[CONTRIBUTION FROM THE DEPT. OF CHEMISTRY, UNIVERSITY OF TORONTO]

DIELS-ALDER ADDITIONS WITH DIALKYL AZODICARBOXYLATES AND AZO-BIS-FORMAMIDINE

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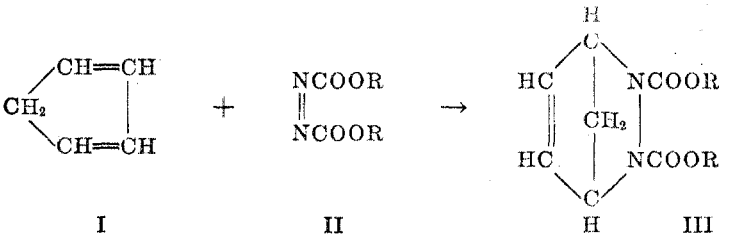
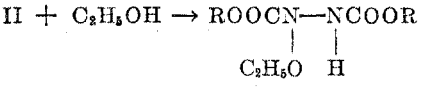
In 1924 Diels, Blum, and Koll (1) reported almost quantitative addition of dialkyl azodicarboxylate (II) to various conjugated dienes alone or in a number of non-polar reaction media. On the other hand Diels and Wulff (2) were unable to isolate the adduct (III) from the reaction of one of these dienes, cyclopentadiene (I), and diethyl azodicarboxylate in methanol or ethanol, although the characteristic color of the ester disappeared.



I II III

Then they investigated the reaction of methanol, ethanol, some mercaptans, and some glycols with diethyl azodicarboxylate (II) and found that addition products were formed slowly. The reaction with ethanol yielded a compound which they designated as diethyl N-ethoxyhydrazodicarboxylate (IV).



IV

The demonstration that these two types of reaction occurred carried the implication that one was alternative to the other.

In contrast to the report of Diels and Wulff we have found that the reaction of cyclopentadiene with dialkyl azodicarboxylates in methanol or ethanol occurs rapidly to give high yields of 1,2-dicarbalkoxy-3,6-endomethylene-1,2,3,6-tetrahydropyridazines (III). The dimethyl ester (III) is a solid. Although the diethyl ester (III) is a liquid it can be characterized easily by conversion to the solid 1,2-dicarbethoxy-4,5-dibromo-3,6-endomethylenepiperidazine of Diels, Blum, and Koll (1).

The addition reaction occurs in alcoholic media with 1,3-butadiene (V_1, R′, R″, R‴ = H), *cis*-2-methylpentadiene-1,3 (V_2, R′ = H, R″ and R‴ = CH_3), and *trans-trans*-1,4-diphenylbutadiene-1,3 (V_3, R′, R‴ = phenyl, R″ = H) and either dimethyl or diethyl azodicarboxylate. The yields in methanol or ethanol are as good as may be obtained in media like diethyl ether, benzene,

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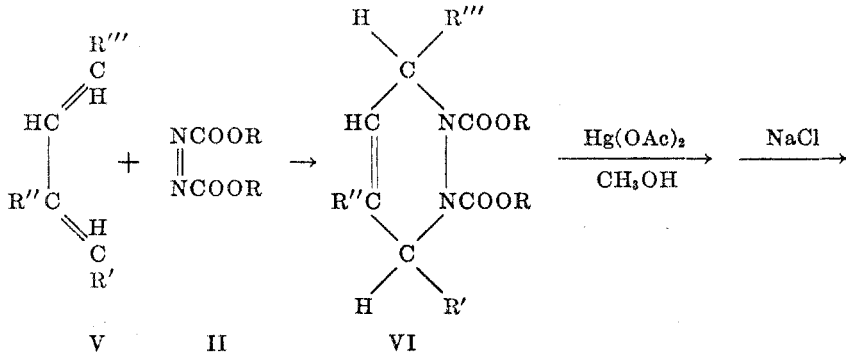
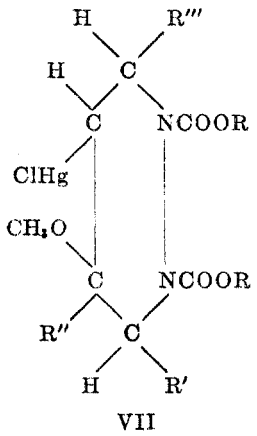
toluene, dioxane, petroleum ether (b.p. 60–70°) or excess diene. The yield of the alternative addition product IV in the alcoholic media is negligible in every instance.



V II VI

V_1 (R′, R″, R‴ = H)
V_2 (R′ = H; R″, R‴ = CH_3)
V_3 (R′, R‴ = phenyl; R″ = H)



VII

Two of the adducts have been characterized as solids. Diels and Alder (3) had previously reported the crystalline 1,2-dicarbomethoxy-3,6-diphenyl-1,2,3,6-tetrahydropyridazine (VI, R′, R‴ = phenyl, R″ = H) obtained from V_3. The adduct from butadiene (V_1), which is liquid, has been converted to 1,2-dicarbethoxy-4-methoxy-5-chloromercuripiperidazine (VII, R′, R″, R‴ = H). The liquid adduct from 2-methylpentadiene-1,3 and diethyl azodicarboxylate could not be converted to a solid derivative either by addition of bromine or by methoxymercuration at the 4,5-positions. It is thought to be 1,2-dicarbethoxy-3,5-dimethyl-1,2,3,6-tetrahydropyridazine (VI, R′ = H; R″, R‴ = CH_3) because of its elemental analysis and its alkaline hydrolysis to an oil which should be 3,5-dimethyl-1,2,3,6-tetrahydropyridazine. The picrates from samples of this oil obtained from VI prepared in methanol or ethanol were identical.

The dialkyl ester adducts just described were prepared in alcoholic media from dialkyl azodicarboxylates which had been synthesized by nitric acid oxidation of the dialkyl hydrazodicarboxylates (4). The results contradict the opinion of Diels and Wulff (1) that adducts could not be obtained in alcoholic media. However the addition in alcohols of diethyl azodicarboxylate to 2-methylpentadiene-1,3 is somewhat less satisfactory when the ester is prepared by the oxidation of diethyl hydrazodicarboxylate with hypochlorite solution as specified by Rabjohn (5).

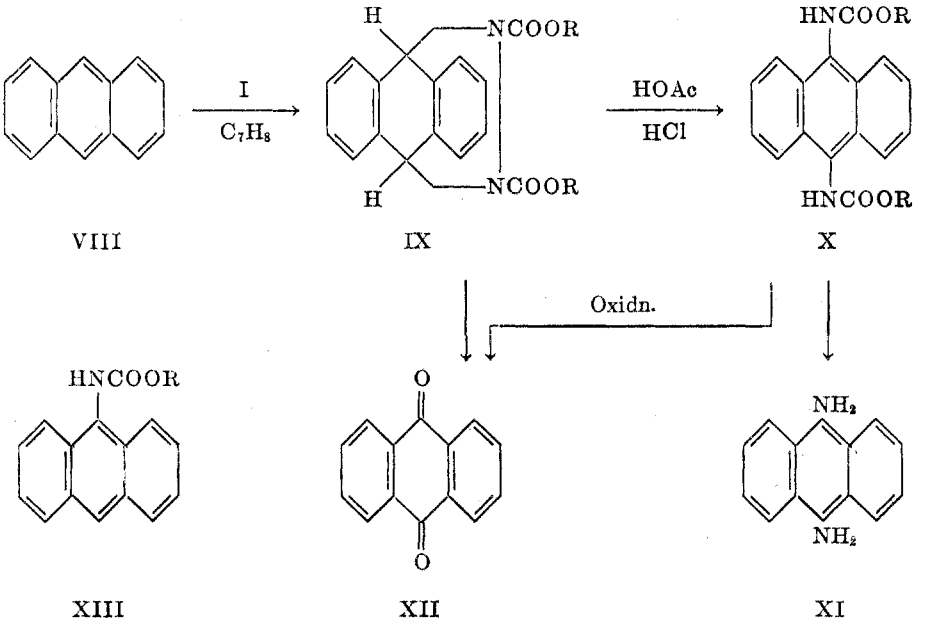
The reagent prepared by Rabjohn's method gives high yields of adduct with 2-methylpentadiene when it is used in media such as diethyl ether or benzene. The reagent also works satisfactorily in methanol after it has been purified rigorously by treatment with aqueous sodium carbonate. Without this purification the yield of adduct VI ($R' = H; R'', R''' = CH_3$) is low and gas is evolved during the reaction. This gas is found to contain an appreciable amount of carbon dioxide.

The presence of diene is not necessary for this gaseous decomposition, since it occurs in methanol alone. It can be accentuated by addition of hydrogen chloride or by presence of cadmium-plated copper, although neither of these catalysts is effective in solvents like diethyl ether or benzene. The rate of decomposition evidently varies with the amount of impurity that is present, but it may be stated in general that the gasification rate is much more rapid than the addition rate of the ester to methanol alone. The disappearance of the color of azoester because of gas formation in methanol is approximately comparable with the rate of addition to 2-methylpentadiene-1,3 in formation of the colorless adduct VI. On the other hand it is slower than the observed rate of addition of pure ester to cyclopentadiene.

These observations lead us to the suspicion that Diels and Wulff were unable to obtain the adduct III from diethyl azodicarboxylate and cyclopentadiene in methanol because their ester was impure. We believe that they failed to observe the evolution of gas and, in consequence, wrongly attributed the disappearance of color to the much slower addition of methanol to the azoester. While we have been unable to isolate the impurity in the ester prepared according to Rabjohn, we know that it contains chlorine. We suspect it to be hydrochloric acid in salt-like coördination. If this coördination is sufficiently weak to be broken by distillation temperature, then recombination will occur in the cool receiver and separation cannot be achieved by distillation. A lesser amount of the same impurity might have been present in the ester prepared by the method of Diels and Paquin (4). Since we shall show in a later report that acids like hydrogen chloride inhibit the addition of azoesters to cyclopentadiene in methanol, it is probable that the impurity in the ester (or the other reagents) not only accelerated the gaseous decomposition in the reaction of Diels and Wulff, but also decelerated the addition of ester to diene.

We do not mean to imply that all of Diels' studies with azoesters were carried out with impure reagents. Indeed we have discovered evidence to the con-

trary. We have repeated the addition of pure diethyl and dimethyl azodicarboxylates to anthracene (6) and have obtained the identical adducts (IX) which were previously described.



These adducts (dimethyl and diethyl esters) had been characterized by Diels, Schmidt, and Witte by reaction with warm acetic acid containing a trace of hydrochloric acid. They specified the highly fluorescent rearrangement product as 9,10-di(N-carbalkoxyamino)anthracene (X). We have repeated this acid treatment; since we were unsuccessful in hydrolyzing the products to 9,10-diaminoanthracene (XI) we have compared their ultraviolet absorption spectra in chloroform with those of anthracene (VIII), 9-carbomethoxyaminoanthracene (XIII, R = CH_3), and 9-carbethoxyaminoanthracene (XIII, R = C_2H_5) (7). The close similarities shown in Table I confirm the opinion of Diels, Schmidt, and Witte that the rearrangement products have structures shown as X.

Since X seems adequately to represent the structures of the products obtained by treatment with hydrochloric and acetic acids it is not unreasonable to assume that X is formed from the adduct IX by a rearrangement of the benzidine (or of the 1,2 type). This assumption is strengthened by the observation that the absorption spectrum of IX (R = CH_3 or C_2H_5) decreases continuously from log E_m = 4.02 at 287 mμ to log E_m = 1.90 at 400 mμ with an inflection at log E_m = 2.82 (320 mμ) and the suggestion of peaks at 305 mμ and 364 mμ. This cannot be interpreted as a spectrum characteristic of anthracene although IX, like X, is oxidized easily to anthraquinone. This seems to be reasonable evidence

that the anthracene-azo ester adducts are indeed bridged dihydroanthracenes (IX).

Having thus assured ourselves of the authentic nature of the adducts (IX) we have sought to prepare IX (R = C_2H_5) in boiling toluene from anthracene and diethyl azodicarboxylate (II) prepared by Rabjohn's method. The trace of acid present in this ester (II) is found to be sufficient to convert the adduct IX entirely to the 9,10-di(N-carbethoxyamino)anthracene during the course of the reaction. Thus it seems evident that Diels and Wulff were purifying their azo esters adequately for reactions other than that with cyclopentadiene in methanol.

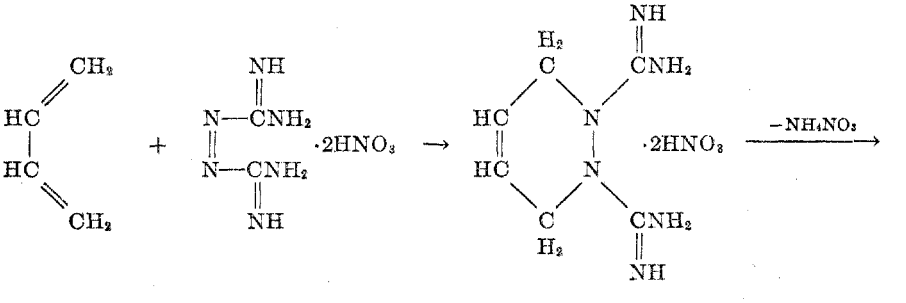
In order to demonstrate that nitric acid in the form of a salt does not cause the decomposition in methanol characteristic of the chloride contaminant in the

TABLE I

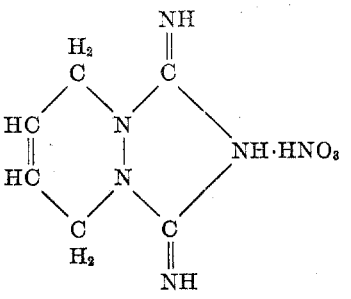
MAXIMA OBTAINED IN THE SPECTROPHOTOMETRIC STUDIES OF COMPOUNDS VIII, X (R = CH_3 OR C_2H_5), AND XIII (R = CH_3 OR C_2H_5)

VIII		X R = CH_3		X R = C_2H_5		XIII R = CH_3		XIII R = C_2H_5	
mμ	log E_m	mμ	log E_m	mμ	log E_m	mμ	log E_m	mμ	log E_m
253	5.23	254	5.20	253	5.18	254	5.14	254	5.15
279	2.88	—	—	—	—	—	—	—	—
290	2.94	—	—	—	—	—	—	—	—
298	2.84	—	—	—	—	—	—	—	—
313	3.08	—	—	—	—	—	—	—	—
327	3.42	334	3.46	333	3.46	334	3.41	334	3.42
342	3.70	350	3.75	350	3.76	350	3.71	350	3.71
359	3.84	369	3.92	369	3.92	368	3.85	368	3.85
379	3.82	390	3.89	389	3.88	387	3.78	388	3.79

azo esters we have treated azo-bis-formamidine dinitrate (XIV) with 1,3-butadiene alone and in methanol solution. No appreciable reaction occurs until azo-bis-formamidine is freed by the addition of pyridine. The slow reaction which then occurs gives a quantitative yield of N,N′-diguanyl-1,2,3,6-tetrahydropyridazine dinitrate (XV) without solvent and a 74% yield of XV in



XIV XV



XVI

methanol. We were unable to detect the formation of an addition product of azo-bis-formamidine and methanol. However we find some decomposition in this solvent, and in consequence a 20% yield of 1,3-diimino-2,8,9-triaza-4,6,8,9-tetrahydroindan nitrate (XVI) contaminated with ammonium nitrate is obtained as well as XV. Indeed XV is sufficiently unstable that it can be converted to XVI by crystallization from hot methanol. This instability probably accounts for the earlier failure (8) to isolate the homolog of XV which may be prepared from 2-methylpentadiene-1,3.

The authors wish to thank Miss Mary van Stone and the staff of the research laboratories, Canadian Industries Ltd., for help in some of the experimental work. They are grateful to the National Cancer Institute (Canada) for a grant-in-aid to one of us (A. R.).

EXPERIMENTAL

Melting points have been corrected against reliable standards.

The dienophiles. Dimethyl azodicarboxylate was prepared and purified according to Ingold and Weaver (9). Diethyl azodicarboxylate obtained by the method of Rabjohn (5) was purified by repeated washing with cold 3% aqueous sodium carbonate and then was distilled in small lots just prior to the experiment in which it was used.

1,2-*Dicarbethoxy-3,5-dimethyl-1,2,3,6-tetrahydropyridazine* (VI). Treatment of 3.48 g. (0.02 mole) of diethyl azodicarboxylate with 1.80 g. (0.022 mole) of freshly distilled 2-methylpentadiene (washed with ferrous sulfate and dried) gave 4.95 g. (94%) of a colorless viscous oil in 22 minutes. Distillation of this oil gave 3.95 g., b.p. 154.5–155.5° (12 mm.), d_4^{25} 1.100, n_D^{20} 1.4689.

Anal. Calc'd for $C_{12}H_{20}N_2O_4$: C, 56.2; H, 7.81; N, 10.9.

Found: C, 55.8; H, 7.93; N, 11.0.

Oxidation of this oil (0.59 g.) with 1.11 g. (0.007 mole) of alkaline potassium permanganate gave 0.15 g. of oil, b.p. 78° (25 mm.), which was converted to a dinitrophenylhydrazone in ethanolic hydrogen chloride. After crystallization from ethanol the derivative melted at 154.5°. A mixture melting point with acetaldehyde dinitrophenylhydrazone was not depressed. The oil is evidently pyruvic acid, since this aldehyde derivative also can be prepared from it.

The yellow solution obtained when VI (2.63 g., 0.0115 mole) was treated with 15 ml. (0.117 mole) of 40% (w/v) methanolic potassium hydroxide was boiled under reflux for 150 minutes, and then was cooled. Potassium carbonate was filtered off and washed with methanol, wt. 3.10 g. or 98% of theoretical. The excess methanol was distilled off. Distillation of the residue yielded 1.08 g. (69%) of an oil assumed to be 3,5-dimethyl-1,2,3,6-

tetrahydropyridazine, b.p. 61–62° (14 mm.). This oil formed a *picrate* in ethanol which, after crystallization from ethanol, melted at 221–224°. The same picrate (m.m.p.) was obtained when VI was prepared either in methanol or ethanol.

When the preparation of VI was carried out in anhydrous methanol with diethyl azodicarboxylate prepared and purified according to Rabjohn (5), carbon dioxide could be detected in the gas which was evolved. This gas was absorbed in an Ascarite-magnesium perchlorate-filled tube saturated with methanol vapor. A mixture of 0.82 g. (0.01 mole) of 2-methylpentadiene-1,3 and 1.74 g. (0.01 mole) of diethyl azodicarboxylate in 30 ml. of methanol under reflux for 130 minutes gave 0.194 g. (0.0044 mole) of carbon dioxide.

1,2-Dicarbethoxy-1,2,3,6-tetrahydropyridazine (VI). When 0.05 mole (8.70 g.) of diethyl azodicarboxylate and an excess (0.55 mole) of 1,3-butadiene was allowed to react at 23° in a pressure bottle for 5 hours the yield of adduct, b.p. 154–155° (11.5 mm.) was quantitative (11.4 g.). This product, n_D^{25} 1.4718, was obtained in 93% yield when an equivalent amount of butadiene was used in 75 ml. of anhydrous methanol.

Anal. Calc'd for $C_{10}H_{16}N_2O_4$: C, 52.6; H, 7.03; N, 12.3.

Found: C, 52.4; H, 7.10; N, 12.3.

1,2-Dicarbethoxy-4-methoxy-5-chloromercuripiperidazine (VII). A solution of 0.32 g. (0.001 mole) of mercuric acetate in 2.5 ml. of methanol was treated with 0.2 g. (0.0009 mole) of 1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine and 3 drops of 30% hydrogen peroxide. After 2 hours dilute aqueous sodium chloride was added. After crystallization had occurred, filtration removed 0.3 g., m.p. 130–141°. This was purified by solution in chloroform to which 2 volumes of diethyl ether was added. The m.p., 143.2–143.6°, was not raised by further purification of this kind.

Anal. Calc'd for $C_{11}H_{19}ClHgN_2O_5$: C, 26.7; H, 4.28; N, 6.25.

Found: C, 27.0; H, 4.14; N, 6.23.

1,2-Dicarbalkoxy-3,6-endomethylene-1,2,3,6-tetrahydropyridazine (III). The cyclopentadiene, b.p. 41.0° (760 mm.), freshly prepared by distillation from dicyclopentadiene through a 40-cm. fractionating column, was treated with the dialkyl azodicarboxylates under the conditions shown in Table II. The dimethyl ester adduct, m.p. 83.6–84.1°, boiled at 150–151° (0.25 mm.). The diethyl ester adduct boiled at 123.5–124.5° (0.75 mm.), and was identified by conversion with bromine in chloroform to 1,2-dicarbethoxy-4,5-dibromo-3,6-endomethylenepiperidazine in 75% yield. This product melted at 67.5–68° (1) after crystallization from 1:1 water-ethanol (8 ml. per g.).

1,2-Dicarbalkoxy-3,6-diphenyl-1,2,3,6-tetrahydropyridazine (VI, *R'*, *R'''* = *phenyl*, *R''* = *H*). *Trans-trans*-1,4-diphenylbutadiene-1,3 prepared by the method of Corson (10) was treated with the azo-esters under conditions shown in Table III. The adduct from the dimethyl ester melted at 180.5–181.5° (3), while that from the diethyl ester melted at 134.5–135.0°. Crystallization from acetonitrile (13 ml. per g.) raised this melting point to 135.7–136.0°.

Anal. Calc'd for $C_{22}H_{24}N_2O_4$: C, 69.4; H, 6.36; N, 7.37.

Found: C, 69.4; H, 6.25; N, 7.44.

1-Carbomethoxy-3,6-diphenyl-1,2,3,6-tetrahydropyridazine. The characterization of 1,2-dicarbethoxy-3,6-diphenyl-1,2,3,6-tetrahydropyridazine (VI, R = C_2H_5; R', R''' = phenyl; R' = H) was effected by alkaline hydrolysis with accompanying ester-interchange. A mixture of 25 g. (0.0658 mole) of VI in 74 g. (0.53 mole) of 40% (w/v) methanolic potassium hydroxide was boiled under reflux for one hour. Dilution with 100 ml. of water and acidification to *p*H 3 with concentrated hydrochloric acid yielded a solid which was washed acid-free and dried, wt. 18.3 g., m.p. 80–115°. Crystallization from ethyl acetate gave 4.72 g. (30%) of 3,6-diphenyl-1,2,3,6-tetrahydropyridazine, m.p. 155–157° (3). The mother liquor was evaporated to leave a gummy solid which crystallized after addition of ethanol, wt. 13.5 g., m.p. 58–68°. This crude 1-carbomethoxy-3,6-diphenyl-1,2,3,6-tetrahydropyridazine (70%) was purified by crystallization from petroleum ether (b.p. 60–70°) until it melted at 76.5–77.0°. Grignard analysis showed that it contained 0.98 active H/mole and that it added 0.4–1.74 moles of Grignard reagent per mole, depending on duration of reaction.

Anal. Calc'd for $C_{12}H_{18}N_2O_2$: C, 73.4; H, 6.16; N, 9.51.
Found: C, 74.3; H, 6.11; N, 9.50.

N,N'-Diguanyl-1,2,3,6-tetrahydropyridazine dinitrate (XV) (all melting points on microscope hot-stage). A. *In butadiene.* A suspension of 4.90 g. (0.02 mole) of azo-bis-formamidine dinitrate (11) in 21.6 g. (0.20 mole) of 1,3-butadiene in a 4-ounce pressure bottle was shaken occasionally for 2 days, but without apparent change. Then 3.16 g. (0.04 mole) of dry pyridine was added. After 12 days the yellow-grey solid was filtered from the colorless liquid medium and washed with ether, wt. 5.84 g., m.p. 164.4–166°. The melt evolved gas

TABLE II

REACTION BETWEEN CYCLOPENTADIENE (I) AND DIALKYL AZODICARBOXYLATES (II)

II, R =	ESTER (Moles)	DIENE (Moles)	SOLVENT (Vol.)	YIELD OF PRODUCT, %	TEMP., °C.
Me	0.05	0.05	Ether (8 ml.)	100	0–5
Me	.002	.002	Benzene (100 ml.)	94	23
Me	.05	.05	Methanol (240 ml.)	93	23
Et	.03	.045	Ether (10 ml.)	97	0–5
Et	.01	.01	Ether (50 ml.)	92	0–5
Et	.01	.01	Methanol (50 ml.)	90	23

TABLE III

REACTION BETWEEN 1,4-DIPHENYLBUTADIENE-1,3 (V_3, R', R''' = PHENYL, R'' = H) AND DIALKYL AZODICARBOXYLATES (II)

II, R =	ESTER (Moles)	DIENE (Moles)	SOLVENT (Vol.)	YIELD OF PRODUCT, %	CONDITIONS
Me	0.0015	0.0015	None	86	Steam-bath, 15 min.
Me	.0015	.0015	Methanol (15 ml.)	82	25° for 48 hours
Me	.0015	.0015	Benzene (15 ml.)	81	25° for 48 hours
Et	.18	.15	None	63	Steam-bath, 15 min.
Et	.0058	.005	Methanol (15 ml.)	48	Reflux, 12 hours
Et	.0086	.008	Methanol (60 ml.)	80	25° for 48 hours
Et	.0025	.0025	Benzene (20 ml.)	70	25° for 48 hours

and resolidified at 169°; it re-melted at 227–229° (decomp.). This crude product (99.4%) was purified by solution in methanol at 25° to which ethyl ether was added immediately, m.p. 168.4–168.6°, remelt at 252–255°.

Anal. Calc'd for $C_6H_{14}N_8O_6$: C, 24.5; H, 4.80; N, 38.1.
Found: C, 24.4; H, 4.86; N, 38.5.

The x-ray diffraction pattern using CuK_α radiation (Ni filtered) for this compound is given in d spacings, Å at relative intensities $[I/I_0]$ as follows: [100] 4.97, 3.19, 3.08; [60] 4.56, 2.97; [50] 3.59; [40] 4.27; [25] 5.96, 3.83, 3.45, 2.40; [13] 7.19, 5.30, 3.94, 2.65, 2.33, 1.97; [10] 2.03; [6] 2.45, 2.22, 1.54; [3] 2.82, 2.73, 2.17, 1.88, 1.71, 1.64, 1.63, 1.34; [2] 2.12, 1.82, 1.60, 1.43, 1.37, 1.28; [1] 1.79, 1.77, 1.74, 1.68, 1.59, 1.40, 1.32.

B. *In methanol.* The procedure described above was repeated with the inclusion of 50 ml. of methanol. After agitation for 7 days the liquid was reddish and the suspension was a mixture of suspended white crystals and heavy yellow agglomerates. Decantation left 1.39 g., m.p. 164–168° (remelted 252–255°). This crude product (24%) was identical with that described above. The decantate was chilled and filtered to remove 1.47 g., m.p. 246–255°, a 20% yield of 1,3-diimino-2,8,9-triaza-4,6,8,9-tetrahydroindan mononitrate, described

below, and probably contaminated with the main product. The filtrate was partially evaporated and then diluted with diethyl ether. The precipitate (1.34 g.) was impure diguanyl tetrahydropyridazine dinitrate, m.p. 150–154° (remelt 230–240°), so the total crude yield of XV was 74%. Further evaporation of the filtrate yielded 0.04 g. (0.7%) of ammonium nitrate, as well as an oil.

1,3-Diimino-2,8,9-triaza-4,6,8,9-tetrahydroindan nitrate (XVI) (all melting points on microscope hot-stage). It is obvious that this substance is formed by fusion of diguanyltetrahydropyridazine dinitrate. Alternatively it was prepared by crystallization of the dinitrate repeatedly from boiling methanol. Ten hours of reflux converted 0.29 g. of the dinitrate to 0.23 g. (79%) of the mononitrate, m.p. 253–255°. When recrystallized from methanol this product melted at 261.2°. Less pure material was obtained by boiling the dinitrate in water. Both products were contaminated with ammonium nitrate.

Anal. Calc'd for $C_6H_{10}N_6O_3$: C, 33.6; H, 4.72; N, 39.2.

Found: C, 32.7; H, 4.68; N, 39.8.

The x-ray diffraction pattern (Cu, K_α, Ni filtered radiation) in d spacings (Å) as relative intensities [I/I_0] are as follows: [100] 4.70, 3.27; [75] 6.83, 4.34, 3.76; [50] 8.71; [25] 2.67, 2.19, 1.63; [13] 4.05, 3.44, 3.00, 2.78; [6] 3.15, 2.87, 2.42, 2.02, 1.99; [3] 5.23, 3.58, 2.39, 2.34, 2.31, 2.24, 1.93, 1.87, 1.82, 1.79, 1.60, 1.57, 1.56, 1.53, 1.50, 1.44, 1.42; [2] 2.10, 1.75, 1.36, 1.34, 1.30; [1] 5.62, 2.48, 1.68, 1.67, 1.48.

9,10-Endo-(N,N-dicarbalkoxyhydrazo)-9,10-dihydroanthracene (IX). These adducts were prepared from anthracene recrystallized from absolute ethanol (m.p. 216.8–217.5°) and the appropriate dialkyl azodicarboxylate according to the method of Diels, Schmidt, and Witte (6). The dimethyl ester melted at 191.6–192.0° and the diethyl ester at 138.8–139.5°. Oxidation of either ester with potassium dichromate in glacial acetic acid gave anthraquinone (XII) in 94% yield. Saponification of either ester with 35% methanolic potassium hydroxide gave a 98% yield of anthracene.

The dimethyl ester (X, R = CH_3) was prepared by the method of Diels, Schmidt, and Witte (6), m.p. 268.0–269.0°. The diethyl ester (X, R = C_2H_5) was prepared in the same manner; alternatively it could be obtained under the conditions used for preparation of IX (R = C_2H_5) if diethyl azodicarboxylate prepared by the method of Rabjohn was used.

Oxidation of the esters X with potassium dichromate in glacial acetic acid gave a 90% yield of anthraquinone (XII). Attempted saponification of X with either 35% (w/v) methanolic potassium hydroxide or 22% hydrochloric acid was unsuccessful; the esters were recovered unchanged in more than 95% yield.

Spectrophotometric studies. The ultraviolet absorption spectra were determined in chloroform solution with use of a Beckman DU instrument at 23° (slit width 0.5 mm.) in 1.0-cm. silica cells. Solutions of VIII, X, and XIII were initially 0.0005–0.0008 molar, while those of the adducts (IX) were initially 0.30 molar. The 9-carbomethoxy- and the 9-carbethoxy-aminoanthracene (XIII) which were used for comparison were prepared by the method of Creech and Franks (7), m.p. 265.0–266.0° and 236.0–237.0° respectively.

TORONTO 5, CANADA

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