solubility in organic solvents simulates that of the above compound.

Anal. Calcd. for $C_{15}N_{15}N_3O_4$: C, 59.80; H, 4.98; N, 13.95. Found: C, 59.57; H, 4.83; N, 13.82.

(B) The reaction was carried out by refluxing a benzene solution of a mixture of the corresponding maleimide (I and VIIa) and diphenyldiazomethane and/or 9-diazofluorene for four hours, during which time the deep color of the reaction mixture faded. The cyclopropane derivatives (IV and IX) were processed as follows: the solvent was evaporated and the solid residue was washed several times with cold ether (15 ml.) and crystallized (*cf.* Table III).

The cyclopropane derivatives are colorless or almost colorless, are easily soluble in hot benzene and hot ethyl alcohol, but sparingly soluble in cold ethyl alcohol and light petroleum, and give a yellow color with cold sulfuric acid. They are insoluble in cold aqueous sodium hydroxide solution (10%), but soluble in hot.

2,3-Dichloro-N-phenylmaleimide (VIIb)[14] was unaffected when treated with diphenyldiazomethane and/or 9-diazofluorene under the above mentioned experimental conditions.

Thermal Decomposition of: (a) Pyrazoline-4,5-(N-phenyl)-dicarboximide (II, X = C_6H_5, R = H).—The thermal decomposition of 0.5 g. of the pyrazoline derivative was carried out under vacuum. The reaction vessel was heated for half an hour at 130° (metal-bath). It was cooled and the oily residue was extracted several times with petroleum ether (b.p. 60–80°) which gave, on cooling, colorless crystals (*ca.* 0.18 g.), m.p. 98°, identified as cyclopropane-2,3-(N-phenyl)-dicarboximide (m.p. and mixed m.p.[15]).

(b) **1-Carbethoxypyrazoline-4,5-(N-phenyl)-dicarboximide** (II, X = C_6H_5, R = $COOC_2H_5$).—The pyrolysis of 0.5 g. of the dicarboximide was carried out as described above. The reaction product was crystallized from ethyl alcohol as colorless crystals (*ca.* 0.21 g.), m.p. 173°. 1-Carbethoxy-

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(12) Crystallization was carried out by adding ether, dropwise, to a clear chloroform solution of the reaction product until the appearance of faint turbidity and then keeping in the ice-chest.

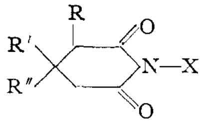
(13) A. Reissert and F. Tiemann, *Ber.*, **19**, 623 (1886).

(14) E. Kauder, *J. prakt. Chem.*, **31**, 17 (1885).

(15) T. W. D. Gregory and W. H. Perkin, *J. Chem. Soc.*, **83**, 788 (1903).

TABLE III

CYCLOPROPANE DERIVATIVES

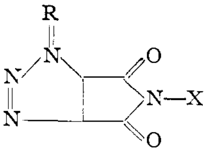


Male-imide derivs.	Diazo-al-kane[c]	Cyclopropane derivs.[a] (X)	M.p.,[b] °C.	Solvent for crystn.[d]	Yield, %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ia	1	C_6H_5	162	A	85	$C_{23}H_{17}NO_2$	81.41	81.32	5.01	5.01	4.13	4.03
	2	C_6H_5	185	B	83	$C_{23}H_{15}NO_2$	81.89	81.68	4.45	4.27	4.15	4.02
Ib	1	$C_6H_4CH_3$-*p*	168	A	65	$C_{24}H_{19}NO_2$	81.58	81.63	5.38	5.26	3.96	3.79
	2	$C_6H_4CH_3$-*p*	205	C	75	$C_{24}H_{17}NO_2$	82.05	82.01	4.84	4.73	3.98	3.84
Ic	1	$C_6H_4OCH_3$-*p*	168	D	55	$C_{24}H_{19}NO_3$	78.04	77.82	5.14	4.78	3.79	3.57
	2	$C_6H_4OCH_3$-*p*	236	C	52	$C_{24}H_{17}NO_3$	78.47	78.42	4.63	4.56	3.81	3.75
Id	1	$C_6H_4OC_2H_5$-*p*	153	D	45	$C_{25}H_{21}NO_3$	78.32	78.12	5.48	5.36	3.65	3.54
	2	$C_6H_4OC_2H_5$-*p*	242	D	45	$C_{25}H_{19}NO_3$	78.74	78.62	4.98	4.94	3.67	3.56
Ie	1	$C_6H_3(CH_3)_2$-2,4	175	D	80	$C_{25}H_{21}NO_2$	81.74	81.43	5.72	5.56	3.81	3.72
	2	$C_6H_3(CH_3)_2$-2,4	214	C	77	$C_{25}H_{19}NO_2$	82.19	82.01	5.20	5.07	3.83	3.69
VIIa	1	C_6H_5	177	D	80	$C_{24}H_{19}NO_2$	81.58	81.42	5.38	5.26	3.96	3.75
	2	C_6H_5	203	C	77	$C_{24}H_{17}NO_2$	82.05	81.94	4.84	4.76	3.98	3.79

[a] R = H except in the case of VIIa, R = CH_3. R′ = R″ = C_6H_5 in the case of cyclopropane derivatives derived from (1) and R′ and R″ = $C_{13}H_8$ (9-fluorenylidene) in the case of (2). [b] Melting points are uncorrected. [c] 1, diphenyldiazomethane; 2, 9-diazofluorene. [d] A, ethyl alcohol; B, petroleum ether (b.p. 80–100°); C, benzene; D, benzene and petroleum ether mixture.

TABLE IV

Δ^2-1,2,3-TRIAZOLINE DERIVATIVES



Male-imide de-rivs.	Aryl azide[g]	Δ^2-1,2,3-Triazoline derivs. X	R	M.p.,[a] °C.	Yield, %	Crystn. sol-vent[f]	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ia	1	C_6H_5	C_6H_5	156	89	A	$C_{16}H_{12}N_4O_2$	65.75	65.56	4.11	4.06	19.17	19.04
	2	C_6H_5	C_6H_4Cl-*p*	164	90	A	$C_{16}H_{11}N_4O_2Cl$	58.81	58.80	3.37	3.43	17.15	17.06[b]
	3	C_6H_5	$C_6H_4NO_2$-*p*	195	78	B	$C_{16}H_{11}N_5O_4$	57.00	56.82	3.26	3.13	20.77	20.57
Ib	1	$C_6H_4CH_3$-*p*	C_6H_5	162	92	A	$C_{17}H_{14}N_4O_2$	66.67	66.56	4.57	4.48	18.30	18.21
	2	$C_6H_4CH_3$-*p*	C_6H_4Cl-*p*	175	88	C	$C_{17}H_{13}N_4O_2Cl$	59.91	59.57	3.82	3.66	16.45	16.43[c]
	3	$C_6H_4CH_3$-*p*	$C_6H_4NO_2$-*p*	186	81	C	$C_{17}H_{13}N_5O_4$	58.12	58.01	3.70	3.56	19.94	19.67
Ic	1	$C_6H_4OCH_3$-*p*	C_6H_5	184	77	C	$C_{17}H_{14}N_4O_3$	63.35	63.12	4.34	4.13	17.39	17.36
	2	$C_6H_4OCH_3$-*p*	C_6H_4Cl-*p*	162	66	A	$C_{17}H_{13}N_4O_3Cl$	57.22	57.01	3.64	3.47	15.70	15.56[d]
	3	$C_6H_4OCH_3$-*p*	$C_6H_4NO_2$-*p*	170	68	A	$C_{17}H_{13}N_5O_5$	55.55	55.38	3.54	3.25	19.07	18.90
Id	1	$C_6H_4OC_2H_5$-*p*	C_6H_5	140	71	A	$C_{18}H_{16}N_4O_3$	64.28	64.15	4.76	4.63	16.66	16.56
	2	$C_6H_4OC_2H_5$-*p*	C_6H_4Cl-*p*	160	65	C	$C_{18}H_{15}N_4O_3Cl$	58.29	58.32	4.05	3.97	15.11	15.01[e]
	3	$C_6H_4OC_2H_5$-*p*	$C_6H_4NO_2$-*p*	174	61	D	$C_{18}H_{15}N_5O_5$	56.69	56.45	3.94	3.56	18.37	18.01
Ie	1	$C_6H_3(CH_3)_2$-2,4	C_6H_5	168	89	E	$C_{18}H_{16}N_4O_2$	67.50	67.32	5.04	4.85	17.50	17.40
If	1	$C_6H_3(OCH_3)_2$-2,4	C_6H_5	160	78	A	$C_{18}H_{16}N_4O_4$	61.36	61.33	4.54	4.45	15.90	15.62
Ig	1	$C_6H_4NO_2$-*o*	C_6H_5	166	72	C	$C_{16}H_{11}N_5O_4$	56.97	56.82	3.26	3.12	20.77	20.54

[a] All melting points are uncorrected and the triazoline compounds melt with decomposition. [b] Cl: Calcd.: 10.87. Found: 10.61. [c] Cl: Calcd.: 10.42. Found: 10.12. [d] Cl: Calcd.: 9.95. Found: 9.78. [e] Cl: Calcd.: 9.58. Found: 9.43. [f] A, benzene–petroleum ether mixture; B, chlorobenzene; C, ethyl alcohol; D, benzene; and E, ethyl acetate. [g] 1, phenyl azide; 2, *p*-chlorophenyl azide; 3, *p*-nitrophenyl azide.

cyclopropane-2,3-(N-phenyl)-dicarboximide (IV, X = C_6H_5, R = $COOC_2H_5$, R′ = H) is easily soluble in benzene, but sparingly soluble in ethyl alcohol and light petroleum, and gives no color with sulfuric acid.

Anal. Calcd. for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.01; N, 5.41. Found: C, 64.73; H, 5.00; N, 5.53.

Action of Aryl Azides on Ia-g.—General Procedure.—To a solution of the N-arylmaleimide (0.005 mole) in 20 ml. of freshly distilled ethyl acetate was added a solution of the aryl azide (0.005 mole) in 15 ml. of ethyl acetate. The reaction mixture was refluxed for four hours and then cooled. The solvent was removed under reduced pressure and the oily residue, so obtained, was washed several times with light petroleum, and then with cold ethyl alcohol (*ca.* 15 ml.). The resulting solid was crystallized from a suitable solvent (*cf.* Table IV).

When working with Id and Ie, a suspension of the imide in ethyl acetate was treated with the corresponding azide, and the reaction mixture was refluxed for eight hours to effect completion of the reaction.

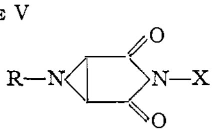
The triazoline derivatives V listed in Table IV form colorless crystals which are insoluble in cold aqueous sodium hydroxide solution (10%), but soluble in hot. They give a yellow solution, accompanied with strong decomposition, when treated with cold sulfuric acid. They are easily soluble in hot benzene, chloroform and ethyl acetate, but sparingly soluble in cold ethyl alcohol and petroleum ether.

VIIa and VIIb were unaffected when treated with phenyl azide under the above-mentioned experimental conditions.

Thermal Decomposition.—The pyrolysis of 1 g. of each of the triazoline derivatives V was carried out as described in

TABLE V

AZIRIDINE DERIVATIVES



Aziridine[b] derivs. X	R	Pyrolysis temp., °C.	M.p.,[a] °C.	Yield, %	Crystn. solvent	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
C_6H_5	C_6H_5	140	120	91	A	$C_{16}H_{12}N_2O_2$	72.73	72.54	4.55	4.36	10.60	10.53
C_6H_5	C_6H_4Cl-*p*	140	98	77	B	$C_{16}H_{11}N_2O_2Cl$	64.32	64.12	3.68	3.61	9.37	9.25[c]
C_6H_5	$C_6H_4NO_2$-*p*	180	240	58	C	$C_{16}H_{11}N_3O_4$	62.13	62.04	3.56	3.32	13.59	13.45
$C_6H_4CH_3$-*p*	C_6H_5	145	140	86	B	$C_{17}H_{14}N_2O_2$	73.38	73.34	5.03	4.78	10.07	9.95
$C_6H_4CH_3$-*p*	C_6H_4Cl-*p*	150	250	81	D	$C_{17}H_{13}N_2O_2Cl$	65.28	65.15	4.16	4.07	8.96	8.72[d]
$C_6H_4CH_3$-*p*	$C_6H_4NO_2$-*p*	160	146	84	B	$C_{17}H_{13}N_3O_4$	63.15	63.01	4.02	3.93	13.00	12.78
$C_6H_4OCH_3$-*p*	C_6H_5	160	178	71	A	$C_{17}H_{14}N_2O_3$	69.38	69.16	4.76	4.61	9.52	9.34
$C_6H_4OCH_3$-*p*	C_6H_4Cl-*p*	150	120	65	B	$C_{17}H_{13}N_2O_3Cl$	62.07	61.96	3.98	3.77	8.52	8.45[e]
$C_6H_4OCH_3$-*p*	$C_6H_4NO_2$-*p*	160	118	58	A	$C_{17}H_{13}N_3O_5$	60.17	60.01	3.83	3.64	12.38	12.14
$C_6H_4OC_2H_5$-*p*	C_6H_5	130	106	61	B	$C_{18}H_{16}N_2O_3$	70.13	69.85	5.19	5.06	9.08	8.84
$C_6H_4OC_2H_5$-*p*	C_6H_4Cl-*p*	140	130	64	B	$C_{18}H_{15}N_2O_3Cl$	63.06	62.85	4.38	4.31	8.17	8.03[f]
$C_6H_4OC_2H_5$-*p*	$C_6H_4NO_2$-*p*	160	180	65	A	$C_{18}H_{15}N_3O_5$	61.20	61.07	4.25	4.21	11.89	11.80
$C_6H_3(CH_3)_2$-2,4	C_6H_5	160	130	92	B	$C_{18}H_{16}N_2O_2$	73.97	73.78	5.48	5.32	9.58	9.46

[a] Melting points are uncorrected. [b] They give yellow solution with cold sulfuric acid, and are regenerated on dilution. A, benzene–petroleum ether (b.p. 80–100°) mixture; B, petroleum ether (b.p. 80–100°); C, xylene; D, ethyl alcohol. [c] Cl: Calcd.: 11.89. Found: 11.77. [d] Cl: Calcd.: 11.36. Found: 11.27. [e] Cl: Calcd.: 10.80. Found: 10.54. [f] Cl: Calcd.: 10.36. Found: 10.21.

the case of the pyrazolines. The oily product was washed several times with light petroleum and the solid, so obtained, was recrystallized.

The aziridine derivatives VI listed in Table V form yellow crystals, are easily soluble in benzene and ethyl alcohol, but sparingly soluble in petroleum ether and cold ethyl alcohol. They dissolve in hot aqueous sodium hydroxide solution (10%) and sublime readily when heated above their melting points.

Action of Sodium Azide on VIIb.—To a suspension of 0.7 g. of VIIb in 20 ml. of ethyl alcohol was added a concentrated aqueous solution of 1 g. of sodium azide The reaction mixture was heated (steam-bath) for five minutes, during which time VIIb gradually went into solution, followed by the separation of a yellow crystalline deposit on cooling. These were filtered off, washed with cold water and crystallized from dilute ethyl alcohol as yellow crystals, m.p. 100° (vigorous decomp.).

Anal. Calcd. for $C_{10}H_5N_7O_2$: C, 47.05; H, 1.96; N, 38.43. Found: C, 46.94; H, 1.76; N, 38.23.

2,3-Diazido-(N-phenyl)-maleimide (XI) is easily soluble in hot ethyl alcohol, but sparingly soluble in ether. It gives a red solution with cold sulfuric acid accompanied with vigorous decomposition.

GIZA, CAIRO, EGYPT

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Bicyclic Carboxylic Acid Derivatives from *cis*-2,5-Bis-(hydroxymethyl)-tetrahydrofuran

BY ARTHUR C. COPE AND BURTON C. ANDERSON

RECEIVED JULY 11, 1955

Bicyclic carboxylic esters (III, VIII and IX) were the only products isolated from the reaction of *cis*-2,5-bis-(hydroxymethyl)-tetrahydrofuran ditosylate (I) with diethyl malonate and ethyl cyanoacetate. The esters were saponified to carboxylic acids V, X and XI. Decarboxylation of the dialkyl malonic acid V formed two isomeric carboxylic acids VI and VII, while the dialkylcyanoacetic acids X and XI on heating alone or in quinoline yielded the isomeric nitriles XIII and XIV. The decarboxylation reaction in quinoline is interpreted as proceeding through a common intermediate such as XV since both X and XI formed the two nitriles in essentially the same proportions.

cis-2,5-Bis-(hydroxymethyl)-tetrahydrofuran ditosylate (I) has been shown to form derivatives of 8-oxa-3-azabicyclo[3.2.1]octane in reactions in which it dialkylates the nitrogen atom of ammonia,[1,2] primary amines[3] and secondary amines.[4] In an attempt to determine whether or not the ditosylate I would form bicyclic derivatives of active methylene compounds, its reactions with diethyl malonate and ethyl cyanoacetate have been studied. In a somewhat analogous case the cyclic dicarboxylic ester, diethyl dibenzo[a,c][1,3]cycloheptadiene-6,6-dicarboxylate, was the only product isolated when 2,2′-bis-(bromomethyl)-biphenyl was allowed to react with diethyl malonate.[5]

Experimental conditions similar to those known to favor dialkylation of diethyl malonate by trimethylene bromide[6] were used in the first experiments of this series. The reaction of the ditosylate I with diethyl malonate and two molar equivalents of sodium ethoxide in ethanol heated under reflux

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