[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

The Osazones of 1,2-Cyclobutanedione and Other Alicyclic α-Diketones

BY FAUSTO RAMIREZ AND RICHARD J. BELLET[1]

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The 2,4-dinitrophenylosazones (DNPO's) of: 1,2-cyclobutanedione (Id), 1,2-cyclopentanedione (IId), 1,2-cyclohexanedione (IIId), and 3,3-dimethyl-1,2-cyclohexanedione (IVd) have been prepared from the corresponding α-halo ketones, and their ultraviolet absorption spectra in chloroform solutions compared to that of biacetyl DNPO (Vd). The alicyclic DNPO's exhibited three absorption maxima in the ultraviolet (352 mμ, *ca.* 400 mμ, and *ca.* 450 mμ) while biacetyl DNPO exhibited only two (*ca.* 400 mμ and *ca.* 440 mμ); this difference is discussed. The similarity between the spectra of the alicyclic DNPO's (Id, IId, IIId and IVd) in the ultraviolet and in the infrared, suggests that the structure of the presumably highly strained 1,2-cyclobutanedione DNPO (Id) does not differ significantly from those of the less strained alicyclic DNPO's (IId, IIId and IVd). 2-Bromocyclobutanone 2,4-dinitrophenylhydrazone was recovered unchanged upon heating in either acetic acid or methanol. These results are consistent with a picture of the reactions of α-halohydrazones previously presented.

Schwarzenbach and Wittwer[2] have demonstrated that the enol content of 1,2-cyclopentanedione is greater than that of 1,2-cyclohexanedione under comparable conditions, and attributed the difference to a greater ring-strain associated with the five-membered α-diketone. The four-membered cyclic diketone, *i.e.*, 1,2-cyclobutanedione, was not included in this study.[3]

We have undertaken the preparation of derivatives of cyclobutane having two vicinal trigonal (coördination number = 3) carbon atoms in order to compare their properties with those of similar derivatives of cyclopentane and cyclohexane. The present paper describes the preparation of the 2,4-dinitrophenylosazones (DNPO's) of 1,2-cyclobutanedione (Id) and 1,2-cyclopentanedione (IId), and compares their ultraviolet absorption spectra with those of the corresponding derivatives of 1,2-cyclohexanedione (IIId), 3,3-dimethyl-1,2-cyclohexanedione (IVd) and biacetyl (Vd).

As shown in Fig. 1, the absorption spectra of 1,2-cyclobutanedione DNPO (Id) and 1,2-cyclopentanedione DNPO (IId) in the 300–500 mμ region are very similar, with maxima at 352, 400 and 450 mμ. The 352 mμ band is also present in 1,2-cyclohexanedione DNPO (IIId) and 3,3-dimethyl-1,2-cyclohexanedione DNPO (IVd) in which, however, a small displacement of the 400 mμ band to about 390 mμ is observed. The 450 mμ maximum has practically disappeared in IVd and is considerably weaker in IIId as compared to Id and IId. No significant change with time was observed in the ultraviolet spectra in chloroform solutions containing *p*-toluenesulfonic acid. In agreement with previous observations[4a,b] biacetyl DNPO was found to exhibit only two absorption maxima, at 395 and 440 mμ, respectively.

The infrared absorption spectrum of 1,2-cyclobutanedione DNPO (Id) was very similar to that of the other alicyclic DNPO's (IId, IIId and IVd, not reproduced) and exhibited the double band at 6.18 and 6.25 μ found in 2,4-dinitrophenylhydrazones.[5]

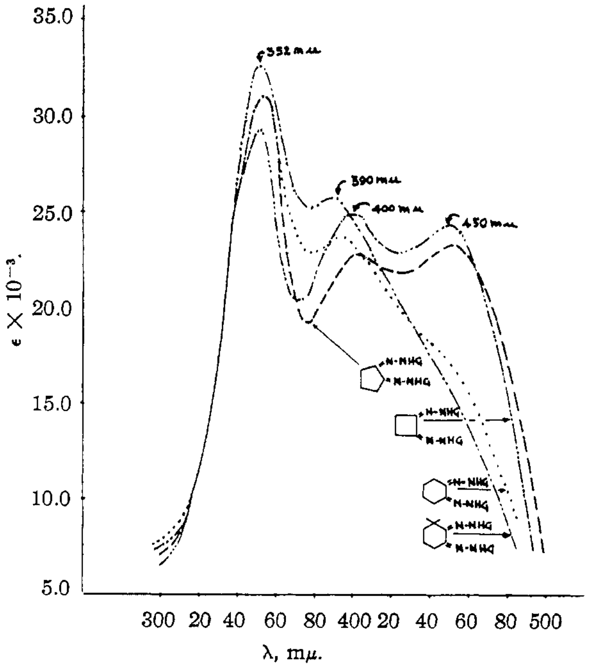
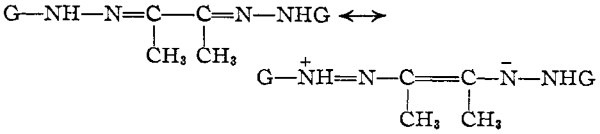


Fig. 1.

It will be noted that tautomerization[6] of the DNPO's, presumably an acid-catalyzed process, could lead to structures such as A and B (Chart 1). The occurrence of this tautomerism is no more in evidence in the ultraviolet and infrared spectra of 1,2-cyclobutanedione DNPO (Id) than in the spectra of the larger, and presumably much less strained,[7] alicyclic DNPO's (IId, IIId and IVd).

In previous discussions of the ultraviolet absorption spectra of osazones,[4] which have been limited to biacetyl DNPO, the observed maxima at 400 and *ca.* 440 mμ have been associated with stabilization of the excited state as in



$$\underset{\textstyle G\text{—NH—N=}}{}\underset{CH_3}{\overset{}{C}}\text{—}\underset{CH_3}{C}\text{=N—NHG} \longleftrightarrow \text{G—}\overset{+}{N}\text{H=N—}\underset{CH_3}{C}\text{=}\underset{CH_3}{C}\text{—}\overset{-}{N}\text{—NHG}$$

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[1] From part of the Ph.D. thesis of R. J. Bellet.

[2] G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 663 (1947).

[3] Unsuccessful attempts to prepare 1,2-cyclobutanedione have been reported recently (K. B. Alberman and F. B. Kipping, *J. Chem. Soc.*, 779 (1951)).

[4] (a) F. Bohlmann, *Chem. Ber.*, **84**, 860 (1951); (b) E. A. Braude and E. H. R. Jones, *J. Chem. Soc.*, 498 (1945).

[5] (a) F. Ramirez and A. F. Kirby, THIS JOURNAL, **74**, 4331 (1952); (b) *ibid.*, **75**, 6026 (1953); (c) *ibid.*, **76**, Feb. (1954). Earlier references are included here.

[6] G. Fodor and P. Szarvas, *Ber.*, **76B**, 334 (1943).

[7] It is conceivable that due to greater ring-strain, structures A or B would be greatly favored in the four-membered ring system as compared to the five-membered homolog; this, irrespective of the actual position of the hypothetical equilibria: DPNO ⇆ A (or B), the assessment of which is beyond the scope of the present work.

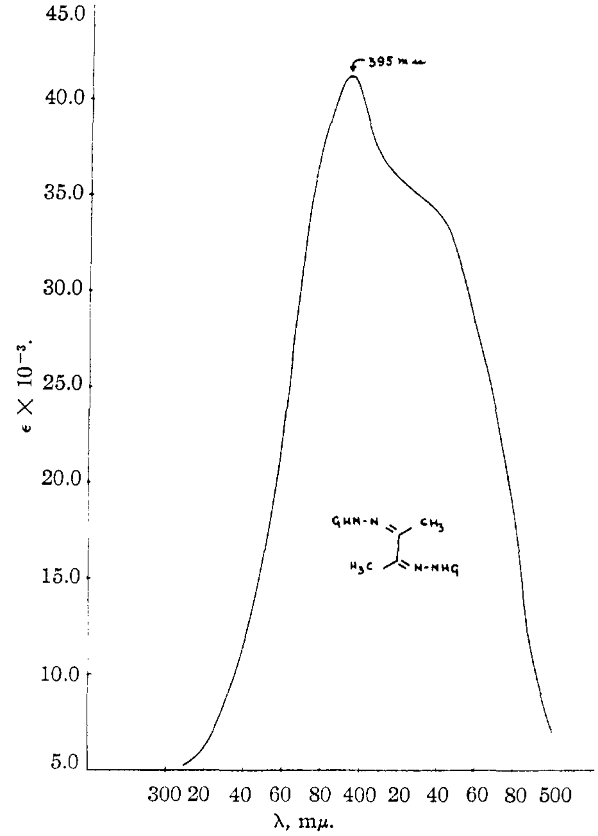


Fig. 2.

in which conjugation between the two hydrazone groups is held responsible for the considerable increase in $\lambda_{\max}$ relative to monodinitrophenylhydrazones. Accordingly, Cook, Raphael and Scott[8] attributed the observed absorption of 1,2-cycloheptanedione DNPO at 356 mμ to a steric interference of the coplanarity of the hydrazone groups necessary for complete conjugation. As previously discussed,[9] the carbonyl groups of 1,2-cycloheptanedione appear from models to be inclined at right angles. It should be noted, however, that 1,2-cyclobutanedione DNPO (Id) and 1,2-cyclopentanedione DNPO (IId) in which the two hydrazone groups are presumably coplanar or nearly so, exhibited also the short wave length maximum (352 mμ). In line with other observations concerning the relationship of structure to ultraviolet spectra in dinitrophenylhydrazones,[5] the short wave length maximum (*ca.* 352 mμ) of alicyclic DNPO's might be associated with the partial dinitrophenylhydrazone chromophore. somewhat displaced toward shorter wave lengths,[10] irrespective of the degree of coplanarity between the two hydrazone groups. In biacetyl DNPO (Vd), in which rotation allows sufficient separation between the hydrazone groups, the short wave length maximum would not be expected to accompany the longer maxima associated with the full osazone chromophore.[4] Id and Vd[11] represent situations of coplanarity between the hydrazone groups under different steric circumstances.

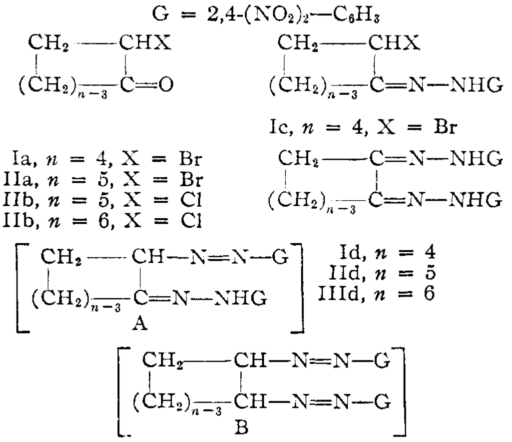
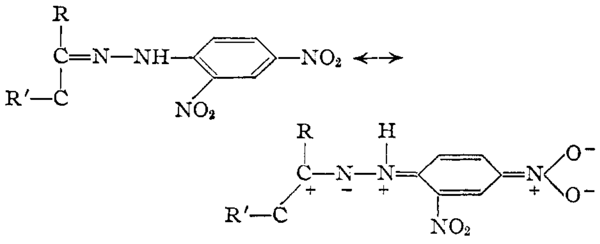
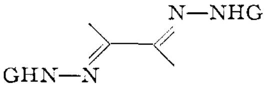
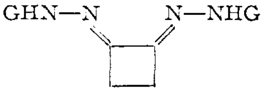


CHART 1





Vd



Id

The preparation of 1,2-cyclobutanedione DNPO (Id) and 1,2-cyclopentanedione DNPO (IId) from the corresponding α-halo ketones utilized the known oxidative-displacement characteristic of the osazone reaction. The intermediate 2-bromocyclobutanone 2,4-dinitrophenylhydrazone (Ic) was isolated, and found to possess a rather unreactive halogen as compared to other α-halo hydrazones studied.[5] Thus, Ic was recovered unchanged after treatment with acetic acid and with methanol under conditions which, in other types of α-halo hydrazones, resulted in dehydrohalogenation and replacement, respectively.[12] These observations are in line with the behavior of four-membered carbon rings in reactions involving a change in coördination number

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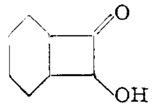
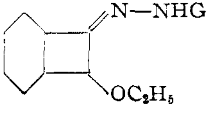
[8] J. W. Cook, R. A. Raphael and A. I. Scott, *J. Chem. Soc.*, 4416 (1952).

[9] N. J. Leonard and P. M. Mader, THIS JOURNAL, **72**, 5388 (1950).

[10] For example, in cyclohexanone dinitrophenylhydrazone: $\lambda_{\max}^{\text{Chl}}$ 366 mμ, (ε 23400); in cyclobutanone dinitrophenylhydrazone: $\lambda_{\max}^{\text{Chl}}$ 362 mμ, (ε 21400).

[11] No evidence concerning the stereoisomerism about the C=N *bond is available. The formulas are written in what appears to be the* less hindered forms.

[12] A. C. Cope and E. C. Herrick (THIS JOURNAL, **72**, 983 (1950)), reported the isolation of two products from the action of 2,4-dinitrophenylhydrazinium sulfate on  in aqueous ethanol solution. One of the products was considered to be the corresponding osazone; the structure of the second product was not elucidated. The published data for this compound agree with the structure 

of the ring atoms from four to five or from four to three.[13] They are also consistent with a picture of the reactions of α-halo hydrazones discussed elsewhere[5] since the distortion of the bond angles should have an adverse effect on the driving force of the elimination and replacement reactions of 2-halocyclobutanone 2,4-dinitrophenylhydrazone.

Experimental[14]

Cyclobutanone.—Prepared as previously described,[15] with the following minor but expedient modifications. To purify the crude pentaerythrityl tetrabromide, recrystallization from ethyl acetate was used, rather than the recommended continuous extraction with ethanol. In the reaction between pentaerythrityl tetrabromide and zinc, addition of some Dow Corning Antifoam A emulsion prevented foaming. In the extraction of 1-hydroxy-1-hydroxymethylcyclobutane and of cyclobutanone, ether can be used. The cyclobutanone was distilled through a 15-plate, helix-packed column; b.p. 97–98°, n^{25}D 1.4179. The infrared spectrum was comparable to that published; the **2,4-dinitrophenylhydrazone**: m.p. 144–145°, $\lambda_{\max}^{\mathrm{Chl}}$ 362 mμ (ϵ 21400).

2-Bromocyclobutanone (Ia).—A solution of 11.43 g. of bromine in 30 ml. of chloroform was added dropwise, over a 1.5-hour period, to a stirred solution of 5.00 g. of cyclobutanone in 125 ml. of chloroform, kept protected from moisture at 27°. The solution was stirred for 15 minutes, washed with cold water and 10% sodium bicarbonate solution, and dried over magnesium sulfate. Removal of the solvent under reduced pressure at *ca.* 30° left 10.56 g. of yellowish oil (crude n^{26}D 1.4991). Distillation through a 3″ Vigreux column gave three fractions: (a) 2.22 g., b.p. 68–70° (14 mm.), n^{25}D 1.5026; (b) 4.40 g., b.p. 70–71° (14 mm.), n^{25}D 1.5038; residue, 1.46 g., n^{25}D 1.526. The infrared spectra of fractions (a) and (b) were very similar; fraction (b): d^{25}_{25} 1.671.

Anal. Calcd. for C_4H_3OBr: C, 32.2; H, 3.4; Br, 53.6; $[R_L]_D$, 26.69. Found: C, 32.3; H, 3.5; Br, 53.4; $[R_L]_D$, 26.38.

2-Bromocyclobutanone 2,4-Dinitrophenylhydrazone (Ic).—To a solution containing 0.20 g. of 2,4-dinitrophenylhydrazine, 0.4 g. of concentrated sulfuric acid, 3 ml. of methanol and 1 ml. of water, was added 0.15 g. of Ia. The yellow precipitate was filtered after 15 minutes; yield of crude 0.240 g., m.p. 114–118°. Several recrystallizations from methylene chloride–petroleum ether gave Ic as yellow needles, m.p. 127–128°, $\lambda_{\max}^{\mathrm{Chl}}$ 357 mμ (ϵ 23400); bands at 3.00, 6.18 and 6.25 μ.

Anal. Calcd. for $C_{10}H_9N_4O_4Br$: C, 36.5; H, 2.8; N, 17.0. Found: C, 36.7; H, 2.8; N, 16.6.

Ic was recovered unchanged from a solution in acetic acid kept at its boiling point for one hour.

Ic was recovered unchanged from a solution in methanol kept at its boiling point for one hour.

1,2-Cyclobutanedione 2,4-Dinitrophenylosazone (Id).—From 0.150 g. of Ic, 0.200 g. of 2,4-dinitrophenylhydrazine, 0.8 g. of concentrated sulfuric acid, 3 ml. of methanol and 1 ml. of water, 0.050 g. of Id (dec. point, *ca.* 270°) was obtained after two hours reflux. The analytical sample melted with decomposition at 282–283° (from chloroform–methanol); $\lambda_{\max}^{\mathrm{Chl}}$ 352 mμ (ϵ 29300); 400 mμ (ϵ 24900); 450 mμ (ϵ 24300); bands at 6.18 and 6.25 μ (Nujol mull).

Anal. Calcd. for $C_{16}H_{12}N_8O_8$: C, 43.3; H, 2.7. Found: C, 43.4; H, 2.8.

1,2-Cyclopentanedione 2,4-Dinitrophenylosazone (IId). (a) **From 2-Bromocyclopentanone.**—The ketone was brominated as described above for cyclobutanone except that the addition of bromine was carried out at 4–7°. From 4.0 g. of cyclopentanone in 50 ml. of chloroform, 8.8 g. of slightly yellow oil was obtained. Distillation gave 2.8 g. of colorless liquid, (b.p. 60° (2 mm.), $n^{24.5}$D 1.5114), which was utilized without delay.[16] To a solution containing 0.60 g. of 2,4-dinitrophenylhydrazine, *ca.* 1.0 g. of concentrated sulfuric acid, 9.0 ml. of methanol and 3.0 ml. of water, was added 0.16 g. of the bromo ketone. The mixture was kept on the steam-bath for 1 hour and at room temperature for 3 hours. The dry orange precipitate (0.36 g.) melted at *ca.* 180–195° dec. Recrystallization from chloroform–methanol (in which it is sparingly soluble) gave IId of m.p. 244° dec., $\lambda_{\max}^{\mathrm{Chl}}$ 352 mμ (ϵ 31000), 403 mμ (ϵ 22800), 452 mμ (ϵ 23300); bands at 6.18 and 6.25 μ (Nujol mull).

Anal. Calcd. for $C_{17}H_{14}N_8O_8$: C, 44.5; H, 3.1; N, 24.5. Found: C, 44.7; H, 3.1; N, 24.6.

(b) **From 2-Chlorocyclopentanone.**—A solution of 3.4 g. of chlorine in 40 ml. of carbon tetrachloride was added to a solution of 4.0 g. of cyclopentanone under conditions analogous to those described under (a). Removal of the solvent gave 6.8 g. of slightly yellow liquid.[16] From 5.4 g. of crude chloro ketone, 10.7 g. of 2,4-dinitrophenylhydrazine, 21.5 g. of concentrated sulfuric acid, 150 ml. of methanol and 50 ml. of water, 7.7 g. of crude IId was obtained after 3 hours on the steam-bath. The crude osazone can be purified to a reproducible decomposition point of *ca.* 245° by recrystallization from chloroform–methanol.

1,2-Cyclohexanedione 2,4-Dinitrophenylosazone (IIId) and 3,3-Dimethyl-1,2-cyclohexanedione 2,4-Dinitrophenylosazone (IVd).—IIId ($\lambda_{\max}^{\mathrm{Chl}}$ 352 mμ (ϵ 31000), 394 mμ (ϵ 23600), *ca.* 450 mμ (ϵ 16900)) and IVd ($\lambda_{\max}^{\mathrm{Chl}}$ 351 mμ (ϵ 32600), 388 mμ (ϵ 25700)) were prepared as previously described.[5]

Biacetyl 2,4-Dinitrophenylosazone (VId).—Made from biacetyl; decomposition point; *ca.* 315°; $\lambda_{\max}$ 395 mμ (ϵ 41000), 440 mμ (ϵ 34000).

Ultraviolet Absorption Spectra.—Taken in chloroform solution in a Cary Recording Spectrophotometer Model 11. The osazones were sparingly soluble, and care was exercised to bring all material in solution. Reproducible values were secured in different samples.

The spectra of the osazones were also determined after the solutions had stood at room temperature in the presence of *p*-toluenesulfonic acid (1 ml. of a solution containing 8 mg. of *p*-toluenesulfonic acid in 100 ml. of chloroform) for variable periods of time (3 minutes, 1 hour, 8 hours, 1 day and 8 days). The values of the extinction coefficients at the indicated maximum wave lengths were checked and found constant within the experimental uncertainty. Thus, for Id: at 352 mμ, $\epsilon \times 10^{-3}$: 29.3 (no acid); 29.3 (3 min. after addition of acid); 28.9 (1 hour); 29.1 (8 hours); 29.4 (24 hours); 29.4 (8 days). At 400 mμ, $\epsilon \times 10^{-3}$: 25.0 (no acid); 25.3 (3 min.); 25.1 (1 hour); 25.1 (8 hours); 25.1 (24 hours); 25.1 (8 days). At 450 mμ, $\epsilon \times 10^{-3}$: 24.3 (no acid); 24.6 (3 min.); 24.4 (1 hour); 24.5 (8 hours); 24.5 (24 hours); 24.6 (8 days).

Infrared Absorption Spectra.—Taken in a Baird Associates, Inc., Spectrophotometer (sodium chloride prism).

NEW YORK, N. Y.

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(13) H. C. Brown, R. S. Fletcher and R. B. Johannssen, THIS JOURNAL, **73**, 212 (1951).

(14) Microanalyses by Micro-Tech Laboratories, Skokie, Ill., and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Melting points are uncorrected.

(15) J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

(16) A. Kotz, K. Blendermann, E. Karpati and R. Rosenbuch, *Ann.*, **400**, 47 (1913).